Russian Chemical Reviews, Volume 49 (1980)

Contents of Volume

Number 1

Stereochemistry of the Reactions of Phosphorus-containing Free Radicals 1
S P Solodovnikov, N N Bubnov, A I Prokof'ev

Catalytic Amination of Alcohols, Aldehydes, and Ketones 14
M V Klyuev, M L Khidekel'

The Chemistry of Sydnone Imines 28
V G Yashunskii, L E Kholodov

Phosphinates ("Hypophosphites") and Their Reactivity 46
V I Yudelevich, L B Sokolov, B I Ionin

Problems of the Theory of Transport Processes in Systems with Intensive Mass Exchange 59
V S Krylov

Extraction Polarography and Its Analytical Applications 74
G K Budnikov, N A Ulakhovich

Thermodynamic Treatment of the Polarity and the Selectivity of Sorbents in Gas Chromatography 88
R V Golovnya, T A Misharina

Number 2

The Present State of the Problem of the Identification of Kinetic Models 99
V V Kafarov, V N Pisarenko

The Basicity of Transition Metal Complexes in Reactions with Aprotic Acids 115
B V Lokshin, A G Ginzburg, E B Nazarova

Photochemical Reactions of Free Radicals in the Solid Phase 131
M Ya Mel'nikov, N V Fok

Cobalt Complexes of Carbaboranes 147
E V Leonova

Theoretical Foundations of the Classification of Molecules by Luminescence Spectra 172
V G Plotnikov

Chemical Chain Reactions in the Devitrification of the Matrix 190
I M Barkalov

Number 3

Thermodynamics of Isotope Exchange Reactions 203
N M Zhavoronkov, D A Knyazev, A A Ivlev, G D Klinskii

Saccharinic Acids 222
R A Gakhokidze

The Formation of the Azoxy-group in Reactions Involving Anions with Nitrogen–Nitrogen Bonds 237
V N Yandovskii, B V Gidaspov, I V Tselinskii

Cathodic Coupling Reactions 249
A V Bukhtiarov, A P Tomilov

Biochemical Applications of Poly(Ethylene Glycol) 260
I N Topchieva

The Structure of Organocyclosiloxanes 272
V E Shklover, Yu T Struchkov

Number 4

Auto-oscillations in the Rates of Heterogeneous Catalytic Reactions 295
M G Slin'ko, M M Slin'ko

Polarographic Study of Complex Formation Equilibria in Solutions 310
E A Mambetkaziev, S I Zhdanov

The Volumes of Mixing of Liquids and Their Importance for the Modern Theory of Solutions 325
A A Tager, L V Adamova

Advances in the Chemistry of Pernitriles 337
N S Zefirov, D I Makhon'kov

Organometallic Derivatives of Diazoalkanes 357
O A Kruglaya, N S Vyazankin

The Synthesis of Active Metabolites and Analogues of Vitamin D_3 371
R I Yakhimovich

Number 5

The Stabilisation of Enzymes — a Key Factor in the Practical Application of Biocatalysis 385
K Martinek, I B Berezin

Problems in the Study of Supported Metal Catalysts 404
A A Slinkin

The Physical Chemistry of Silatranes 414
V F Sidorkin, V A Pestunovich, M G Voronkov

Advances in the Chemistry of Azaindoles 428
L N Yakhontov, A A Prokopov

Structure and Properties of Networks in Heat-resistant Polymers 445
A A Askadskii, Yu S Kochergin

Chemospecific (Covalent) Chromatography of Biopolymers 460
V I Lozinskii, S V Rogozhin

Reproducibility of Retention and Identification Data in Gas–Liquid Chromatography 473
A N Korol'

Gas-chromatographic Analysis of Nucleic Acids 488
V V Tets

Number 6

The Use of Mass Spectrometry to Study the Structure of Flames and Combustion Processes 497
O P Korobeinichev

Theoretical Calculation of the Spatial Distribution of Molecules in Crystals 509
T V Timofeeva, N Yu Chernikova, P M Zorkii

Mechanism of the Adsorption of Organic Sulphur Compounds by Oxides and Zeolites 526
N K Lyapina, V I Lygin, A D Ulendeeva

The Electrochemistry of Hydroxide Melts 536
O G Zarubitskii

Nucleophilic Substitution Reactions of Cyclopropane Derivatives 549
V S Aksenov, G A Terent'eva, Yu V Savinykh

Aromatic Monocarbonylpolyfluoro-compounds 558
T N Gerasimova, E P Fokin

The Synthesis of Carbohydrates from Formaldehyde 570
T I Khomenko, M M Sakharov, O A Golovina

Photoageing of Aliphatic Polyamides 585
A L Margolin, L M Postnikov

Number 7

Thermochemistry of Organic Derivatives of Non-transition Elements 603
V I Tel'noi, I B Rabinovich

Methods of Calculating pK_{BH^+} for Weak Bases 623
Yu L Khaldna

Outer-sphere Interactions in Solutions of Labile Complexes 631
Yu A Makashev, V E Mironov

Diastereotopy in Transition Metal Complexes 645
G B Shul'pin

Stereochemistry of Four-coordinate Chelate Compounds of Schiff Bases and Their Analogues 655
G V Panova, N K Vikulova, V M Potapov

Advances in the Chemistry of Organofluorine Hypohalites and Related Compounds 668
F M Mukhametshin

Concentration Methods for the Determination of Trace Elements 683
Yu A Zolotov

Number 8

Possible Approaches to the Development of Photo-catalytic Solar Energy Converters 695
K I Zamaraev, V N Parmon

Electrocatalysis on Metalloporphyrins 718
M R Tarasevich, K A Radyushkina

Determination of the Useful Lifetime of a Polymeric Material as a Physicochemical Problem 731
O N Karpukhin

Prediction of the Variation of the Properties of Polymeric Materials after Prolonged Storage and Use 748
B D Goikhman, T P Smekhunova

Kinetic Models for the Prediction of the Lifetime of Polymeric Materials 759
E V Deyun, G B Manelis, E V Polianchik, L P Smirnov

Photochemical Oxidation of Polyolefins and Prediction of Their Useful Lifetime 771
E M Slobodetskaya

Synthesis of Bisbenzylisoquinoline Alkaloids 784
O N Tolkachev, E P Nakova, R P Evstigneeva

Number 9

Grigorii Alekseevich Razuvaev 799
A M Sladkov

Organometallic Compounds with Heteroatomic Chains 800
M N Bochkarev

The Formation of Inorganic Coatings in the Decomposition of Organometallic Compounds 810
G A Domrachev, O N Suvorova

Spectroscopic Study of π-Acceptor Effects in Compounds of Silicon Subgroup Elements 820
A N Egorochkin, S Ya Khorshev

The Mechanisms of the Rearrangements of Peroxides 833
V A Yablokov

α-Ketophosphonic Acid Esters — Synthesis, Structure, and Reactions 843
Yu A Zhdanov, L A Uzlova, Z I Glebova

Arylated Cyclopentadienes and Cyclopentadienylides 854
Ya N Kreitsberga, O Ya Neiland

Prop-2-ynyl Ethers 865
S F Karaev, Sh V Garaeva

α,β-Unsaturated Heteroatomic Compounds in 1,3-Dipolar Addition Reactions 880
V A Galishev, V N Chistokletov, A A Petrov

Organometallic (Non-transition Metals) Free Radicals 893
A G Milaev, O Yu Okhlobystin

Number 10

Boris Petrovich Nikol'skii 907
A M Sladkov

Oxidation-reduction Measurements and Their Applications in the Study of Interactions in Solutions 908
V V Pal'chevskii, Kh M Yakubov

Dynamics of the Potential and the Mechanism of Action of Ion-selective Glass Electrodes 920
A A Belyustin

Inorganic Ion-exchange Materials Based on Insoluble Antimony(V) Compounds 933
F A Belinskaya, E A Militsina

Ion-selective Electrodes in the Study of Cholinesterases 953
E A Materova, E B Nikol'skaya

Rhenium Fluorides 958
E G Rakov, A S Dudin, A A Opalovskii

The Isotope Effect for Diffusion in Solids 968
A N Murin, I V Murin, V I Portnyagin

Reversible Recombination of Radicals 982
I V Khudyakov, P P Levin, V A Kuz'min

The Spectra and Structure of Transition Metal Complexes with Tetradentate Macrocyclic Ligands 1003
K B Yatsimirskii, Ya D Lampeka

Number 11

The Influence of Solvation on the Acid-Base Properties of Organic Compounds in Various Media 1021
K M Dyumaev, B A Korolev

The Structure of the Electronic Excitation of Molecules in Quantum-chemical Models 1033
A V Luzanov

Heptavalent Bromine Compounds 1049
V V Gavrilov, V K Isupov

Synthesis of Corroles and Octadehydrocorrins 1056
N S Genokhova, T A Melent'eva, V M Berezovskii

Chemistry of α-Halogenonitroalkanes 1068
A L Fridman, V D Surkov, S S Novikov

Studies in the Field of Boron-substituted Functional Derivatives of Carbaboranes(12) 1084
V N Kalinin

The Mechanism of the Catalytic Polymerisation of Olefins Based on the Number of Active Centres and the Rate Constants for Individual Stages 1097
V A Zakharov, G D Bukatov, Yu I Ermakov

The Attaching of Biologically Active Compounds to the Surfaces of Optical Materials 1112
A Baigozhin

Number 12

Oxidative Decarboxylation of Carboxylic Acids 1119
Yu A Serguchev, I P Beletskaya

The Synthesis of Polymers by Modification Methods 1135
V V Korshak

Advances in the Chemistry of Compounds with the Cyclodisilazane Structure 1149
D Ya Zhinkin, Yu M Varezhkin, M M Morgunova

Kinetics and Mechanism of the Reaction of Ozone with Double Bonds 1163
S D Razumovskii, G E Zaikov

Internuclear Distances in Carbaboranes 1181
V S Mastryukov, O V Dorofeeva, L V Vilkov

The Formation, Structure, and Properties of the Extracomplexes of Porphyrins 1188
B D Berezin, O I Koifman

Polyimides Based on Heterocyclic Monomers 1204
A L Rusanov, I Batirov

© 2008, No Rights Reserved.

RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

January 1980

Translated from *Uspekhi Khimii*, 49, 3-27 (1980)

U.D.C. 541.515

Stereochemistry of the Reactions of Phosphorus-containing Free Radicals

S.P.Solodovnikov, N.N.Bubnov, and A.I.Prokof'ef

The stereochemical characteristics of phosphoranyl radicals and β-phosphorus-substituted radicals as well as tautomeric transformations involving phosphorus-containing phenoxy-radicals, which reflect the stereochemical properties of quinquevalent phosphorus, are discussed.
The bibliography includes 58 references.

CONTENTS

I.	Introduction	1
II.	Stereochemical characteristics of phosphorus-containing free radicals	1
III.	Stereochemical transformations of phosphoranyl radicals	3
IV.	The conformation of β-phosphorus-substituted radicals	6
V.	Tautomerism of phosphoranylphenoxy-radicals	8

I. INTRODUCTION

Phosphorus-containing free radicals and reactions involving them have been vigorously investigated in recent years. The results of experimental and theoretical studies on the structures and reactivities of numerous phosphorus-radicals published until 1974 have been compiled in two reviews[1,2]†.

In the study of the structures and reactivities of phosphorus-containing free radicals a research field associated with the stereochemistry of the radical reactions of organophosphorus compounds has been established. Ideas have been put forward, according to which the stereochemical transformations occuring in organophosphorus free radicals influence the mode and rate of reaction and also the stereochemical properties of the reaction products.

II. STEREOCHEMICAL CHARACTERISTICS OF PHOSPHORUS-CONTAINING FREE RADICALS

According to the established classification, phosphorus-centred free radicals are divided into phosphinyl, phosphonyl, and phosphoranyl radicals. In these radicals the unpaired electron is either wholly or largely localised at the phosphorus atom. There exists a large class of radicals in which the free valence is located at atoms in the β-positions relative to the phosphorus atom. The radical-anions and radical-cations of organophosphorus compounds are widely known[1,2].

A planar structure with the localisation of the unpaired electron in the *p* orbital of the phosphorus atom has been attributed to the phosphinyl radicals $\dot{P}R_2$.[1] It is believed that

† After the present review had been sent to the printers, the monograph by Ya.A.Levin and E.I.Vorkunova, "Gomoliticheskaya Khimiya Fosfora" (The Homolytic Chemistry of Phosphorus), Izd.Nauka, Moscow, 1978, was published; here the reader will find a more detailed discussion of a number of the problems dealt with in the present review.

the phosphonyl radicals $R_2\dot{P}O$ have a non-planar structure and the unpaired electron is in the 3*s* and 3*p* phosphorus orbitals and the 2*p* oxygen orbital[1]. The greatest amount of data are available on the structures of phosphoranyl radicals of the type $\dot{P}R_4$. Depending on the nature of the substituents, either a trigonal bipyramid (TBP) or a tetrahedral structure is attributed to them.

The non-equivalence of the fluorine atoms in the $\dot{P}F_4$ radical[3,4] or the hydrogen atoms in the $\dot{P}H$ radical[5] and the hydrogen atoms in the methyl groups in the $H_3\dot{P}O$–t-Bu, $Me\dot{P}H_2$–O–t-Bu, and $Me_3\dot{P}O$–t-Bu radicals[6], which follows from the EPR spectra, shows that the radicals have a structure close to that of a TBP, which is characteristic of phosphorus(V) compounds.

The following stereochemical problems arise in the study of phosphoranyl radicals[7].

(a) Is the formation of a phosphoranyl radical following the addition of an attacking radical (for example in the apical position, as in the nucleophilic attack on PX_4^+, $X_3P=O$, and possibly $:PX_3$) stereoselective?

(b) Is there a possibility of the interconversion of the configurational isomers during the lifetime of the radicals, which naturally can vary as a function of the experimental conditions?

(c) Is the fragmentation of phosphoranyl radicals stereoselective, particularly when the phosphoranyl radical contains a pair of identical ligands, one of which is in the apical position and the other in the equatorial position and which one of them is susceptible to more or less ready α- or β-cleavage?

$$A{-}B^{\cdot} + PX_3 \rightarrow AB{-}\dot{P}X_3 ,$$

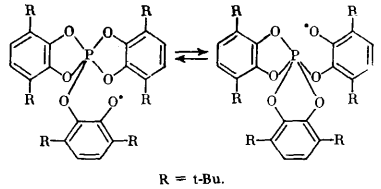
$$AB\dot{P}X_3{-}\left|\begin{array}{l}\xrightarrow[\alpha\text{-elimination}]{} A{-}B{-}PX_3 + X^{\cdot} ,\\ \xrightarrow[\beta\text{-elimination}]{} A^{\cdot} + B{=}PX_3 .\end{array}\right.$$

(d) The question arises which isomer of the phosphoranyl radicals recorded or not recorded by EPR undergoes faster fragmentation and which is the main source of the fragmentation products:

(e) Finally it is necessary to establish to what extent the stereochemical characteristics of the disposition of the substituents and the frequency of the interconversions of the stereoisomers of phosphoranyl compounds differ compared with phosphorus(V) compounds.

In the study of radicals where the free valence is localised on atoms in the β-positions relative to the phosphorus atom stereochemical problems associated with the steric requirements of the radical fragments also arise.

Exchange reactions involving radicals of the following type have been discovered recently:



R = t-Bu.

(I)

where the rapid transfer of the unpaired electron between the ligands results in the phosphorus(V) compound having the structure of a hexacoordinate phosphorus compound on the EPR time scale[8]. The study of this reaction led to the problem of the stereospecificity of the substitution reaction involving bonds and radicals with the TBP structure.

The main aspects of the stereochemical problem under consideration is the possibility of the interconversion of the configurational isomers of the radicals, their frequency and activation barriers, the mechanisms of stereochemical transformations, and their role in the overall mechanism of the radical reactions of organophosphorus compounds. The study of the stereochemistry of phosphoranyl radicals is based on the findings obtained in the study of phosphorus(V) compounds with which the radicals have much in common according to experimental data.

X-Ray diffraction and NMR data established that the geometry of these compounds corresponds to either a TBP or a tetragonal pyramid (TP). In agreement with calculations, the energy differences between these conformations are small (~0.5 kcal mol^{-1}). It has come to be assumed that in the liquid phase the majority of phosphorus(V) compounds have the TBP geometry[9].

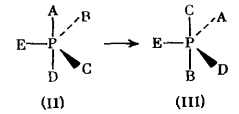
The so-called polarity rule has been established[9,10], according to which electron-donating substituents occupy equatorial positions in TBP, while electronegative substituents occupy apical positions (the vacant *d* orbitals of the phosphorus atom interact effectively with electron-donating substituents via the formation of dative bonds in the equatorial positions). Apart from the donor–acceptor interactions, steric effects play a major role, the apical position being more shielded. All these features make the apical bonds longer than the equatorial bonds.

It has been noted that for cyclic ligands, particularly oxygen-containing cyclic ligands, five-membered rings occupy preferentially the equatorial-apical positions because the internal strain is reduced in this configuration. Six-membered rings are located mainly in the equatorial positions[10]. The presence of identical ligands leads to additional stabilisation as a result of the ligand symmetry. It consists in the fact that isomers having identical ligands in either apical or equatorial positions are more stable.

Thus the disposition of the substituents in phosphorus(V) compounds is a complex function of several parameters. The concept of "apicophilicity" of particular ligands, based on empirical data, is used to describe this function[9,10].

The use of NMR made it possible to follow, in an enormous number of examples, the dynamics of the mutual exchange of ligands in a TBP, in which the substituents exchange between the apical and equatorial positions. It was found that the frequencies of such transformations depend significantly on the nature of the ligands and the activation energy varies within wide limits (1.5–25 kcal $mole^{-1}$).[9]

The ligand exchange in the chiral phosphorane



(II) (III)

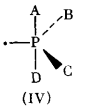
can be explained within the framework of two models: (1) Berry's pseudorotation mechanism[11], taking into account the change in the angles in the TBP, which leads to a TP as an intermediate conformation with formation of a new TBP, and (2) the Ramirez turnstile mechanism[10], which postulates the rotation of three ligands relative to two others and reflects the transposition mechanism of the pseudorotation. The turnstile mechanism is more applicable to the explanation of ligand exchange involving cyclic phosphorus compounds, where Berry's pseudorotation is accompanied by an increase of ring strain when the angles are altered.

Five different types of rearrangements of the TBP of the phosphorane P(ABCDE), denoted by *M*1–*M*5, are distinguished[12]. The rates of different rearrangements and the stability of the conformers depend on the nature of the ligands. In the stereochemistry of nucleophilic substitution at a tetracoordinate phosphorus atom the formation of an

intermediate (or transition state) with a pentacoordinate phosphorus atom, having the TBP geometry, is postulated. The empirical rule that the attacking nucleophile enters the apical position and the substituted ligand leaves the apical position has been established and has been widely confirmed on numerous examples[10]. Hexacoordinate phosphorus species are anions and have the octahedral configuration.

III. STEREOCHEMICAL TRANSFORMATIONS OF PHOSPHORANYL RADICALS

A TBP structure with the free valence located in the equatorial plane has been attributed to phosphoranyl radicals:

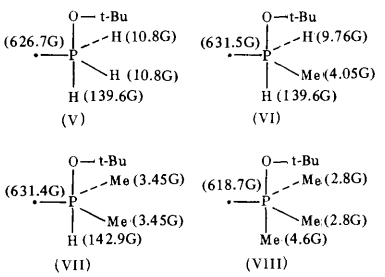


(IV)

This geometry has been established on the basis of the study of EPR spectra and theoretical analysis.

The EPR spectra of the simplest phosphoranyl radicals $\dot{P}F_4$ and $\dot{P}H_4$ show a non-equivalent hyperfine interaction (HFI) of the unpaired electron with the fluorine and hydrogen nuclei. In $\dot{P}F_4$ two fluorine atoms have an HFI constant of 259 G, while two others have a constant of 59 G; in $\dot{P}H_4$ two hydrogen atoms have an HFI constant of 198 G and two others have a constant of 6 G. The high HF constants involving the phosphorus atom (a_P), which amount to 1330 G in $\dot{P}F_4$ and 519.3 G in $\dot{P}H_4$, are associated with the appreciable *s* character of the hybrid *spd* orbital of the unpaired electron. Theoretical analysis[13,14] made it possible to assign the higher values of a_F and a_H to the apical positions and the lower values to the equatorial positions.

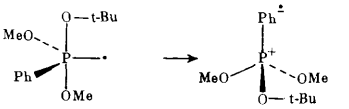
The EPR spectra of $\dot{P}F_4$ and $\dot{P}H_4$ were obtained in solid matrices. However, numerous examples of phosphoranyl radicals with a marked non-equivalence of the apical and equatorial substituents have also been obtained in solution. A number of phosphoranyl radicals in solutions in hydrocarbons have been obtained[6] at a low temperature by the addition of the t-butoxy-radical to the phosphines PH_3, CH_3PH_2, $(CH_3)_2PH$, and $(CH_3)_3P$. The structure of the radicals is shown in the diagram below, the values of the HFI constants being indicated opposite the corresponding atoms:



Thus the structure of phosphoranyl radicals is similar to that of phosphorus(V) compounds (phosphoranes), where the orbital of the unpaired electron acts as one of the substituents. It is therefore of great interest to follow the stereochemistry of the disposition of the substituents in phosphoranyl radicals and to compare it with the stereochemistry of the corresponding phosphoranes.

Roberts and coworkers carried out extensive studies in this field. They established that the chlorine atoms in chlorophosphoranyl radicals occupy apical positions preferentially. The EPR spectra of phosphoranyl radicals of the type t-Bu–O–$(RO)_n\dot{P}Cl_{3-n}$ and t-Bu–O–$R_n\dot{P}Cl_{3-n}$ have been investigated and show electron–Cl HF constants of 30–40 G.[15] In the EPR spectrum of $\dot{P}Cl_4$ the splitting by the apical chlorine atoms is 62 G and that by the equatorial atoms is 7 G.[16]

In the study of phenyl-substituted phosphoranyl radicals the fundamental problem of their structure arose (a TBP or tetrahedral structure). Doubts about the TBP structure of phenyl-substituted phosphoranyl radicals arose in view of the extremely low phosphorus hyperfine interaction constants in the corresponding radicals. Thus $a_P = 9.7$ G for t-Bu–O(Ph)$\dot{P}$·(OMe)$_2$ and we have $a_H^{para} = 9.7$ G, $a_H^{ortho} = 5.5$ G, and $a_H^{meta} = 0.9$ G.[17,18] On the basis of these data, it was suggested that the structure of phenyl-substituted phosphoranyl radicals changes from a TBP to a tetrahedron and that the radical itself acquires the betaine structure:



(IX) (X)

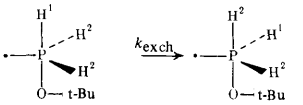
Numerous examples of radicals of this type have been presented in reviews[1,2].

Analysis of the hyperfine structure of the EPR spectra of a large number of phosphoranyl radicals established the apicophilicity series for substituents at the phosphorus atom[19,20]:

$$F, Cl, RC(O)O > CF_3, \overline{CH_2CH_2CH_2C(O)N}, OCN > RO, R_2N > H > H_3C.$$

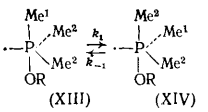
This apicophilicity series agrees on the whole with the electronegativities of the substituents and is consistent with the general characteristics established in the study of phosphorus(V) compounds. The study of the EPR spectra of phosphoranyl radicals over a wide temperature range showed that, with increase of temperature, an interchange of the ligand positions at a frequency of 10^6–10^8 s^{-1} is observed in some cases.

Krusic and Meakin[21] measured the frequency of exchange between two types of hydrogen atoms in t-BuO$\dot{P}H_3$ and the corresponding activation barrier and found that $\Delta G^{\neq} = 5.3$ kcal mole^{-1} at −75 °C and $k_{exch} = 3 \times 10^6$ s^{-1} at −80 °C:



(XI) (XII)

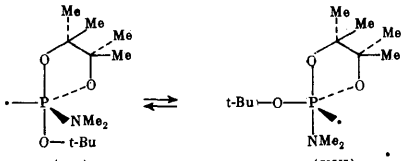
A similar example is provided by the t-butoxytrimethylphosphoranyl radical, in which the methyl groups change positions[22]:



(XIII) (XIV)

$k_1 = 4 \times 10^6$ s^{-1} at −70 °C. The temperature dependence of the rate constant is of the form $\lg k_1 = (10.4 \pm 1) - (13 \pm 4)$ kcal mole^{-1} θ^{-1}, where $\theta = 2.3\,RT$ kcal mole^{-1}. The rate of ligand exchange involving methyl groups is independent of the nature of the alkoxy-group (R = Et, t-Bu, or t-pentyl). It has been stated that[18] in certain trimethyl (R,R′) phosphoranes similar methyl exchange frequencies are observed.

Another example where the ligands change positions is provided by the aminophosphoranyl radical[23]:



(XV) (XVI)

In contrast to the previous case, the states of the radicals (XV) and (XVI) are energetically different. The spectroscopic characteristics of the radicals (XV) and (XVI) differ appreciably:

Radical	(XV)	(XVI)
a_P, G	849	784
a_N, G	8.4	24

At −120 °C the ratio of the radical concentrations is (XVI)/(XV) = 0.25. With increase of temperature, the rate of interconversion of radicals (XV) and (XVI) increases, which is manifested by a characteristic broadening of the hyperfine structure (HFS) components associated with the nitrogen nuclei. Agreement between the experimental and calculated spectrum was achieved for $k_1 = 2.0 \times 10^7$ s^{-1}, $k_{-1} = 8.0 \times 10^7$ s^{-1}, and (XVI)/(XV) = 0.25 at −120 °C and $k_1 = 10^8$ s^{-1}, $k_{-1} = 3.3 \times 10^9$ s^{-1}, and (XVI)/(XV) = 0.3 at −80 °C.[23]

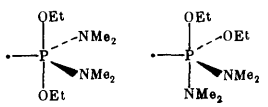
The following equation holds in the range between −120 °C and −80 °C:

$$\lg k_1 = 10.7 - 2.4/\theta,$$

where $\theta = 2.3\,RT$.

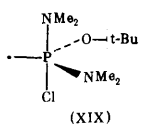
The temperature dependence of the equilibrium constant K = (XVI)/(XV) in the range from −160° to −120 °C makes it possible to determine $\Delta H^\circ \cong \Delta G^\circ \cong 0.4$ kcal mol^{-1} and $\Delta S^\circ \cong 0$.

The interaction of EtO· with $EtOP(NMe_2)_2$ gives rise to two radicals, namely (XVII) and (XVIII):



(XVII) (XVIII)

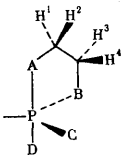
At −126 °C the concentration ratio [XVIII]/[XVII] = 6. At −140 °C each component of the phosphorus doublet in the spectrum of radical (XVIII) is split into a 1 : 1 : 1 triplet ($a_N = 11.5$ G). With increase of temperature to −110 °C, the three lines are replaced by five lines with a splitting of 7.5 G, and at −90 °C their intensity ratios become close to 1 : 2 : 3 : 2 : 1. These changes are attributed to the rapid exchange between the NME_2 groups in the apical and equatorial positions in the radical (XVIII) ($k_{exch} = 10^8$ s^{-1} at −110 °C).[23] In the radical[24]



(XIX)

the exchange of the dimethylamino-groups takes place at a rate of 2×10^7 s^{-1}, i.e. is somewhat slower than in the radical $(EtO)_2\dot{P}(NMe_2)_2$.

In the EPR spectra of the radicals of 1,3,2-dioxaphospholane and 1,3,2-diazaphospholane derivatives[23,24]

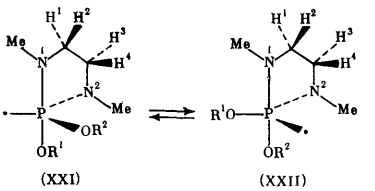


(XX)

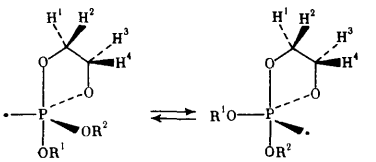
where A = B = O or A = B = N–Me, a hyperfine splitting by the quasi-apical ring protons H^1 or H^2 is observed and can serve as a source of information about the stereochemical mobility of these radicals.

For the above radicals, different stereochemical reactions are possible:

Exocyclic process 4*M*

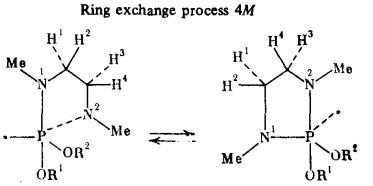


(XXI) (XXII) (1)

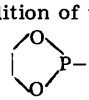


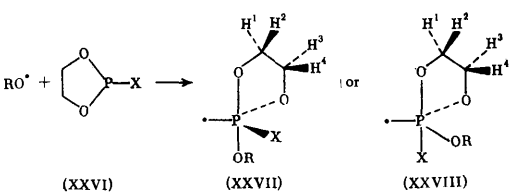
(XXIII) (XXIV) (2)

Ring exchange process 4*M*



(XXI) (XXV)

The addition of the alkoxy-radical RO· to 1,3,2-dioxaphospholane  as well as 1,3,2-diazaphospholane can proceed stereospecifically depending on the electronegativity of X:

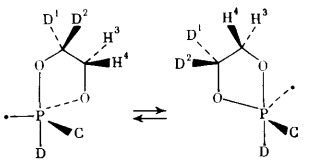


(XXVI) (XXVII) (XXVIII)

At a low temperature hyperfine splitting by one H^1 or H^2 proton is observed in the spectra of radicals formed from 1,3,2-dioxaphospholane when RO and X have markedly different apicophilic properties; the hyperfine interactions with the H^1 and H^2 protons are different owing to the differences between the steric orientations of these protons relative to the unpaired electron. When X and RO are identical, hyperfine splitting by the two equivalent protons ($a_H = 2$ G), caused by by the rapid exchange via reaction (2), is observed.

For C = D = OEt, the exocyclic process 4*M* takes place with $k_{exch} > 6 \times 10^9$ s^{-1} over the entire experimental temperature range. When C = OEt, D = Cl, and Cl is much more apicophilic than OEt, the groups change positions in the ring. The same process is observed for D = $MeCO_2$, CF_3CO_2, BzO, and $(EtO)_2P(O)O$. On the other hand, if D = F, OCN, and $CH_2(CH_2)_2C(O)N$, changes in line form are not observed, which indicates the absence of ligand position interchange[23,24].

The exocyclic 4*M* process and the exchange process in the ring were resolved using 4,4-dideutero-1,3,2-dioxaphospholanes. The resolution was achieved on the basis of the different HFS changes in spectra of the protonated and 4,4-dideutero-derivatives of the radicals when the temperature is varied:

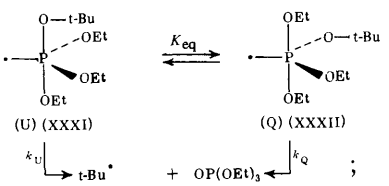


(XXIX) (XXX)

In the interchange of positions in the rings of radicals of 4,4-dideutero-derivatives of 1,3,2-dioxaphospholanes, the spectra are altered; with increase of temperature, there is a transition from the superposition of the doublet due to one proton in one pseudoapical CH_2 group (with a splitting of 4 G) on to a singlet due to one pseudoapical CD_2 group to a doublet with a splitting of 2 G, which corresponds to rapid migrations of the CH_2 and CD_2 groups between the apical and equatorial positions. In the exocyclic 4*M* process involving the protonated form there should be a change from a doublet with a splitting of 4 G to a 1:2:1 triplet with a splitting of 2 G. For the deutero-derivative at a high temperature, a singlet due to the deutero-group should be superimposed on the triplet and the resultant spectrum should have intensity ratios of 1:6:1, which has been observed experimentally[24].

The results show that the ligand positions are interchanged in the phosphoranyl radicals; the rate and nature of these processes are determined by the structural characteristics of the radicals.

The study of ligand exchange processes in phosphoranyl radicals involves the investigation of the chemical reactions of these radicals. Thus the mobility of the leaving group in the apical and equatorial positions is very important for the β-elimination reaction. The equilibrium between the stereoisomers can influence the observed β-elimination rate constant in the following way:



(U) (XXXI) (Q) (XXXII)

$$k_{obs} = (k_U + k_Q K_{eq})/(1 + K_{eq}).$$

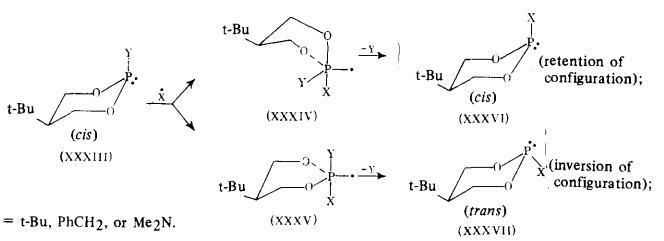
Thus in the elimination of the t-butyl radical with equilibrium between the stereoisomers, cleaved at different rates, will influence significantly the rate of the chemical reaction.

Kinetic studies have revealed definite stereochemical relations for α- and β-elimination reactions involving phosphoranyl radicals[22,25-28]. It has been suggested that in tetraalkoxyphosphoranyl radicals β-elimination takes place preferentially in the equatorial position, while α-elimination in alkoxyalkylphosphoranyl radicals takes place from the apical position[22,25].

A definite relation has been observed between the stability of phosphoranyl radicals and the change in the number of alkyl and alkoxy-groups in the radical[27]. The maximum stability is observed when the numbers of alkyl and alkoxy-groups are equal. This is attributed to the fact that, in conformity with their more pronounced apicophilic properties, the alkoxy-groups are located in the apical positions, while the alkyl groups are in the equatorial positions[27]. Thus the groups involved in α- and β-elimination are located in chemically inactive positions.

Stereochemical transformations are important in homolytic substitution reactions involving phosphorus(III) compounds. Bentrude and coworkers[29,30] studied the stereochemistry of radical substitution and oxidation of phosphorus(III) compounds[29,30] In the course of the investigation of these reactions the problem arose of the configurational stability of the phosphoranyl radicals formed and of its influence on the yield of the isomers.

The stereochemistry of the substitution reaction was studied in the following example[29];

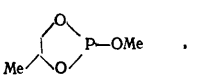


(*cis*) (XXXIII) (XXXIV) (XXXV) (*cis*) (XXXVI) (retention of configuration); (*trans*) (XXXVII) (inversion of configuration);

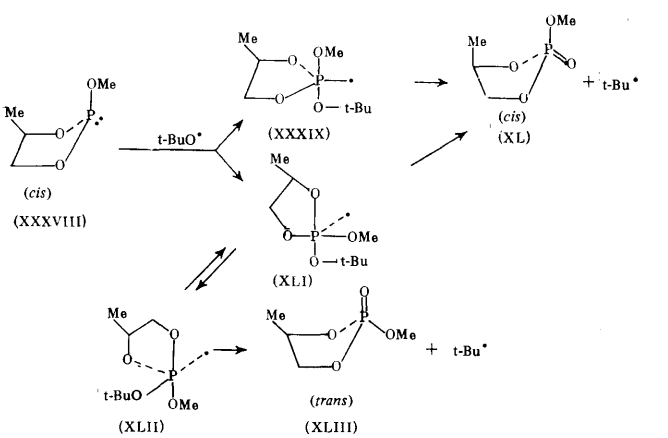
Y = t-Bu, $PhCH_2$, or Me_2N.

The radical X· was Me_2N·, obtained in the decomposition of the tetrazene $Me_2NN{=}NNMe_2$ under the influence of ultraviolet light. These reactions proceed with a high degree of stereoselectivity and lead mainly to inversion of configuration. It has been suggested that the disposition of X and Y in the apical positions in structure (XXXV) is responsible for the observed inversion of configuration.

The stereochemistry of the oxidation reactions of phosphorus(III) compounds has been studied[30] for the compound

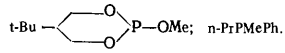


It was found that the reaction is stereospecific and proceeds with retention of configuration. The retention of configuration implies that the β-decomposition of phosphoranyl radicals is faster than the ligand exchange (XLI) → (XLII):



(*cis*) (XXXVIII) (XXXIX) (*cis*) (XL) (XLI) (XLII) (*trans*) (XLIII)

The retention of configuration was observed previously[31] in the study of the oxidation of the following compound:

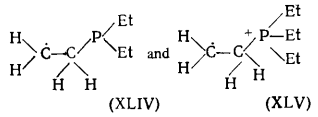


The stereospecificity of the above reactions implies a "memory" of the pathways followed in the formation of the phosphoranyl radical. On the other hand, the intramolecular migrations of the ligands should abolish this effect. In order to observe the "memory" effect, Hay and Roberts[32] obtained radicals of the type $(RO)_2\dot{P}(OR^1)OR^2$ in two ways: by the reaction between $(RO)_2POR^1$ and $R^2O^\cdot$ and by the reaction between $(RO)_2POR^2$ and $R^1O^\cdot$. The relative yields of the radicals $R^{1\cdot}$ and $R^{2\cdot}$, formed as a result of β-elimination, are independent of the source of the intermediate phosphoranyl radicals. It follows from these date that the tetraalkoxyphosphoranyl radicals do not retain a "memory" of their origin. The authors[32] concluded that the high rate of exchange of the alkoxy-ligands in phosphoranyl radicals precludes the observation of a "memory" effect in reactions involving the oxidation of phosphites by alkoxy-radicals. It follows from the above results[32] that the "memory" effects observed previously by Bentrude and coworkers in the oxidation of phosphites by alkoxy-radicals were not confirmed in their repeated investigations.

Thus the influence of the interchange of ligand positions in phosphoranyl radicals on the yield of the stereoisomers of the final products depends on the rates of these processes and on the rate of decomposition of the phosphoranyl radicals.

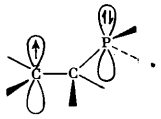
IV. CONFORMATION OF PHOSPHORUS-SUBSTITUTED RADICALS

There exists a wide class of phosphorus-containing radicals in which the unpaired electron is localised at carbon atoms in the β-positions relative to the phosphorus atom. In such radicals the hyperfine interaction of the unpaired electron with the phosphorus nucleus depends significantly on their geometrical structure. Symons and coworkers[33,35] investigated the EPR spectra of the radicals

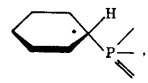


(XLIV) (XLV)

obtained by the γ-irradiation of powdered specimens of the corresponding phosphines and phosphonium salts at 77 K. The isotropic HFI constants calculated from the spectra proved to be $a_P = 251$ G for (XLIV) and $a_P = 120$ G for (XLV). The much higher values of a_P for the former radical can be accounted for by the homoconjugation of the $2p_z$ unpaired electron orbital and the phosphorus orbital occupied by the lone electron pair:

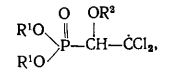


The mechanism of the delocalisation of the unpaired electron over the quadrivalent phosphorus atom in radical (XLV) is not so evident. Presumably the transfer of unpaired electron spin density to the quadrivalent phosphorus atom proceeds via $p_\pi - d_\pi$ conjugation. However, Symons believes[35] that this mechanism is unlikely, since it is inconsistent with the isotropic nature of the HFI constant. As an alternative hypothesis, a hyperconjugation mechanism involving the C–P bond was postulated. The strong hyperfine interaction with the phosphorus nucleus in the cyclohexadienyl radical



obtained by the γ-irradiation of phenylphosphonous acid PhPO(O)H at 77 K, can be accounted for by an analogous mechanism[36]. An isotropic EPR spectrum was observed for this radical and the following HFI constants were calculated from it: $a_H = 40$ G for the methylene proton, $a_H = 10$ G for the *ortho*- and *para*-protons of the benzene ring, and $a_P = 200$ G.

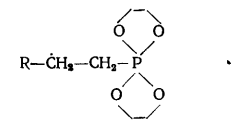
Damerau and coworkers[37–40] obtained radicals of the type



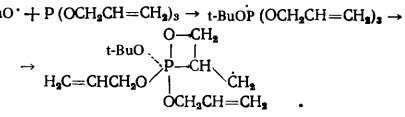
in aqueous solution for which a_P varies from 60 to 69 G, depending on the size of R^1 and R^2, and in addition it depends on temperature. The latter finding is related to the angular dependence of the phosphorus hyperfine interaction constant and constitutes significant evidence in support of the hyperconjugation mechanism[37].

A number of β-phosphorus-substituted alkyl radicals have been obtained in the liquid phase by the addition of phosphorus-centred radicals to unsaturated compounds. For such radicals, the phosphorus hyperfine interaction constant is in the range from 30 to 180 G and is determined mainly by the conformation of the radical. Thus Beckwith[41] investigated the EPR spectra of the radicals formed as a result of the addition of HPO_2, $H\dot{P}O_3$, and $\dot{P}O_3^{2-}$ to unsaturated compounds of the type $R_2C=CR'_2$, where R, R' = H, CH_3, CO_2H, or the aci-anions of nitroalkanes ($H_2C=NO_2$). The phosphorus hyperfine interaction constants in the resulting adducts varied in the range from 60 to 100 G; the phosphorus hyperfine interaction is treated within the framework of the hyperconjugation mechanism with participation of 3*d* orbitals. Radicals of an analogous type were also obtained by Gilbert et al.[42] The phosphorus hyperfine interaction constants in these adducts vary with temperature, which shows that they depend on the conformation.

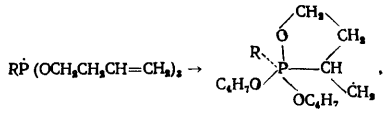
Davies et al.[43] investigated the EPR spectra of the radicals formed following the addition to the double bond of dialkoxyphosphonyl radicals of the type $(RO)_2\dot{P}O$, for which the phosphorus hyperfine interaction constant in the range 94–112 G and this corresponds to β-phosphorus-substituted alkyl radicals. Radicals have been obtained similarly by the addition of spirophosphoranyl radicals to olefins[44]:



Davies et al.[45] also observed an interesting reaction involving the intramolecular addition of the phosphoranyl radical to the double bond of an olefinic substituent. Phosphoranyl radicals containing 2-alkenyloxy-substituents cyclise to oxaphosphotans, in which the unpaired electron is localised at an exocyclic carbon atom:



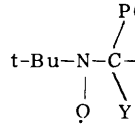
Depending on the substituents, a_P varies from 176 to 199 G. On the other hand, if the phosphorus atom is linked to 3-alkenyloxy-groups, cyclic oxaphospholan radicals are formed;



for which the isotropic HFI constant is $a_P = 127-136$ G.[45]

From the standpoint of conformational analysis, more or less stable nitroxy-radicals incorporating phosphorus-containing fragments proved to be very interesting. Il'yasov and coworkers[46] obtained a large number of such radicals using 2-methyl-2-nitrosopropane as the spin-trapping agent and analysed in detail their EPR spectra. The presence of one or two magnetic phosphorus nuclei in nitroxy-radicals of this kind leads to the appearance of hyperfine interaction of the unpaired electron with these nuclei; the HFI constant can serve as a criterion of the conformation of the molecules and of its dependence on the steric and electronic effects of the substituents. Additional information is provided by the hyperfine interaction β-proton constant when a β-proton exists.

Table 1. The HFI constants for radicals of the type



obtained in a 1:3 (by volume) water–alcohol mixture at room temperature.

No.	Y	a_N, G	a_P, G	a_H, G
(XLVI)	$P(O)(OEt)_2$	14.2	42.1; 42.5	1.6
(XLVII)	H	16.3	45.0	10.3 (2H)
(XLVIII)	COOMe	14.3; 14.2	29.2; 28.8	2.0; 2.4
(XLIX)	COOEt	14.3; 14.3	28.7; 28.5	2.3; 2.5
(L)	$COOC_3H_7$	14.3; 14.3	28.8; 28.4	2.4; 2.8
(LI)	COC_6H_5	14.3; 14.3	22.6; 22.5	4.7; 4.8

Table 1, taken from the paper by Il'yasov and coworkers[46], lists the EPR data for nitroxy-radicals with phosphorus-containing fragments. We shall consider the nitroxy-radical (XLVI), which incorporates two phosphorus atoms. The presence of two different ^{31}P hyperfine interaction constants and the low value of the single β-proton hyperfine interaction constant ($a_H = 1.6$ G) are striking. These data agree with the conformation proposed by the authors[46], which has the form, in terms of the Newman projection, illustrated in Fig.1. The low values of the β-proton hyperfine interaction constant shows that the angle between the direction of the C–H bond and the axis of the $2p_z$ orbital of the unpaired electron is close to 90° ($\alpha \to 0$). For the same reason, the difference between the two phosphorus hyperfine interaction constants is only 0.4 G. With increase of temperature, the phosphorus HFI constants become even more similar but the complete equivalence of the two phosphorus nuclei could not be attained up to 100 °C. A further increase of temperature is limited owing to the inadequate stability of the radical.

For the phosphononitroxy-radical (XLVII), which has one phosphorus atom and two β-protons, there is a complete equivalence of the protons even at room temperature. It might have been thought that the equivalence of the two protons is due to the free rotation of the $C(P)H_2$ fragment about the C–N bond. However, the experimental value of the constant $a_H^\beta = 10.3$ G, the lower limit of which is 13 G according to Chapelet-Letournux et al.[47], is inconsistent with this hypothesis. In order to account for the equivalence of the β-protons in radical (XLVII), the authors[46] therefore postulated a rapid transition between two conformations, which would lead to the averaging of the hyperfine interaction with the protons H_a and H_b (Fig.2).

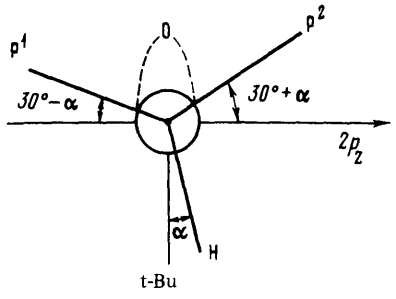


Figure 1. Schematic representation of one of the conformations of the nitroxy-radical (XLVI).

The two conformations are energetically equivalent and the average value of a_H under the conditions of a rapid transition is therefore determined by the simple relation:

$$\langle a_H \rangle = \frac{1}{2} B_2^N \rho_N^\pi (\langle \cos^2 90° \rangle + \langle \cos^2 30° \rangle)$$

where $\beta_2^N \rho_N^\pi = 26 \pm 2$ G is characteristic of the majority of nitroxy-radicals[47].

Stone and Maki[48] developed a theory, according to which the the values of $\langle \cos^2\theta \rangle$ are related to the barrier V_0 to the conformational transitions. Using conclusions from this theory, Il'yasov and coworkers[46,49] showed that the experimental β-proton hyperfine interaction constant in radical (XLVII) $a_H^\beta = 10.3$ G corresponds to the barrier $V_0 = 2$ kcal mole^{-1}.

Table 1 shows that a_P for the phosphononitroxy-radicals (XLVIII)–(LI) is greatly reduced compared with the values for radicals (XLVI) and (XLVII), which indicates an increase of the angle θ_P, which can be estimated from the β-proton splitting. For example, $\langle \theta_H \rangle = 80°$ when $V_0 = 3$ kcal mole^{-1} has been found for the nitroxy-radical (L) from the expression

$$a_H^\beta = \rho_N^\pi (B_0 + B_2 \langle \cos^2 \theta_H \rangle)$$

on the assumption that $B_0 \cong 0$ [50] and using the experimental value $a_H^\beta = 2.8$ G. Here it is evident that $\langle \theta_P \rangle = 40°$. The expression

$$a_P^\beta = \rho_N^\pi (B_0 + B_2^P \langle \cos^2 \theta_P \rangle)$$

with $B_0 \cong 0$ and $\rho_N^\pi B_2^P = 56$ G [46] yields $a_P = 31$ G, which is very close to the experimental value $a_P = 28.8$ G.

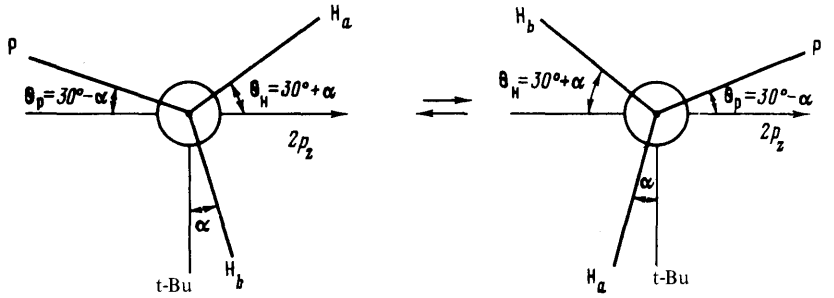
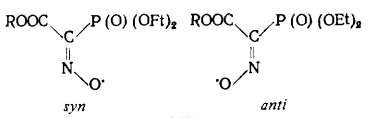


Figure 2. Schematic illustration of the conformational transitions in the nitroxy-radical (XLVII).

With decrease of temperature, the EPR spectra of the two forms of the nitroxy-radicals (XLVIII)–(LI) are resolved. In their study of the temperature dependence of the concentration of the two forms, Il'yasov and coworkers[46] estimated the difference between the energies of these forms. Thus $\Delta H = -0.36$ and -0.77 kcal mole^{-1} for radicals (XLVIII) and (L) respectively.

The unpaired electron in the nitroxy-radicals examined above is localised mainly in the 2*p* orbitals of the nitrogen and oxygen atoms. The angular dependence of the ^{31}P hyperfine interaction constant shows that the transfer of spin density to the phosphorus atom proceeds via the hyperconjugation mechanism.

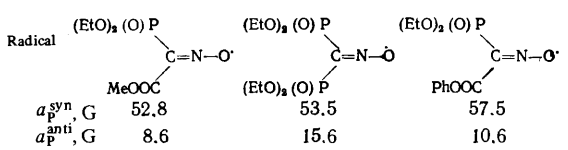
Il'yasov and coworkers[51] obtained phosphorus-containing iminoxy-radicals of another type:



(LII)

A characteristic feature of these radicals is the possibility of spin density transfer to the phosphorus atom via the system of σ bonds, since the unpaired electron is located mainly in the σ plane. The EPR spectra showed that in solution the radicals (LII) exist in the form of stable *syn*- and *anti*-isomers with markedly different HFI constants and *g*-factors. The spectroscopic parameters of some of the radicals investigated are listed in Table 2, which shows that the phosphorus hyperfine interaction constant is much greater for the *syn*-isomers than for the *anti*-isomers. The authors[51] found from the temperature dependence of the relative concentrations of the isomers that the equilibrium is displaced towards the *anti*-isomer, which is thermodynamically more favourable ($\Delta H = -1.1$ kcal mol^{-1}).

It is interesting to compare the influence of the electronic properties of substituents on the phosphorus hyperfine interaction constant in the *syn*- and *anti*-isomers. For this purpose, we shall compare the values of a_P for the following three radicals[49]:



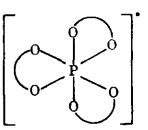
The data show that the electronic properties of the substituents have a greater influence on the a_P constants for the *anti*-isomers. One can therefore postulate that in these isomers the σ–π polarisation and the delocalisation of the unpaired electron over the σ bonds make a significant contribution to the phosphorus hyperfine interaction. In the *syn*-isomers the spin density is largely transmitted via a mechanism involving the direct overlap of the orbitals of the unpaired electron with the σ orbitals of the C–P bond.

Table 2. Parameters of the EPR spectra of radicals (LIII).

R	Isomer	a_N	a_P	g^{iso}
Me	*syn*	32.4	52.8	2.0038
	anti	32.4	8.6	2.0041
Et	*syn*	32.5	52.9	2.0038
	anti	32.8	8.5	2.0041
Pr	*syn*	32.3	53.0	2.0038
	anti	32.3	8.6	2.0041

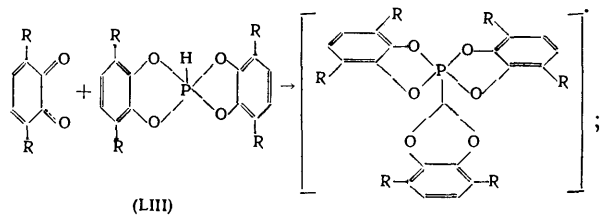
V. TAUTOMERISM OF PHOSPHORANYLPHENOXY-RADICALS

The previous sections dealt with radicals in which the free valence was localised either in the hybrid orbitals of the phosphorus atom (phosphoranyl radicals) or in the *p* orbitals of the carbon or oxygen atoms linked directly to the phosphorus atom. Here we shall deal with radicals where the free valence migrates between the oxygen atoms of catechol ligands attached to the phosphorus atom. In these radicals the phosphorus is formally hexacoordinate[8]:



The arcs drawn between two oxygen atoms represent different *ortho*-phenylene groups[53]. The migration of the free valence in these radicals involves the stereochemical features of quinquevalent phosphorus (see above).

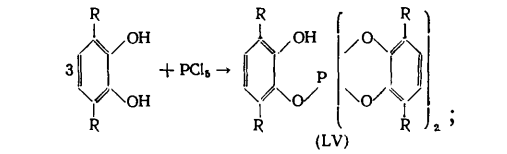
The photoinitiated reaction of 3,6-di-t-butyl-o-quinone with the spirophosphorane (LIII) leads to the formation of an analogue of the phosphate anion (LIV) which carries an unpaired electron instead of a negative charge[8]:



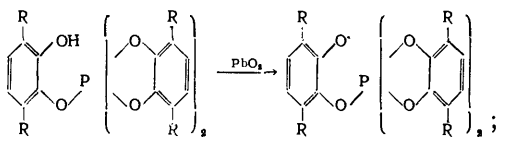
(LIII) (LIV)

R = t-Bu.

The same free radical can be obtained by the oxidation with lead dioxide of the hydropyrophosphorane (LV), which is synthesised in its turn from 3,6-di-t-butylcatechol and phosphorus pentachloride[58]:



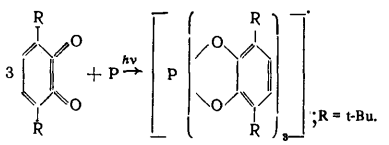
(LV)



(LIV)

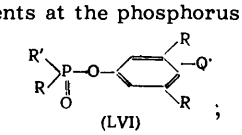
R = t-Bu.

Radical (LIV) is also obtained by the photoaddition of 3,6-di-t-butyl-o-quinone to elemental phosphorus[53]



R = t-Bu.

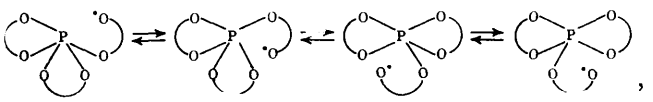
Solutions of the free radicals (LIV), obtained in different ways, exhibit identical EPR spectra with similar temperature variations. Fig.3 illustrates the EPR spectrum of radical (LIV) in ether. At 20 °C the spectrum consists of a doublet with a phosphorus splitting of 4.0 G; each component of the doublet consists of seven lines with the intensity ratios 1:6:15:20:15:6:1 (the splitting by the six equivalent protons is $a_H = 1.45$ G). Thus the unpaired electron interacts with all six protons of the three benzene rings and with the phosphorus atom. The spin density at the phosphorus atom itself is then low: the splitting constant of 4.0 G can be compared with the splitting in the spectrum of the phenoxy-radical (LVI), which amounts to 6–7 G (depending on the nature of the substituents at the phosphorus atom):[52]



(LVI)

R = t-Bu.

One must assume that the unpaired electron spin density is localised mainly in the catechol fragments. With decrease of temperature, the components are broadened at −80 °C the spectrum is converted into a doublet of triplets (Fig.3)—a doublet due to the phosphorus atom and a triplet with a splitting of 4.35 G due to the two protons of one ring[8,53]. Thus at 20 °C and above the free valence "migrates" between all six equivalent oxygen atoms:



etc., while at low temperatures the EPR spectra reveal the interaction with the protons of only one ring.

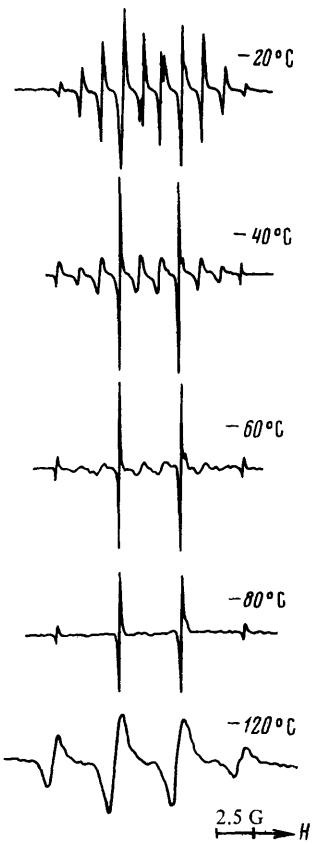


Figure 3. The EPR spectrum of radical (LIV) in ether at different temperatures.

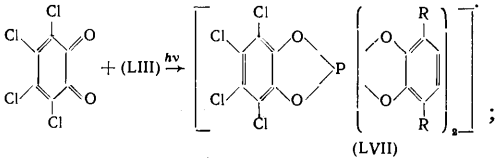
The temperature-induced changes in the spectrum have been studied in greater detail in solution in ether[53]. At low temperatures a quartet splitting was observed (by two protons and a phosphorus atom; 1:3:3:1), but the intermediate spectra are particularly distinct and convenient for the kinetic analysis of the exchange process. It was found that, with decrease of temperature, both interligand and intraligand exchange reactions are retarded to approximately the same extent, but, whereas the interligand exchange is already "frozen", the rapid-exchange spectral conditions are maintained for the intraligand exchange, which

has approximately the same intrinsic frequency, and we observe splitting by two protons. The exchange frequency is

$$\nu_{exch}=3.4\cdot10^{12}\exp[(-4300\pm500)/RT]\ s^{-1}.$$

The frequency of the "migration" of the unpaired electron at 20 °C (toluene) is $2.2\times10^9\ s^{-1}$. Thus at 20 °C the unpaired electron passes through all six oxygen atoms with a jump frequency of 2×10^9 per second.

The interaction of the spirophosphorane (LIII) with *o*-chloranil on irradiation also gives rise to the radical (LVII), which contains a formally hexacoordinate phosphorus atom[8]:

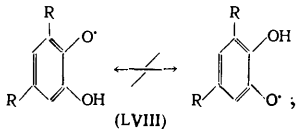


(LVII)

R = t-Bu.

The presence of four chlorine atoms in a single ring suggested that the unpaired electron spin density is preferentially concentrated in two other catechol fragments and at the phosphorus atom. Indeed the 1:3:3:1 quartet is observed in the EPR spectrum at −80 °C (splitting by the phosphorus atom and the two protons—interaction of the unpaired electron with the protons of a single ring), while on increase of temperature the spectrum is transformed into a doublet of 1:4:6:4:1 quintets corresponding to four equivalent protons. The splitting by phosphorus is 4.35 G and that in the quintet is 2.18 G#. It is remarkable that the splitting in the quintet is 1.5 times greater than that (1.45 G) in the septet and the symmetrical radical (LIV). The explanation is that the same spin density in the former case is distributed over six protons, while in the latter case it is distributed over four protons. Hence the entire spin density, previously distributed over three ligands, is now concentrated in two ligands, i.e. we have a "four-well" system[8].

Hitherto we have considered only radicals with a symmetrical ligand—the 3,6-di-t-butylphenylenedioxy-group. A series of studies have been carried out with an asymmetric ligand—the 3,5-di-t-butylphenylenedioxy-group. In the first place one should note that neither hydrogen nor deuterium migrate in the corresponding semiquinone radical—the 4,6-di-t-butyl-2-hydroxyphenoxy-radical (LVIII)—up to 200 °C:[54]

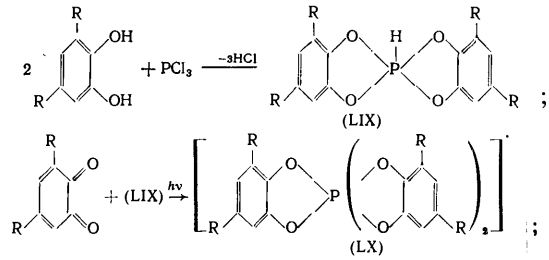


(LVIII)

R = t-Bu.

From our point of view, this can be explained by the non-equivalence of the oxygen atoms; the transfer of the proton to the oxygen atom adjoinging the t-butyl group actually becomes relatively unfavourable owing to the steric shielding by this group§. One could therefore assume that there is no intramolecular exchange in "multiwell" systems containing this fragment.

The photoinitiated reaction of 3,5-di-t-butyl-*o*-quinone with the spirophosphorane (LIX), obtained from 3,5-di-t-butylcatechol and phosphorus trichloride, leads to the formation of the free radical (LX) with three 3,5-di-t-butylphenylenedioxy-ligands[56]:

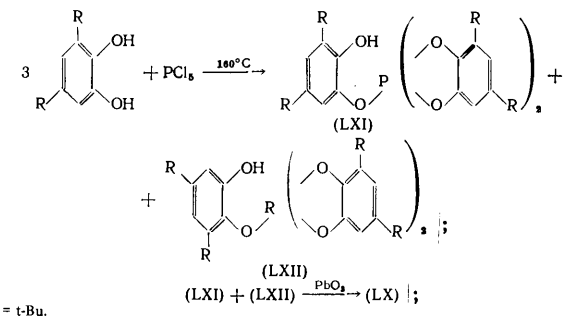


(LIX)

(LX)

R = t-Bu.

The same radical is formed in the oxidation with lead dioxide of a mixture of the spirophosphoranes (LXI) and (LXII) obtained from 3,5-di-t-butylcatechol and phosphorus pentachloride. When these reactants are fused together, a mixture of the isomers (LXI) and (LXII) is produced; on oxidation, both isomers give rise to the same three-ligand radical (LX):[56]

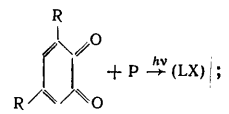


(LXI)

(LXII)

R = t-Bu.

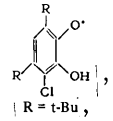
The same radical is formed in the photoinitiated reaction of elemental phosphorus with 3,5-di-t-butyl-*o*-quinone[53]:



R = t-Bu.

At a low temperature (−100 °C, toluene) the EPR spectrum of this radical consists of a triplet due to the hyperfine interaction with the proton in the 5-position and the phosphorus

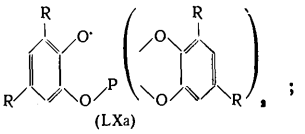
§ This does not imply that the absence of symmetry in the radical inevitably leads to the absence of migration. This happens only for large energy differences between different forms. In other cases, for example, for the 4,6-di-t-butyl-3-chloro-2-hydroxyphenoxy-radical



all the characteristics of hydrogen-tropic tautomerism[55] (non-degenerate!) are observed.

Radical (LVII) is unstable and disproportionates even at −40 °C, which complicates the spectrum.

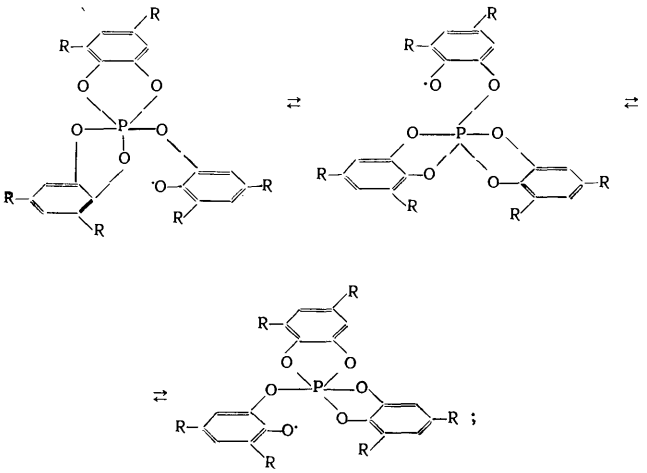
atom ($a_H^5 = a_P = 4.35$ G). Under these conditions, the structure (LXa), with the unpaired electron localised at one of the oxygen atoms of one of the ligands, should be assigned to this radical:



(LXa)

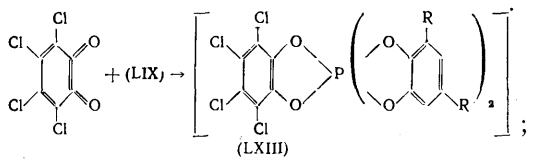
R = t-Bu.

With increase of temperature, additional broad lines appear and at −40 °C a doublet of 1:3:3:1 quartets arises (a_H = 1.45 G)—the unpaired electron interacts with three equivalent protons of three benzene rings; this is a "three-well" system, with one well for each ligand, and only interligand exchange takes place[56]:



R = t-Bu.

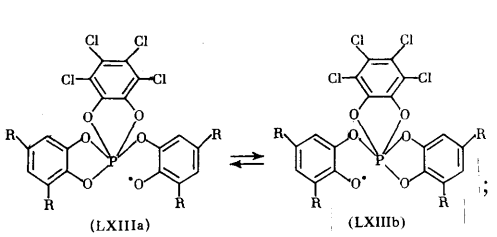
If *o*-chloranil is involved in the reaction with the spirophosphorane (LIX) instead of di-t-butyl-*o*-quinone, a new three-ligand radical (LXIII) is formed[56]:



(LXIII)

R = t-Bu.

As noted previously, the *o*-chloranil ligand is in this case excluded from the exchange. The EPR spectrum at −100 °C in toluene therefore shows a 1:2:1 triplet ($a_H^5 = a_P = 4.35$ G) and at −40 °C a doublet of 1:2:1 triplets ($a_H = 2.17$ G). In the first case there is a "frozen" structure (LXIIIa) or (LXIIIb), while in the second case there is rapid interligand exchange with splitting by one proton in each ligand:



(LXIIIa) (LXIIIb)

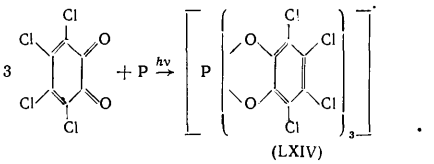
R = t-Bu.

For the low-temperature spectrum (splitting by one proton), the splitting constant is 4.35 G and in the "two-well" system at −40 °C it amounts to 2.17 G, i.e. the splitting by each proton is smaller by a factor of two, while in the "three-well" system the contant is 1.45 G, i.e. the splitting is smaller exactly by a factor of three[56].

The exchange process involving thse radicals belongs to the category of rapid processes. At 20 °C the exchange frequency is 1.2×10^9 s^{-1} for the "three-well" system and 4×10^9 s^{-1} for the "two-well" interligand system[56]. The kinetic parameters of the exchange reactions (s^{-1}) are as follows:

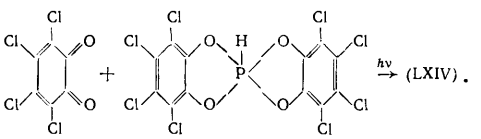
$$\nu_{(LX)} = 4.8 \cdot 10^{12} \exp\{-(4800 \pm 500)/RT\}\ s^{-1};$$
$$\nu_{(LXIII)} = 2 \cdot 10^{14} \exp\{-(6300 \pm 500)/RT\}\ s^{-1}.$$

The reaction of white phosphorus with *o*-chloranil under irradiation gives rise to the highly chlorinated three-ligand radical (LXIV):[53]



(LXIV)

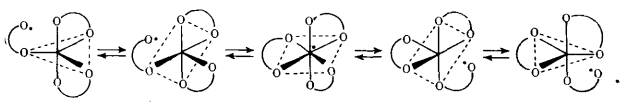
The same radical is formed in the photochemical reaction of *o*-chloranil with a perchlorospirophosphorane:



The EPR spectrum of this radical naturally contains only one doublet with a splitting of 3.4 G by the phosphorus atom, because the hyperfine interaction with the chlorine nuclei is not manifested. Nothing can be said about the characteristic features of this radical.

The examples of the free valence and bond exchange reactions examined involve intramolecular radical substitution at a pentacoordinate phosphorus atom of the "synchronous" type[57]. The instantaneous structure of the given radicals, with the localisation of the unpaired electron at one oxygen atom, consists of a trigonal bipyramid. The pseudorotation characteristic of pentacoordinate phosphorus compounds, as a result of which the apical and equatorial positions change places, has a broad frequency spectrum which depends on the nature of the substituents in these compounds. In particular, the pseudorotation frequencies for hydroxyspirophosphoranes are $>10^5$ s^{-1} and the energy barrier is <8 kcal mole^{-1}.[10]

Thus the kinetic equivalence of the intra- and inter-ligand exchange processes can be indissolubly linked to pseudorotation. When the trigonal bipyramid passes through the stage of a tetragonal pyramid on pseudorotation, it is attacked from the "rear" (from the side of the base) by an oxygen atom with an unpaired electron. The intermediate octahedral structure constitutes in this case a transition state[53]:



bipyramid pyramid octahedron pyramid bipyramid

If the pseudorotation frequency is higher than the rate of intramolecular exchange, then any oxygen atom can be located at the apical positions of the bipyramid or at the

vertex of the tetragonal pyramid (positions subjected to radical attack). Evidently the intra- and inter-ligand exchange reactions should be indistinguishable from this point of view. However, it can be assumed that the octahedral configuration constitutes a transition state in which all the oxygen atoms become equivalent and the loss of any of them is equally probable, which is consistent with experimental data; the requirement for high pseudorotation frequencies of the bipyramid then loses significance. Both concepts are evidently fairly speculative in view of the lack of correct pseudorotation frequencies for pentacoordinate phosphorus compounds (above 10^5 s^{-1}). One can only say that the low phosphorus HFI constant and the similarity of the unpaired electron density distribution in the radicals under consideration (when the interligand exchange is "frozen") to that in semiquinone radical-anions with a similar structure indicates the localisation of the unpaired electron almost entirely in the catechol ligand. This constitutes important evidence in support of an octahedral transition state in the intramolecular free valence and bond exchange reactions considered.

The above mechanism apparently determines the nature of the exchange involving radicals containing non-equivalent and asymmetric ligands. The intra- and inter-ligand exchange processes are then manifested as a result of radical attack on the phosphorus atom and the equal probabilities of the appearance of a free valence at any of the oxygen atoms (for symmetrical and identical ligands).

REFERENCES

1. V.V.Pen'kovskii, Uspekhi Khim., **44**, 969 (1975) [Russ. Chem.Rev., No.6 (1975)].
2. P.Schipper, E.H.J.H.Jansen, and H.M.Buck, Topics in Phosphorus Chemistry, **9**, 407 (1977).
3. R.W.Fessenden and R.H.Schuler, J.Chem.Phys., **45**, 1845 (1966).
4. W.Nelson, G.Jackel, and W.Gordy, J.Chem.Phys., 52, 4572 (1970).
5. A.J.Colassi, J.R.Morton, and K.F.Preston, J.Chem. Phys., **62**, 2004 (1975).
6. P.J.Krusic, W.Wahler, and J.K.Kochi, J.Amer.Chem. Soc., **94**, 6033 (1972).
7. R.W.Dennis and B.P.Roberts, J.Chem.Soc., Perkin Trans.II, 140 (9175).
8. A.I.Prokof'ev, N.A.Malysheva, N.N.Bubnov, S.P.Solodovnikov, I.S.Belostotskaya, N.L.Komissarova, V.V.Ershov, and M.I.Kabachnik, Dokl.Akad.Nauk SSSR, **229**, 1396 (1976).
9. R.Luckenbach, "Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements", Stuttgart, 1973.
10. F.Ramirez and I.Ugi, Bull.Soc.chim.France, 453 (1974).
11. R.S.Berry, J.Chem.Phys., **32**, 933 (1960).
12. Y.I.Musher, J.Chem.Educ., **54**, 94 (1974).
13. J.Higuchi, J.Chem.Phys., **50**, 1001 (1969).
14. J.M.Howell and J.H.Olsen, J.Amer.Chem.Soc., **98**, 7119 (1976).
15. D.Griller and B.Roberts, J.Chem.Soc., Perkin Trans. II, 1333 (1973).
16. G.F.Kokoszka and F.E.Brinckmann, J.Amer.Chem. Soc., 92, 1199 (1970).
17. G.Bockestein, E.Jansen, and H.Buck, Chem.Comm., 118 (1974).
18. A.Davies, M.Parrot, and B.Roberts, Chem.Comm., 973 (1974).
19. J.W.Cooper, M.J.Parrot, and B.P.Roberts, J.Chem. Soc., Perkin Trans.II, 730 (1977).
20. R.W.Dennis, I.H.Elson, and B.P.Roberts, J.Chem. Soc., Perkin Trans.II, 819 (1977).
21. P.J.Krusic and P.Meakin, Chem.Phys.Letters, **18**, 347 (1973).
22. J.W.Cooper and B.P.Roberts, J.Chem.Soc., Perkin Trans.II, 808 (1976).
23. R.W.Dennis and B.P.Roberts, J.Chem.Soc., Perkin Trans.II, 140 (1975).
24. J.W.Cooper, M.J.Parrot, and B.P.Roberts, J.Chem. Soc., Perkin Trans.II, 730 (1977).
25. A.G.Davies, D.Griller, and B.P.Roberts. J.Chem. Soc., Perkin Trans.II, 224 (1972).
26. A.G.Davies, D.Griller, and B.P.Roberts, J.Chem. Soc., Perkin Trans.II, 993 (1972).
27. A.G.Davies, R.W.Dennis, and B.P.Roberts, J.Chem. Soc., 1101 (1974).
28. G.W.Wafts, D.Griller, and K.U.Ingold, J.Amer.Chem. Soc., **94**, 8754 (1972).
29. W.G.Bentrude, W.A.Khan, M.Murakami, and Han Van Tan, J.Amer.Chem.Soc., **96**, 5566 (1974).
30. H.W.Tan and W.B.Bentrude, J.Amer.Chem.Soc., 96, 5950 (1974).
31. W.G.Bentrude, J.H.Karsis, and P.E.Russek, Chem. Comm., 296 (1969).
32. R.S.Hay and B.P.Roberts, J.Chem.Soc., Perkin Trans.II, 770 (1978).
33. M.C.R.Symons, Chem.Phys.Letters, **19**, 61 (1973).
34. A.R.Lyons and M.C.R.Symons, Chem.Comm., 1068 (1971).
35. A.R.Lyons and M.C.R.Symons, J.Chem.Soc., Faraday Trans.II, **68**, 622 (1972).
36. S.P.Mishra and M.C.R.Symons, Tetrahedron Letters,, **41**, 4061 (1973).
37. W.Damerau, G.Lassman, and Kh.Lohs, J.Magn.Res., **5**, 408 (1971).
38. W.Damerau, G.Lassman, and Kh.Lohs, Z.Chem., 11, 182 (1971).
39. W.Damerau, G.Lassman, and Kh.Lohs, Z.Naturforsch, **B25**, 152 (1970).
40. G.Lassman, D.Damerau, and Kh.Lohs, Z.Naturforsch, **B24**, 1375 (1969).
41. A.L.J.Beckwith, Austral.J.Chem., **25**, 1887 (1972).
42. B.C.Gilbert, J.P.Larkin, R.O.C.Norman, and P.M.Storey, J.Chem.Soc., Perkin Trans.II, 1508 (1972).
43. A.G.Davies, D.Griller, and B.P.Roberts, J.Amer. Chem.Soc., 94, 1782 (1972).
44. D.Griller and B.P.Roberts, J.Chem.Soc., Perkin. Trans.II, 1416 (1973).
45. A.G.Davies, M.J.Parrott, and B.P.Roberts, Chem. Comm., 27 (1974).
46. Ya.A.Levin, A.V.Il'yasov, A.Sh.Mukhtarov, and M.S.Skorobogatova, Teor.Eksper.Khim., 612 (1975).
47. G.Ghapelet-Letourmux, H.Lemaire, R.Lenk, M.A.Marechal, and A.Rassat, Bull.Soc.chim.France, 3963 (1968).
48. E.W.Stone and A.H.Maki, J.Chem.Phys., **37**, 1326 (1962).
49. A.Sh.Mukhtarov, Candidate's Thesis, A.E.Arbuzov Institute of Organic and Physical Chemistry, USSR Academy of Sciences, Kazan, 1977.
50. Ya.A.Levin, A.V.Il'yasov, I.D.Morozova, A.Sh.Mukhtarov, and M.S.Skorobogatova, Izv.Akad. Nauk SSSR, Ser.Khim., 315 (1975).
51. A.V.Il'yasov, Ya.A.Levin, A.Sh.Mukhtarov, and

M.S.Skorobogatova, Izv.Akad.Nauk SSSR, Ser.Khim., 1651 (1975).
52. E.Müller , A.Rieker, K.Scheffler, and A.Moosmauer, Angew.Chem., **78**, 98 (1966).
53. A.I.Prokof'ev, A.A.Khodak, N.A.Malysheva, N.N.Bubnov, S.P.Solodovnikov, I.S.Belostotskaya, V.V.Ershov, and M.I.Kabachnik, Dokl.Akad.Nauk SSSR, **240**, 358 (1978).
54. A.I.Prokof'ev, S.P.Solodovnikov, N.N.Bubnov, and A.S.Masalimov, Izv.Akad.Nauk SSSR, Ser.Khim., 2490 (1976).
55. A.S.Masalimov, A.I.Prokof'ev, N.N.Bubnov, S.I.Solodovnikov, and M.I.Kabachnik, Dokl.Akad.Nauk SSSR, **236**, 116 (1977).
56. A.I.Prokof'ev, A.A.Khodak, N.A.Malysheva, N.N.Bubnov, S.I.Solodovnikov, and M.I.Kabachnik, Dokl.Akad.Nauk SSSR, **240**, 92 (1978).
57. K.U.Ingold and B.P.Roberts, "Free-Radical Substitution Reactions" (Translated into Russian), Izd.Mir, Moscow, 1974.
58. I.S.Belostotskaya, N.L.Komissarova, T.I.Prokof'eva, A.I.Prokof'ev, V.V.Ershov, and M.I.Kabachnik, Izv. Akad.Nauk SSSR, Ser.Khim., 1222 (1978).

Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow

Translated from *Uspekhi Khimii*, **49**, 28 - 53 (1980) U.D.C. 542-97

Catalytic Amination of Alcohols, Aldehydes, and Ketones

M.V.Klyuev and M.L.Khidekel'

Data on the catalytic amination of alcohols and carbonyl compounds are examined, the catalysts for these processes are described, and the problems of their effectiveness, selectivity, and stability are discussed. The possible mechanisms of the reactions indicated are presented.
The bibliography includes 266 references.

CONTENTS

I. Introduction 14
II. Catalytic amination of alcohols 14
III. Catalytic reductive amination of carbonyl compounds 19

I. INTRODUCTION

Amines are the most important products of basic and fine organic syntheses. They are used extremely widely and for different purposes in the national economy. Amines and their derivatives are employed, in particular, as antioxidants in fuel oils and as rubber stabilisers, in the manufacture of water-impermeable fabrics and effective medicinal drugs, in road building, in the manufacture of detergents, as extractants of rare metals (U, Th, Pu, Au, Zr, V. Pa, and others), and in the manufacture of herbicides. They have found applications in the synthesis of dyes and accelerators of the polymerisation of rubber. A wide variety of plastics are obtained from alicyclic and aromatic amines.

Amines are obtained by the amination of saturated and unsaturated hydrocarbons, alcohols, halogeno-compounds, and carbonyl compounds, by the reduction of a wide variety of nitro-compounds, and by the Hofmann, Curtius, and other reactions. The synthesis of amines from alcohols was first achieved by Sabatier and Mailhe[1] in 1909 and the reductive amination of aldehydes and ketones was first carried out by Mignonac[2] in 1919. Since then, numerous studies on particular aspects of the above reactions as well as a number of reviews have been published[3-7], the results of pre-war investigations (particularly those of Emerson[3]) being surveyed most completely.

This review is devoted to the literature on the synthesis of amines by the catalytic amination of alcohols and carbonyl compounds. An attempt is made to reflect the achievements and trends in the study of these reactions.

II. CATALYTIC AMINATION OF ALCOHOLS

The modern industrial method for the preparation of primary, secondary, and tertiary aliphatic amines consists in passing the vapour of the corresponding alcohol and ammonia over oxide catalysts such as Al_2O_3, ThO_2 etc. heated to 350–450 °C. Apart from amines, unsaturated and saturated hydrocarbons, water, nitriles, aldehydes or ketones, hydrogen, and ethers are detected in the reaction products. The presence of these substances in the reaction medium has been explained in different ways by various investigators. There is as yet no unanimous view concerning the mechanism of the amination of alcohols.

The original discoverers of the reaction assumed that[8] the alcohol initially reacts with the catalyst (thorium oxide) and forms an unstable ester—alkyl thorate [reaction (1)], which then reacts rapidly with ammonia [reaction (2)]. The authors assumed that the olefins obtained are the products of secondary reactions. Secondary and tertiary amines are formed by the interaction of alkyl thorate with primary [reaction (3)] and secondary [reaction (4)] amines:

$$ROH + ThO_2 \rightarrow ThO(OR)_2 + H_2O\,, \quad (1)$$

$$ThO(OR)_2 + NH_3 \rightarrow RNH_2 + ThO_2 + H_2O\,, \quad (2)$$

$$ThO(OR)_2 + RNH_2 \rightarrow R_2NH + ThO_2 + H_2O\,, \quad (3)$$

$$ThO(OR)_2 + R_2NH \rightarrow R_3N + ThO_2 + H_2O\,. \quad (4)$$

Baum[9] assumed that the ethers formed from the alcohols via reaction (5) are intermediates in the synthesis of amines in the presence of alumina [reaction (6)–(8)]:

$$RCH_2OH \rightarrow (RCH_2)_2O + H_2O\,, \quad (5)$$

$$(RCH_2)_2O + NH_3 \rightarrow RCH_2OH + RCH_2NH_2\,, \quad (6)$$

$$(RCH_2)_2O + RCH_2NH_2 \rightarrow (RCH_2)_3NH + RCH_2OH\,, \quad (7)$$

$$(RCH_2)_2O + (RCH_2)_3NH \rightarrow (RCH_2)_3N + RCH_2OH\,. \quad (8)$$

Schwegler and Adkins[10] suggested that the alcohols are initially dehydrogenated via reaction (9) to aldehydes or ketones, which react with ammonia to form imines [reaction (10)]. The latter are then reduced with hydrogen to primary amines via reaction (11). While reacting with fresh molecules of the carbonyl compounds via reactions (12)–(14), the primary amines give rise in their turn to secondary and tertiary amines via the intermediate Schiff bases:

$$RCH_2OH \rightarrow R-C\begin{matrix}O\\ \diagdown H\end{matrix} + H_2\,, \quad (9)$$

$$R-C\begin{matrix}O\\ \diagdown H\end{matrix} + NH_3 \rightarrow RCH{=}NH + H_2O\,, \quad (10)$$

$$RCH{=}NH + H_2 \rightarrow RCH_2NH_2\,, \quad (11)$$

$$RCH_2NH_2 + RC\begin{matrix}O\\ \diagdown H\end{matrix} \rightarrow RCH_2N{=}CHR + H_2O\,, \quad (12)$$

$$RCH_2N{=}CHR + H_2 \rightarrow (RCH_2)_2NH\,, \quad (13)$$

$$RCH_2N{=}CHR + RC\begin{matrix}O\\ \diagdown H\end{matrix} \xrightarrow{+H_2} (RCH_2)_3N + H_2O\,. \quad (14)$$

Popov[11] assumed that the first stage in the amination process is reaction (15) involving the dehydration of alcohols with formation of olefins, which then react with ammonia, primary, and secondary amines to form primary [reaction (16)]. secondary [reaction (17)], and tertiary [reaction (18)] amines respectively:

$$RCH_2CH_2OH \rightarrow RCH{=}CH_2 + H_2O\,, \quad (15$$

$$NH_3 + RCH{=}CH_2 \rightarrow RCH_2CH_2NH_2\,, \quad (16$$

$$RCH{=}CH_2 + RCH_2CH_2NH_2 \rightarrow (RCH_2CH_2)_2NH\,, \quad (17)$$

$$RCH{=}CH_2 + (RCH_2CH_2)_2NH \rightarrow (RCH_2CH_2)_3N \ . \qquad (18)$$

It has been shown[12-14] that amines are formed in the amination of alcohols by direct substitution of the alcoholic hydroxy-group by the amino-group [reaction (19)]. Secondary [reaction (20)] and tertiary [reaction (21)] amines are obtained similarly:

$$RCH_2OH + NH_3 \rightarrow RCH_2NH_2 + H_2O \ , \qquad (19)$$

$$RCH_2OH + RCH_2NH_2 \rightarrow (RCH_2)_2NH + H_2O \ , \qquad (20)$$

$$RCH_2OH + (RCH_2)_2NH \rightarrow (RCH_2)_3N + H_2O \ . \qquad (21)$$

The alcohols, unsaturated hydrocarbons, carbonyl compounds, and ethers formed in the amination process were regarded[13] as the products of the dehydration and dehydrogenation [side reactions (5), (9), and (15)] occurring on the surface of the catalysts at elevated temperatures.

In contrast to this view, Bashkirov and coworkers showed in relation to the amination of deuteroalcohols[15-20] that the reaction proceeds via the mechanism proposed by Schwegler and Adkins[10]. In their study of the interaction of labelled ethanol with ammonia, they noted[15-20] that the ethanol is initially dehydrogenated, the abstraction of hydrogen atoms from the α-position in the alcohol molecule being the rate-limiting stage of the process. The β-hydrogen atoms in the alcohol are not involved in the rate-limiting stage. It was found that this stage proceeds with participation of two active centres of the catalyst. Secondary amines are formed in consequence of the addition of primary amines to the double bonds of aldimines. On raising the temperature and at a low hydrogen partial pressure, aldimines can be dehydrogenated to nitriles. It was established that ammonia and primary and secondary amines as well as the saturated hydrocarbons produced do not influence the rate of reaction. The addition of water greatly lowers the rate of amination. The authors[15-20] proposed the following reaction mechanism (Z is a catalyst active centre):

$$RCH_2OH + Z \rightleftarrows RCH_2OHZ \ , \qquad (22)$$

$$H_2 + Z \rightleftarrows H_2Z \ , \qquad (23)$$

$$NH_3 + Z \rightleftarrows NH_3Z \ , \qquad (24)$$

$$RCH_2OHZ + Z \rightarrow RCHOZ + H_2Z \ , \qquad (25)$$

$$RCHOZ + NH_3Z \rightarrow RCH{=}NHZ + H_2OZ \ , \qquad (26)$$

$$RCH{=}NHZ + H_2Z \rightleftarrows RCH_2NH_2Z + Z \ , \qquad (27)$$

$$RCHOZ + RCH_2NH_2Z \rightarrow RCH{=}N{-}CH_2RZ + Z \ , \qquad (28)$$

$$RCH{=}N{-}CH_2RZ + ZH_2 \rightarrow (RCH_2)_2NHZ + Z \ , \qquad (29)$$

$$RCH_2NH_2Z \rightleftarrows RCH_2NH_2 + Z \ , \qquad (30)$$

$$(RCH_2)_2NHZ \rightleftarrows (RCH_2)_2NH + Z \ , \qquad (31)$$

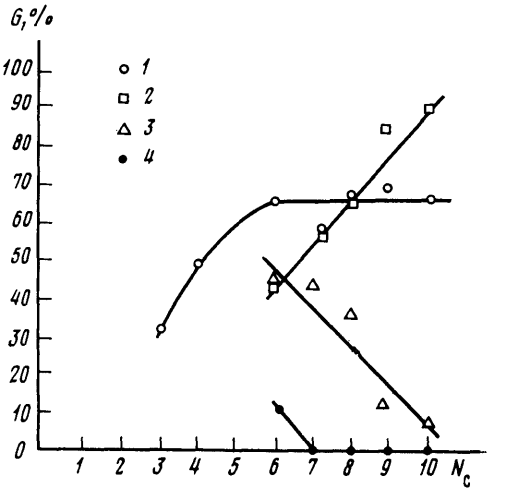
$$H_2OZ \rightleftarrows H_2O + Z \ . \qquad (32)$$

Stage (25) is slow, while all the remaining stages are fast or correspond to equilibrium. We believe that this mechanism is the most probable.

1. The Synthesis of Aliphatic Amines

(a) The Synthesis of Aliphatic Amines in the Presence of Dehydrating Catalysts

The principal disadvantage of the synthesis of amines from alcohols is the occurrence of a number of side reactions, particularly the dehydration of the initial alcohols. One of the ways of suppressing the dehydration involves the use of a high ammonia pressure in the reaction zone. With the aid of this method, Kozlov and coworkers established[21,22] that with increase of ammonia pressure the yield of amines rises. With increase of the molecular weight of the alcohol, the yield of amines falls (Table 1, Nos.1–7). For alcohols having the same molecular weight[22], the yield of amines depends on the degree of branching of the carbon chain, other conditions being equal. Indeed the yield of amines obtained from 1-butanol was 89.9% while that from triethylmethanol was only 25.5% with respect to the alcohol which has reacted (Table 1, Nos.1 and 8). It is noteworthy that secondary and tertiary amines are obtained with lower yields than primary amines. This probably occurs because a transamination reaction takes place when amines are passed over heated oxide catalysts, i.e. ammonia and two new amines are obtained from the initial amine[23,24]. It has been established[25] that the predominance of the primary amine in the products is associated with the fact that an increase of ammonia pressure greatly displaced the reaction equilibrium between the alcohol and ammonia towards the formation of the primary amine. This was confirmed in a study of the thermodynamics of the reaction[26].



Dependence of the yield of amines G on the number of carbon atoms in the alcohol N_C (according to the data of Kozlov and Kirichenko[27]); 350–400 °C; $p_{NH_3} = 7$–11.5 atm; Al_2O_3–SiO_2 catalyst: 1) overall yield of amines; 2) primary amines; 3) secondary amines; 4) tertiary amines.

Another approach to the problem of improving the selectivity in the amination of alcohols involved the promotion of alumina by other metal oxides. It has been shown[27] that a mixed aluminosilicate catalyst dehydrogenates alcohols to a lesser extent, so that C_3–C_{10} straight-chain aliphatic alcohols can be converted into amines in yields up to 70%. The Figure shows that, with increase of the length of the carbon chain of the alcohol, there is not only an increase of the yield of amines in the presence of this catalyst under conditions analogous to the use of activated alumina but there is also an increase of selectivity in relation to primary amines

Table 1. Catalytic amination of aliphatic alcohols in the presence of dehydrogenating catalysts.

No.	Alcohol	Catalyst	t, °C	p, atm	Overall yield of amines, %	Yields of amines, %			Remarks	Refs.
						primary	secondary	tertiary		
1	1-Butanol	act. Al_2O_3	370—380	9	89.9	62.0	29.8	8.2	yield w.r.t. alcohol which has reactd.	21,22
2	Isobutyl alcohol	act. Al_2O_3	370—380	9	68.8	51.4	40.7	7.7	ditto	21,22
3	Isopentyl alcohol	act. Al_2O_3	370—380	9	76.4	51.2	30.6	18.2	" "	21
4	Methylpropylmethanol	act. Al_2O_3	370—380	9	44.2	—	—	—	" "	21
5	Ethyldimethylmethanol	act. Al_2O_3	370—380	9	25.8	—	—	—	" "	21
6	1-Octanol	act. Al_2O_3	370—380	9	18.1	53.5	34.4	12.1	" "	21
7	1-Nonanol	act. Al_2O_3	370—380	9	11.9	61.0	25.5	13.5	" "	21
8	Trimethylmethanol	act. Al_2O_3	370—380	9	25.3	—	—	—	" "	21
9	1-Butanol	$Al_2O_3 + Cr_2O_3$	330	9	42.8	25.5	17.3	—	$C_4H_9OH:NH_3 = 1:4$	31
10	1-Butanol	$Al_2O_3 + V_2O_5$	347	9	54.1	24.9	29.2	—	$C_4H_9OH:NH_3 = 1:4$	32
11	1-Butanol	$Al_2O_3 + 5\%$ TiO_2	370	8,5	36.1	80.1	19.9	—	yield w.r.t. alcohol used	13
12	Isobutyl alcohol	$Al_2O_3 + 5\%$ TiO_2	370	8,5	35.3	76.8	23.2	—	ditto	13
13	Ethanol	$Al_2O_3 + 10\%$ Fe_2O_3	370—380	7—10	45	—	—	—	$C_2H_5OH:NH_3 = 1:3$	37
14	1-Butanol	bauxite + 3% Fe_2O_3	320	—	58.5	20.6	28.8	9.1	$C_4H_9OH:NH_3 = 1:1.6$	39
15	1-Butanol	mordenite	200	—	70	—	—	—	—	40
16	1-Dodecanol	12% $Th(SO_4)_2$ on kieselguhr	360	—	95	—	—	95	$(CH_3)_2NH$: alcohol = 2 : 1	53

The decrease of the yield of secondary amines and the disappearance of tertiary amines from the reaction mixture are probably associated either with a decrease in the surface area of the catalyst or with steric hindrance. However, the aluminosilicate catalyst was less active and the yield of amines in its presence was lower than in the presence of alumina. From earlier studies[21-22,27-29], Kozlov et al.[30] suggested that the catalysts described be used to synthesise amines from the waste in the manufacture of synthetic methanol and ethanol.

Catalysts based on Al_2O_3 and SiO_2, promoted with chromium, nickel, vanadium, molybdenum, magnesium, iron, titanium, and other oxides, have been investigated[13,31-38]. Typical examples of the conditions in the amination processes in their presence as well as the yields of products are listed in Table 1 (Nos. 9–13).

Natural aluminosilicates (bauxites, gumbrin, mordenite, etc.) have been studied as amination catalysts[39-44]; even under fairly severe conditions, the yield of amines is as a rule low (Table 1, Nos. 14 and 15). We may note that in the presence of H-substituted mordenite ($Na_2Al_2Si_{10}O_{24}.7H_2O$), only the formation of primary and secondary amines is observed[40]. The author[40] believes that the reaction selectivity depends on the pore size in the catalyst and the associated steric hindrance to the formation of tertiary amines.

It has been suggested that methylamines be synthesised in the presence of various mixtures of H_3BO_3 and H_3PO_4 on kieselguhr or pumice[45,46] or in the presence of pure Al_2O_3.[47-49] It is of interest that, when acid-treated alumina was employed, the preferential formation of secondary amines was observed[50], other conditions being equal. Alumina[51] or thorium sulphate[52] have been used in the amination of alcohols by primary or secondary amine. A particularly high yield of *N*-alkylated amines (95%) was obtained in the presence of a catalyst containing 12% $Th(SO_4)_2$ on kieselguhr[53] (Table 1, Nos. 16).

(b) The Synthesis of Aliphatic Amines in the Presence of Hydrogen

Dehydration and hydrogenation[54] or dehydrogenation and hydrogenation[55] catalysts have been used in succession to synthesise amines in a number of studies. Thus a mixture of alcohol vapour with ammonia was passed initially[54] over an iron catalyst at 300–470 °C and the resulting condensate was then hydrogenated on a nickel catalyst at 80–160 °C and a hydrogen pressure of 100–150 atm, the product consisting mainly of primary amines. Up to 100% of amines was obtained[55] when nickel on kieselguhr at 200 °C (a dehydrogenation catalyst) and copper at 180 °C or nickel at 100 °C (hydrogenation catalysts) were used in succession.

Very many studies have been devoted to the amination of alcohols on hydrogenation catalysts. Raney nickel has been widely used; with its aid, amines have been alkylated by alcohols[56,57], aminoalcohols have been synthesised[58], and amines have been obtained from butyl[59] and isooctyl[60] alcohols. Raney nickel proved to be a non-selective catalyst and in addition it must be consumed in large amounts for high yields of amines to be attained. Other nickel-containing catalysts[61-67] suffer from the same disadvantages (Table 2, Nos. 1 and 2). When nickel and Cr_2O_3 on kieselguhr were used (Table 2, No. 1), water was continuously removed from the reaction mixture, which made it possible to displace the equilibrium towards the formation of the tertiary amine[61].

Catalysts containing cobalt[68-70] or noble metals[71-73] proved to be much more active than nickel catalysts; up to 97% of amines has been obtained in their presence (Table 2, Nos. 3–5). Their high selectivity, the relatively mild conditions required for their application, and their low cost make cobalt catalysts extremely promising for the amination of alcohols.

Bashkirov and coworkers[74] suggested that fused Fe_3O_4, promoted by acid and amphoteric oxides, be used for the amination of alcohols. This catalyst has been employed in a number of subsequent studies[15-20,75-89]. The authors found the optimum conditions for the synthesis of butylamines[76] (Table 2, No. 6) and investigated in detail the amination of octyl alcohols with a wide variety of structures[77]. It was shown that the branching of the carbon skeleton entails a sharp increase in the yield of side products. At the same time the branching of the carbon chain of the initial alcohol lowers its capacity for the formation of secondary and tertiary amines, probably owing to the increasing steric hindrance.

In the amination of various aliphatic alcohols (C_5–C_{18}) the authors[79] found that, with increase in the length of the carbon chain of the alcohol, its capacity for the formation of

secondary amines also increases. Subsequently Bashkirov and coworkers showed that it is possible to obtain preferentially either primary[80], or secondary[81], or tertiary[82] amines by altering the reaction conditions. By using an optimisation method, the authors[83–86] determined the best conditions for the synthesis of normal primary, secondary, and tertiary amines as well as branched amines (Table 3). If the alcohol is in the liquid state then, other conditions being equal, the amount of secondary amines obtained increases by a factor of 1.5.

The kinetics of the amination of 1-octanol have been studied in detail[88]. In particular, it was shown that the addition of water lowers the rate of reaction, while the addition of hydrogen and the concentrations of other reactants do not influence the rate of amination.

Using primary amines (CH_3NH_2, $C_4H_7NH_2$, $C_7H_{10}NH_2$) as the aminating agents, Bashkirov and coworkers[89] obtained between 60 and 85% of secondary amines (with respect to the alcohol which has reacted). They used Fe_3O_4 with added 0.8–1.0% of beryllium or vanadium oxide as the catalyst at 230–240 °C and a hydrogen pressure of 20 atm.

The catalytic properties of the fused iron catalyst[74], iron ε-nitride (ε-Fe_2N), and iron carbonitride ($Fe_2C_{0.29}N_{0.71}$) were compared[90] in the amination of butanol. It was found that mainly primary amines are obtained in the presence of ε-Fe_2N, secondary amines are the main products in the presence of $Fe_2O_3 + V_2O_5$, while the carbonitride can serve as a catalyst for the synthesis of butyronitrile.

2. The Synthesis of Alicyclic Amines

There are very few data on the amination of alicyclic alcohols, although this reaction has much in common with the amination of aliphatic analogues and proceeds in the presence of similar catalysts.

Thus Al_2O_3 has been used[91] (Table 4, No.1). The authors found that the application of an increased ammonia pressure suppresses (as for aliphatic alcohols[21]) the dehydration of cyclohexanol and drives the process towards the formation of cyclohexylamines.

Subsequently the amination of cyclohexanol and cyclopentanol was investigated[92] over Al_2O_3, Al_2O_3–SiO_2, Al_2O_3 activated with 2% KOH or 2% LiOH, Cu/Al_2O_3, and Ni/Al_2O_3. It was found that, for a copper content above 0.5%, cyclohexylamine was obtained with a maximum yield (76.5%); with increase of the copper content to 20%, the main amination product became dicyclohexylamine.

When Ni/Al_2O_3 was used, aniline and *N*-cyclohexylaniline as well as pyridine and 2-methylpyridine were detected in the reaction products. It is noteworthy that the formation of pyridines was observed also in the presence of copper catalysts. It had been suggested earlier[93] that 2-methylpyridine may be obtained from cyclohexylamine. This was subsequently confirmed by Kozlov et al.[92] Under the conditions of the amination of alicyclic alcohols, these workers obtained 52–70% of 2-methylpyridine and 5–10% of pyridine respectively from cyclohexyl- and cyclopentyl-amines. It

Table 2. Catalytic amination of aliphatic alcohols in the presence of hydrogen.

No.	Alcohol	Catalyst	*t*, °C	*p*, atm	Overall yield of amines, %	Yield of amines, %			Remarks	Refs.
						primary	secondary	tertiary		
1	Isononyl alcohol	Ni, Cr_2O_3 on kieselguhr	190	—	—	—	—	83.0	$NH_3:H_2=1:1$	61
2	1-Propanol	Ni on Al_2O_3 treated with $Ba(OH)_2$	195	20	—	24.3	42.6	12.0	—	63
3	Isopropyl alcohol	Co, Mn, Cr	300	—	97	90.5	6.5	—	—	69
4	1-Dodecanol	Co, ZnO, Al_2O_3	180	—	—	95.3	—	—	$NH_3:H_2=3:1$	70
5	Isobutyl alcohol	Pt on SiO_2	400	—	86.34	15.33	11.90	59.11	—	72
6	1-Butanol	Fe_3O_4	250	20	76	95.7	4.3	—	—	76

Table 3. Optimum conditions for the synthesis of amines in the presence of a fused iron catalyst.

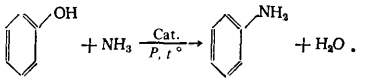
No.	Alcohol	*t*, °C	*p*, atm	Rate of supply of alcohol, mol litre^{-1} h^{-1}	Flow rate of gas mixture, cm s^{-1}	NH_3 content, vol.%	Overall yield of amines, %	Yield of amines, %			References
								primary	secondary	tertiary	
1	Normal C_6–C_{13}	258	50	14.4	1.8	43	90–93	88–92	—	—	83
2	Normal C_6–C_{12}	280	50	11.0	0.16	35	50–59	11–25.5	45–49	29.5–35	84
3	Normal C_6–C_{12}	295	50	12.3	0.03	23	60–70	12.5–20.5	18.5–25.5	59–69	85
4	2-Ethyl-1-hexanol	293	50	8.5	18	45	—	99	—	—	86

has been suggested that alicyclic alcohols be aminated in the presence of aluminosilicates[94-97]. The yield of the corresponding amines was 51–90% (Table 4, Nos.2–4).

Catalysts working under hydrogenation conditions have been investigated[93-104]. Whereas in the presence of nickel or iron catalysts the amination products are the corresponding amines (Table 4, No.5), in the presence of noble metals anilines are obtained (Table 4, Nos.6–8). Richardson and coworkers believe[101] that the reaction proceeds in the presence of these catalysts via the intermediate cyclohexylamine, which is strongly retained and is then dehydrogenated with the desorption of aniline.

3. The Synthesis of Aromatic Amines

In industry aromatic amines are obtained mainly by the reduction of the corresponding nitro-compounds. Together with the wide-scale development of this method, reports have appeared of the synthesis of aniline and its homologues by the catalytic amination of phenol and its analogues:



It has been found[21,105] that industrial activated alumina catalyses the conversion of phenol, *o*- and *p*-cresols, and *m*-xylenol into the corresponding primary amines. The highest yield (88% of aniline) was obtained in the amination of phenol (Table 5, No.1). The effectiveness of Al_2O_3 increases after its preliminary treatment with alkali and a carboxylic acid[106] or H_3BO_4 [107] (Table 5, Nos.2 and 3). The same catalysts have been proposed also for the synthesis of *m*- and *p*-toluidines, diphenylamine, β-naphthylamine, etc. The above amines are also obtained when (2–10% $AlCl_3$)/Al_2O_3 or Al_2O_3–SiO_2 are used under analogous conditions (365 °C, $p_{NH_3} = 16$ atm).[108] In addition, other oxide catalysts have been proposed[109-115]. The yield of aniline is 80–99% (Table 5, Nos.4–6).

The properties of mixed oxide catalysts in the amination of phenol have been studied in detail[116-119] and it has been established that SiO_2–TiO_2, TiO_2–WO_3, TiO_2–Nb_2O_5, TiO_2–ZrO_2, ZrO_2–Nb_2O_5, and other mixtures of oxides showed a higher catalytic activity and selectivity in this reaction than SiO_2–Al_2O_3. It has been found with the aid of thermogravimetric analysis[119] that the amination proceeds via the adsorption of phenol on the acid centres of the catalyst and that the more acid centres of the mixtures of oxide proved to be more effective than the less acid centres of SiO_2–Al_2O_3. It is noteworthy that phenol and aniline poison catalysts containing highly acid and therefore highly active centres.

Yamamoto et al.[120] investigated the amination of phenol in the presence of type Y zeolites at 350–380 °C. In terms of their catalytic activity, the zeolites can be arranged in the following sequence: HY > CaY > CuY. The yield of aniline is 11–14 mol.%. In addition, the influence of the amount of Cu^{2+} in the zeolite on the yield of products has been studied. The maximum yield of aniline was obtained in the presence of 80% of the metal. It is noteworthy that, when aniline or pyridine is added to CuY, the yield of aniline falls, while in the presence of added HCl it increases. This suggests that amination proceeds in this case via the adsorption of phenol on the acid centres of the zeolites.

Hydrogenation catalysts have been used to aminate benzyl and β-phenylethyl alcohols as well as phenol[69,121-123] (Table 5, Nos.7–9). When catalysts based on noble metals

Table 4. Catalytic amination of alicyclic alcohols.

No.	Alcohol	Catalyst	*t*, °C	*p*, atm	Product	Yield, %	Remarks	Refs.
1	Cyclohexanol	Al_2O_3	260-300	8-10	cyclohexylamine	90-95	yield w.r.t. reacted alcohol	91
2	Cyclohexanol	$Ca/Al_2O_3.SiO_2$	245-330	14	" "	67-82	NH_3:alcohol = 8:1-15:1	94
3	Cyclohexanol	gumbrin + 8% Fe_2O_3	300	1	" "	90.6	ditto	95
4	1-Methyl-1-cyclopentanol	gumbrin + 8% Fe_2O_3	280	1	1-methyl-1-cyclopentylamine	51.08	" "	97
5	Cyclohexanol	Fe_3O_4	240-260	50	cyclohexylamine	85	" "	99
6	Cyclohexanol	Pt/C	315	1.8	aniline cyclohexylamine	89 5	NH_3:H_2:alcohol = 16:1:1	102
7	Cyclohexanol	Pd/SiO_2	330	–	N-methylaniline	70	$MeNH_2$:H_2:alcohol = 5:5:1	102
8	Cyclohexanol	Pt/SiO_2	315	4	aniline	89	NH_3:H_2:alcohol = 8:4:1	103

Table 5. Catalytic amination of aromatic alcohols [and phenol].

No.	Alcohol	Catalyst	*t*, °C	*p*, atm	Product	Yield, %	Remarks	Refs.
1	Phenol	Al_2O_5	475	9	aniline	88.3	–	21
2	Phenol	γ-Al_2O_3, treated with H_3BO_3	365	16	aniline	87.0	phenol:NH_3 = 1:20	106
3	Phenol	γ-Al_2O_3, treated with acid and alkali	365	16	aniline	98.0	phenol:NH_3 = 1:20	107
4	Phenol	Al_2O_3 + 1% Na_2O	363	16.9	aniline	98.9	phenol:NH_3 = 1:20	112
5	Phenol	SiO_2-Al_2O_3 + V_2O_5	300-600	7	aniline	80.0	–	114
6	Phenol	9.9% Al_2O_3 on SiO_2	383	16.8	aniline	93	–	115
7	Benzyl alcohol	Fe_3O_4	200	50	benzyl- and dibenzylamines	53.5	H_2:NH_3:alcohol = 9.7:22.2:1	121
8	β-Phenylethyl alcohol	Co, Cr, Mn	220	300	phenylethylamine Di(phenylethyl)amine	90.0 10.0	–	69
9	Phenol	NH_4Cl	400	1000	aniline	90	–	122
10	Phenol	5% Ru on charcoal + sodium phenoxide	110	13-14	cyclohexylamine	85.2	–	126
11	Phenol	5% Pd on charcoal	110	10	dicyclohexylamine	82.5	–	127

were used, the hydrogenation of the aromatic ring was observed and cyclohexylamines and cyclohexanol were obtained from phenol[124,125]. It was found[126] that the addition of 0.015–10 wt.% of sodium phenoxide lowers the fraction of cyclohexanol in the product and that cyclohexylamine is obtained in 85.2% yield (Table 5, No.10). In the presence of (5% Pd)/C phenol is converted preferentially into dicyclohexylamine[127] (Table 5, No.11).

We shall consider separately data for the alkylation of aniline by alcohols and for the amination of phenol–aliphatic alcohol mixtures. Evans and Bours[128] postulated that the best catalyst for the gas-phase alkylation of aniline by methanol is activated alumina; it has been established[39] that natural aluminosilicates can also be used to alkylate aniline by alcohols. Thus, in the presence of bauxite containing 6% Fe_2O_3 at 275 °C, at atmospheric pressure, and for the ratio ethanol : aniline = 1.45, 83.9% of ethylaniline and 3.3% of diethylaniline were obtained. It has been shown[129] that, when aniline and ethanol are passed over Nb_2O_5 heated to 350–408 °C, 10% of *N,N*-dimethylaniline and 20–25% of *N*-ethylaniline are obtained during one pass.

Alumina, various aluminosilicates, as well as Al_2O_3 promoted by other metal oxides and hydroxides have been investigated[130–133] in the amination of the phenol–aliphatic alcohol system. The best catalyst proved to be the Al_2O_3 + 1% LiOH mixture[132]. The yield of arylamines in the presence of this catalyst at 450 °C and $p_{NH_3} = 12$ atm was in excess of 60%. With increase of the LiOH content, the yield of amines fell to 28%, probably owing to the blocking action of the lithium cations, which covered a proportion of the aprotic centres of Al_2O_3 responsible for the amination reaction. It has also been found that, with increase of the molecular weight of the alcohol, the yield of arylamines falls from 69% (for CH_3OH) to 18% (for C_4H_9OH) and that for branched alcohols the yield is smaller by a factor of two than for normal alcohols.

It has been suggested[134–136] that aniline be alkylated by alcohols in the presence of acids. Thus using H_2SO_4, 99% of *N,N*-dimethylaniline was obtained on heating a methanol–aniline mixture to 190–210 °C under a pressure of 5 atm.[135]

A number of studies[57,137–140] have been devoted to the synthesis of mixed amines by the reaction of aromatic amines with aliphatic alcohols in the presence of Raney nickel. The yield of amines is fairly high (41–90%) and the alkylation conditions in the presence of Raney nickel are comparatively mild. The main disadvantage of the method is the high consumption of the catalyst.

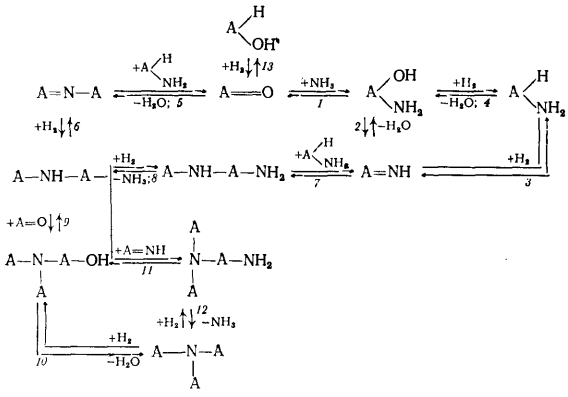
It has been found[141] that phenylacetylmethanols can be alkylated by primary amines also by a non-catalytic procedure, in the presence of sodium tetrahydroborate. The main disadvantage of this method is the high cost of $NaBH_4$.

III. CATALYTIC REDUCTIVE AMINATION OF CARBONYL COMPOUNDS

The catalytic reductive amination of carbonyl compounds is usually carried out in the presence of catalysts based on transition metals. Studies on the use of complex catalysts have been carried out recently. In addition, there have been reports of the electrocatalytic synthesis of amines from ketones and by non-catalytic amination with the aid of tetrahydroborates.

We shall consider certain general postulates underlying the reductive amination of carbonyl compounds. The synthesis of amines by this procedure (Scheme 1) consists in the addition of ammonia to a carbonyl compound with subsequent reduction of the adduct (pathway *1*, *4*)

Scheme 1



where A=O represents R–C(=O)–R′ and R, R′ = alkyl, aryl, or H.

It may be that the adduct is initially dehydrated and the dehydration product is subsequently reduced (pathway *1–2–3*). The primary amine formed ultimately can also behave as an aminating agent for carbonyl compounds, forming Schiff bases, which are reduced to secondary amines (pathway *5–6*). The addition of a primary amine to imines with subsequent reduction of the adduct also leads to secondary amines (pathway *7–8*). Secondary amines react similarly in their turn with carbonyl compounds (pathway *9–10*) or with an imine (pathway *11–12*), forming tertiary amines. The principal side reactions involve the formation of an alcohol (pathway *13*) and aldol condensation. In order to prevent the formation of an alcohol, it has been recommended in a number of studies that ammonium[6,147–148] or sodium[149] acetates or chlorides be added to the reaction mixture. The aldol condensation is retarded or is not observed at all when the reaction mixture is cooled before hydrogenation[6] or when the contact time between the carbonyl compound and ammonia is reduced[150]. The kinetics of the reductive amination of aldehydes and ketones have been studied in detail[142–146] and we shall not consider them in the present review.

Numerous catalysts for the reductive amination of carbonyl compounds have now been investigated. From these, Freifelder[6] selected nickel catalysts, believing them to be the most effective and most readily available. Together with nickel catalysts, Augustine[151] recommends also platinum catalysts for this reaction. The use of catalysts containing platinum group metals has been most fully described by Rylander[7]. This review covers studies which are not included in the books by Freifelder[6] and Rylander[7] and in Augustine's review[151].

(a) Reductive Amination of Aliphatic Aldehydes and Ketones

Nickel catalysts have been used in many studies on the synthesis of amines from aliphatic carbonyl compounds. Raney nickel has been investigated[152–160]. Table 6 (Nos.1–11) shows that the yield of amines depends on the structure of the carbonyl compound. The rate of reaction also depends on the structure of the substrate employed. Thus it has been established[155] that the rate of amination decreases in

the sequence ethyl methyl ketone > isobutyl methyl ketone > diethyl ketone. The advantages of Raney nickel as a catalyst include ready availability, the possibility of carrying out experiments under mild conditions, and fairly high selectivity, while its main disadvantages are high consumption and lack of safety. These disadvantages can be eliminated by employing catalysts containing nickel on various carriers.

Nickel deposited on alumina proved to be an effective catalyst for the amination of carbonyl compounds[161-174]. Analysis of the literature data showed that the conditions under which Ni/Al_2O_3 is used are as a rule similar to those employed for Raney nickel (Table 6, Nos.12–14), but, in contrast to the latter, it is more active and stable in the reaction under discussion. Thus it has been shown[164] that Ni/Al_2O_3 is three times more active than freshly prepared Raney nickel and it has been reported[161] that Ni/Al_2O_3 is stable for 2000 h.

In some cases, when the amination reaction was carried out in the presence of Ni/Al_2O_3, nitriles were detected in the reaction mixture. Popov and Shuikin[168] suggested that the amination proceeds via the formation of nitriles and put forward the following reaction mechanism:

$$R{-}CHO + NH_3 \rightarrow R{-}C(H)(OH)(NH_2) \xrightarrow[-H_2O]{} R{-}C(H)=NH \xrightarrow[-H_2]{} RC{\equiv}N \xrightarrow{+2H_2} RCH_2NH_2 .$$

Next the primary amine is converted into a secondary amine and the secondary amine is converted into a tertiary amine.

Among other carriers, kieselguhr has been widely used. Thus, considerable amounts of ethylamines have been obtained[175] by the amination of acetaldehyde in the presence of a catalyst containing 52.2% Ni, 14% Cu, 2% Mo, and 31.5% of kieselguhr (Table 6, No.15); the synthesis of tertiary amines by the reaction of ketones with secondary amines in the presence of a catalyst consisting of 50% Ni and 2% Zr on kieselguhr has been reported in a number of patents[176,177].

Analysis of studies in which cobalt catalysts for reductive amination have been used[178-180] shows (Table 6, Nos.16–18) that these catalysts give rise to a high yield of amines, but require more severe conditions than nickel catalysts. Copper catalysts have been studied in a number of investigations[181-183]. Among these, the greatest interest attaches to the hydroamination of ketones by benzonitrile in the presence of $(20\%\ Cu)/Al_2O_3$. Various *N*-alkylated benzylamines have been obtained by this method. It has been reported in a patent[184] that alkylidenealkenylamines are obtained in yields up to 98% when a mixture of the corresponding aldehyde and ammonia is passed through a column heated to 150–400 °C and filled with pumice containing 7.5% Zn and 1.5% Cr. Catalysts based on platinum[148,185,186] work under milder conditions (20–100 °C, $p_{H_2} = 1$–4 atm), but the yield of amines is as a rule low (10–65%). With increase of hydrogen pressure to 50–125 atm, the use of PtO_2,[187] Pd/C,[188,189] and Rh/Al_2O_3 [190] gives rise to 81–95% of secondary amines (Table 6, Nos.19–21).

There is very little information about the electrocatalytic amination of carbonyl compounds. It has been reported[191,192] that, using electrodes activated by Raney nickel, it was possible to convert acetone into isopropylamine in 78% yield. On these electrodes, ketones with identical hydrocarbon groups are aminated more readily than those with different hydrocarbon groups[149]. When a porous palladium electrode was used[193], the opposite behaviour was noted: the yield of the primary amine from ethyl methyl ketone was higher than that from diethyl ketone.

(b) Reductive Amination of Alicyclic Carbonyl Compounds

Nickel catalysts have been widely investigated, most studies being devoted to the synthesis of cyclohexylamine. Analysis of the literature data on the use of reduced nickel and Raney

Table 6. Reductive amination of aliphatic carbonyl compounds.

No.	Carbonyl compound	Catalyst	*t*, °C	*p*, atm	Product	Yield, %	Remarks	Refs.
1	Diethylaminoacetone	Raney Ni	20	1	3-diethylamino-2-propylamine	65	—	153
2	4-Diethylamino-2-butanone	Raney Ni	20	1	4-diethylamino-2-butylamine	75	—	153
3	5-Diethylamino-2-pentanone	Raney Ni	20	1	5-diethylamino-2-pentylamine	85	—	153
4	Acetone	Raney Ni	60—100	15	isopropylamine	98.7	acetone : NH_3 = 1 : 3	154
5	Ethyl methyl ketone	Raney Ni	150	45	2-aminobutane	93	—	155
6	Isobutyl methyl ketone	Raney Ni	150	45	3-amino-2,2-dimethylbutane	97	—	155
7	Diethyl ketone	Raney Ni	150	45	3-aminopentane	12—22	—	155
					bis(-α-ethylpropylamine)	40—66	—	
					3-pentanol	4	—	
8	Acetaldehyde	Raney Ni	150—160	35	ethylamine	83	—	156
9	Glyoxal	Raney Ni	200—210	77	imidazole	85	—	158
10	1-Butanal	Raney Ni	90	5—10	n-butylamine	74—80		160
11	1-Butanal	Raney Ni	80	15	dibutylamine	50	1-butanal : n-butylamine = 1 : 2	160
12	Acetone	Ni/Al_2O_3	150	46	isopropylamine	92		161
13	Acetone	Ni/Al_2O_3	100—150	1—4	isopropylamine	70—96	acetone : H_2 : NH_3 = 1:4:4–1:5:5	162
					dipropylamine	0.1—21.0		
					2-propanol	3—11		
14	1-Butanal	Ni/Al_2O_3	240	—	mixture of butylamines	50	1-butanal : NH_3 = 1 : 3	168
15	Acetaldehyde	Ni, Cu, and Mo on kieselguhr	180	—	ethylamine	53.4	acetaldehyde : H_2 : NH_3 = 1 : 5 : 5	175
					diethylamine	38.8		
					triethylamine	7.9		
16	Ethyl methyl ketone	17% Co; 0.9% Cr; 0.5% H_3PO_4 on Al_2O_3	110	300	s-butylamine	95.5	—	176
17	Acetone	77.5% Co; 4.5% Mg; 18% Mn	>140	100÷125	isopropylamine	95.5	—	179
18	C_{13}-C_{15} aldehydes	Co, 5% Zr	110—120	140—160	mixture of primary amines	97.1	—	180
19	Isobutyl methyl ketone	PtO_2	20	50	*N,N'*-dialkylhexamethylenediamines	85	aminating agent—hexamethylenediamine	187
20	Ethyl methyl ketone	Pd/C	85—105	65—100	s-butylmethylamine	88.3	aminating agent—methylamine	188,189
21	1-Butanal	(5% Rh)/Al_2O_3	0—125	180	dibutylamine	95	1-butanal : n-butylamine = 1 : 1.1	190

nickel[194-199] shows that these catalysts proved to be extremely selective and effective in the synthesis of cyclohexylamine (Table 7, Nos.1–3). In the reductive amination of more complex alicyclic compounds it is impossible to achieve a high yield of amines even under severe conditions (Table 7, No.4). It has been established[196] that the yield of amines depends on the solvent employed and falls in the sequence ethanol > water > methanol > isopropyl alcohol. The authors suggest that in alcoholic solution the reaction proceeds via the intermediate cyclohexanone–cyclohexylimide. Cyclohexylamine is obtained also in the electrocatalytic reduction of cyclohexanone[200] in the presence of Raney nickel electrodes.

Other nickel-containing catalysts are also known. It is suggested in a patent[201] that nickel be modified by the addition of H_3PO_4 or H_3BO_3 for the synthesis of cyclohexylamine. A number of studies have been made[202-204] on nickel–chromium catalysts. They do not require high pressures and are more stable than Raney nickel, although they are inferior to it as regards selectivity (Table 7, No.5).

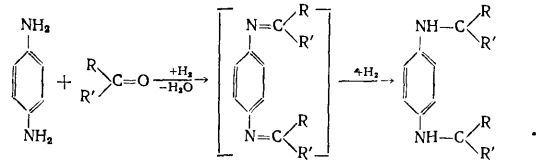
Nickel on alumina proved to be a less effective catalyst[205], but in its presence certain aliphatic ketones have been aminated[206] by pyridine bases, while dicyclohexylamine has been obtained from cyclohexanone and aniline at $p_{H_2} = 20$ atm at 250 °C.[207] We may note that, in the presence of Cu/Al_2O_3, *N*-cyclohexylaniline was obtained under the same conditions. Aliphatic cyclic amines have been synthesised using a catalyst containing Ni, MgO, and kieselguhr[208], and 1-*N*-cycloalkylaminocyclododecene which has been obtained[209] from cyclododecanone and morpholine, piperidine, and pyrrolidine in the presence of $TiCl_4$.

Table 7 (Nos.6–11) shows that catalysts based on noble metals[148,185,186,188,190,210,213] proved to be effective, with the exception of the study of Popov and Shuikin[185], only for the synthesis of secondary and tertiary amines. We may note that, when platinised quartz or certain other catalysts are used, mainly aniline is obtained from cyclohexanone[214].

(c) Reductive Amination of Aromatic Carbonyl Compounds

Raney nickel proved to be extremely suitable for the amination of aromatic carbonyl compounds[153,215-219]. Examples of its use (Table 8, Nos.1–5) shows that the yield of amines is fairly high and depends on the structure of the initial carbonyl compounds and on the reaction conditions.

As in the reductive amination of aliphatic and alicyclic carbonyl compounds, catalysts based on noble metals[148,190,220-228] proved to be effective only for the synthesis of secondary and tertiary aromatic amines (Table 8, Nos.6–8). The use for this purpose of platinum group metal sulphides[229-233] or catalysts based on these metals with added sulphur-containing compounds[234,235] (Table 8, Nos.9–11) proved to be particularly successful. It has been suggested[232] that the alkylation of *p*-phenylenediamine proceeds via the intermediate formation of Schiff bases:



In another study by the same workers[236] it was shown that, in the presence of the same catalysts and under similar conditions, the reduction of Schiff bases does indeed occur.

Among non-noble metal sulphides, rhenium sulphide proved to be the most active catalyst[232,237] (Table 8, No.12). The sulphides of basic metals proved to be relatively insensitive to poisons and in their presence virtually no hydrogenation of the benzene ring was observed and in many instances the initial carbonyl compound was not reduced to the corresponding alcohol.

Copper catalysts modified with barium sulphate[182] or chromium oxide[238,239] have been used[182,238,239] to synthesise secondary aromatic alkylamines. The yield of amines under conditions close to those employed for sulphide catalysts is appreciably lower (38–74%).

(d) Reductive Amination of Carbonyl Compounds in the Presence of Tetrahydroborates

Lane[240] believes that the reductive amination of an aldehyde or ketone is possible when the carbonyl compound interacts with an amine or ammonia at pH 6–8 in the presence of $NaCNBH_3$. The explanation is that the imino-group is reduced much faster than the carbonyl group. It has been suggested[241-245] that $LiCNBH_3$ in methanol at pH 5–6 and 25 °C be used together with $NaCNBH_3$ for reductive amination. However, lithium cyanotrihydroborate proved to be

Table 7. Reductive amination of alicyclic carbonyl compounds.

No.	Carbonyl compound	Catalyst	*t*, °C	*p*, atm	Product	Yield, %	Remarks	References
1	Cyclohexanone	Ni	140	28	cyclohexylamine	98.5	—	194
2	Cyclohexanone	Ni	130	30	cyclohexylamine	97.5	—	195
3	Cyclohexanone	Raney Ni and Co	80	5–15	cyclohexylamine	90–95	—	196
					dicyclohexylamine	0.2		
					cyclohexanol	0.2–3.1		
4	Cycloheptanone	Raney Ni	70	100	cycloheptylamine	61	—	199
5	Cyclohexanone	45% Ni; 1.8% Cr on kieselguhr	140	—	cyclohexylamine	84–86	—	204
					dicyclohexylamine	12–14	—	
6	Cyclohexanone	Pd/C	89–94	60–130	dicyclohexylamine	86.2	—	188
7	Cyclohexanone	PtO_2	20	1–3	cyclohexylamine	44–50	—	148
8	Cyclohexanone	Pt/SiO_2	200	—	cyclohexylamine	89.6	—	185
9	Cyclopentanone	Pt/SiO_2	170–240	—	cyclopentylamine	11.3	—	186
10	Formaldehyde	(5% Rh)Al_2O_3	20	180	cyclohexylmethylamine	68.8	aminating agent–cyclohexylamine	190
11	Cycloalkanones	AgO, PdO, and MnO on SiO_2	150–180	200	secondary and tertiary amines	98	aminating agent–secondary amines	212

a milder reductant than $NaBH_4$ and reductive amination did not go to completion in its presence. This may be associated with the choice of solvent. It is known[246] that $NaBH_4$ reduces the $>C=N$ bond more readily in dimethyl sulphoxide than in alcohols.

Using sodium cyanotrihydroborate, Borch and coworkers aminated cyclohexanone with methyl- and propyl-amines[243], methyl phenyl ketone with ammonia[242], and formaldehyde with aniline[245]. This yielded 78.5% of cyclohexylpropylamine, 53% of cyclohexyldimethylamine, 76% of 1-phenyl-1-aminoethane, and 92% of dimethylaniline. Together with the examples described, a considerable number of analogous syntheses of primary, secondary, and tertiary amines have been carried out[241-245] at room temperature and atmospheric pressure. This undoubtedly demonstrates the importance of the synthetic application of tetrahydroborates in the reductive amination of aldehydes and ketones. At the same time, in view of the high cost of tetrahydroborates, the large scale industrial production of amines by this procedure is not very promising.

(e) Reductive Amination of Carbonyl Compounds in the Presence of Complex and Catalysts

The reductive amination of carbonyl compounds in the presence of complex catalysts has been so far inadequately investigated. In a number of studies[247-252] the reductant was the complex tetracarbonylhydroferrate $[HFe(CO)_4]^-$ in an equimolar amount relative to the carbonyl compound. The reaction was carried out in an atmosphere of CO at room temperature in alcohol; $[HFe(CO)_4]^-$ was obtained *in situ* by the reaction of $Fe(CO)_5$ with alkali. Under these conditions, Watanabe et al. synthesised *N*-alkyl- and *N*-aryl-glycines from glyoxylic acid[249] and *N*-substituted piperidines from glutaraldehyde[250] and also carried out the amination[247] of acetone by isopropylamine (Table 9, No.1), of butanol by aniline (Table 9, No.2), and of cyclohexanone by cyclohexylamine (Table 9, No.3). *N,N*-Dimethyl-, *N,N*-diethyl, *N,N*-dipropyl-, *N,N*-dibutyl-, *N,N*-ethylmethyl-, and other *N,N*-substituted anilines have been obtained from aniline and the corresponding aldehydes in quantitative yields[248]. The reaction has been shown to proceed via *N*-substituted anilines[251].

Certain aromatic amines have been alkylated by formaldehyde under analogous conditions[252]. The yield of the corresponding secondary and tertiary amines was ~80%. The authors suggested that the reaction proceeds via the formation of intermediate Schiff bases, which are reduced irreversibly by $[HFe(CO)_4]^-$ to the corresponding amines. The $[HFe(CO)_4]^-$ ion cannot be regarded as a catalyst, since it is active only in stoichiometric amounts.

The reductive amination of aldehydes and ketones by ammonia and primary and secondary amines has been investigated[253] in the presence of catalytic amounts of cobalt and rhodium carbonyls at 100–160 °C and $p_{H_2} = 100$–300 atm. Amines were obtained in very high yields in this homogeneous process. Thus (2-ethylhexyl)isopropylamine (Table 9, No.4), cyclohexylisopropylamine (Table 9, No.5), and benzylmethylamine (Table 9, No.6) have been obtained from α-ethylhexanal and isopropylamine, from cyclohexanone and isopropylamine, and from benzyl methyl ketone and ammonia respectively.

A cobalt cyanide complex has been used[254,255] as a catalyst of the homogeneous reductive amination of benzylacetone (Table 9, No.7) and benzylacetophenone (Table 9, No.8). Previously aminoacids had been obtained[256-258] from α-hydroxyacids with the aid of this catalyst.

In enzymatic catalysis reductive amination constitutes the main pathway for the conversion of ammonia into compounds with α-amino-groups[259]. It is to be expected that compounds which are models of enzymes will prove active in the reductive amination reaction. Indeed it has been reported[260] that *N*-methylaniline can be obtained from aniline and formaldehyde under mild conditions in the presence of vitamin B_{12r} or its model—diaquocobaloxime(II).

It has been found[261] that hydridobis(dimethylglyoximato)-aquorhodium(III) is a catalyst of the reductive amination of formaldehyde by aniline and of cyclohexanone by ammonia (Table 9, No.9). At the same time, in contrast to claims by Schrauzer and Windgassen[260], it has been shown[261] that in the presence of diaquocobaloxime(II) the process is not catalytic and stops at the stage involving the formation of the complex

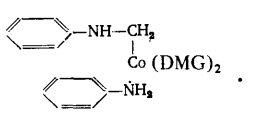


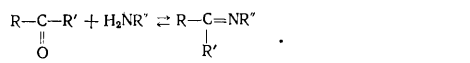
Table 8. Reductive amination of aromatic carbonyl compounds.

No.	Carbonyl compound	Catalyst	*t*, °C	*p*, atm	Product	Yield, %	Remarks	Refs.
1	Phenylacetone	Raney Ni	20	1	2-amino-3-phenylpropane	85	—	153
2	Benzylacetone	Raney Ni	20	1	2-amino-4-phenylbutane	67	—	153
3	Acetophenone	Raney Ni	110—130	25	α-phenylethylamine	90.7	—	215
4	Acetophenone	Raney Ni	110—150	50—150	α-phenylethylamine	94	—	216
5	2,5-Dimethoxyphenylacetone	Raney Ni	90	70	2-amino-3-(2,5-dimethoxyphenyl)propane	95	aminating agent—CH_3COONH_4	218
6	1-Butanal	(5% Rh)/Al_2O_3	75	50	N-butylaniline	93	aminating agent—aniline	190
7	Acetophenone	PtO_2	20	1—3	α-phenylethylamine	69	—	148
8	Octadecanone	Pt	26	—	2-benzylaminooctadecane	89.9	aminating agent—benzylamine	222
9	Acetone	(5% RhS)/C	140	80	*N,N*-diisopropyl-1,5-naphthylenediamine	96	aminating agent—1,5-naphthylenediamine	233
10	Ketones	PdS	150—200	110—150	*N,N*-dialkyl-*p*-phenylenediamines	60—90	aminating agent—*p*-phenylenediamine	232
11	Ketones	Pt/Al_2O_3+0,005÷2% S	120—175	14—105	*N,N*-dialkyl-*p*-phenylenediamines	50—90	aminating agent—*p*-phenylenediamine	235
12	Acetone	Re_2S_7	140	80	*N*-isopropylaniline	90	aminating agent—aniline	237

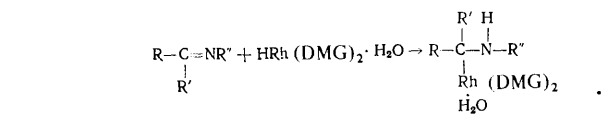
Table 9. Reductive amination of aldehydes and ketones in the presence of complex compounds.

No.	Carbonyl compound	Complex compound	*t*, °C	*p*, atm	Product	Yield, %	Remarks	Refs.
1	Acetone	$Fe(CO)_5$	20	1	diisopropylamine	93	amination with isopropylamine in an atmosphere of CO	247
2	1-Butanal	$Fe(CO)_5$	20	1	*N*-n-butylaniline	100	aminating agent—aniline; in an atmosphere of CO	247
3	Cyclohexanone	$Fe(CO)_5$	20	1	dicyclohexylamine	100	aminating agent—cyclohexylamine; in an atmosphere of CO	247
4	α-Ethylhexanal	$Rh_6(CO)_{16}$	110—160	100—300	(2-ethylhexyl)isopropylamine	98	aminating agent—isopropylamine; in an atmosphere of CO and H_2	253
5	Cyclohexanone	$Rh_6(CO)_{16}$	110—160	100—300	cyclohexylisopropylamine	100	ditto	253
6	Benzyl methyl ketone	$Co_2(CO)_8 + P(C_4H_9)_3$	150—180	100—300	benzylmethylamine	69	reaction in an atmosphere of H_2 and CO	253
7	Benzylacetone	cobalt cyanate complex	70	50	2-amino-4-phenylbutane	73.2	ditto	255
8	Benzylacetophenone	cobalt cyanate complex	70	50	2-amino-1,4-diphenylbutane	53.3	" "	255
9	Cyclohexanone	$HRh(DMG)_2.H_2O$	45	1	cyclohexylamine, dicyclohexylamine	74 9	yield w.r.t. cyclohexanone employed	261

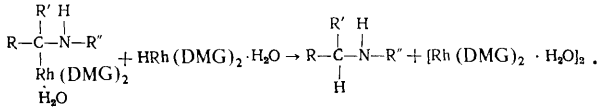
It has been postulated[261] that the reaction proceeds via the following mechanism: there is initial condensation of the carbonyl compound with ammonia or the amine:



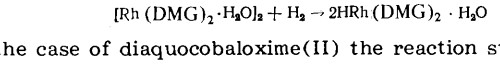
The resulting imine or Schiff base reacts with the catalyst to form an intermediate complex:



The complex reacts with a new catalyst species and forms amines:



The resulting dimer is reduced in its turn by hydrogen with formation of two molecules of the initial catalyst:



In the case of diaquocobaloxime(II) the reaction stops in the second stage. In this connection one may note that, in a number of other reduction reactions, rhodium complexes proved to be more active than the corresponding cobalt analogues[262].

---o0o---

It is seen from the data presented that considerable advances have been made in recent years in the catalytic amination of carbonyl compounds and alcohols. Thus, on the basis of developments in recent years, a large-scale industrial production of aniline from phenol has been established in the USA;[263] many valuable medicinal drugs have been obtained[6] by the reductive amination of various carbonyl compounds.

Despite the fact that the vast majority of amines are obtained nowadays by traditional methods (from alcohols or halogeno-compounds or by the reduction of nitro-compounds), in the immediate future the reductive amination of carbonyl compounds may become one of the main procedures for the synthesis of amines. This appears possible primarily because of the considerable advances in the field of oxo synthesis (see, for example, Alekseeva et al.[264]), which made it possible to reduce the cost of carbonyl compounds. Many aldehydes and ketones are now cheaper than the corresponding alcohols[265].

The most important task at the present time is the selection of highly effective and selective catalysts for the reductive amination of carbonyl compounds, because only on the basis of such catalysts is it possible to set up a modern waste-free industry. Great expectations are associated with the employment of the principles of molecular catalysis[266]. The first studies on the use of complex catalysts for reductive amination give rise to the hope that in their presence it will be possible to carry out the process under mild conditions and extremely selectively.

REFERENCES

1. P.Sabatier and A.Mailhe, Compt.rend., **148**, 898 (1909).
2. M.C.Mignonac, Compt.rend., **169**, 237 (1919).
3. W.Emerson, in "Organic Reactions" (Translated into Russian), Inostr.Lit., Moscow, 1951, Vol.5, p.347.
4. V.A.Nekrasova and N.I.Shuikin, Uspekhi Khim., **34**, 1945 (1965)[Russ.Chem.Rev., No.11 (1965)].
5. M.I.Yakushkin, Khim.Prom., **7**, 13 (1966).
6. M.Freifelder, "Practical Catalytic Hydrogenation", Wiley and Sons, New York, 1970, p.333.
7. P.Rylander, "Catalytic Hydrogenation over Platinum Metals", Acad.Press, New York, 1967.
8. P.Sabatier, "Catalysis in Organic Chemistry" (Translated into Russian), Goskhimizdat, Leningrad, 1932.
9. G.Baum, "Über der Katalytishe Alkylierung von Ammoniack", Zürich, 1945.
10. E.D.Schwegler and H.Adkins, J.Amer.Chem.Soc., **61**, 3499 (1939).

11. M.A.Popov, Candidate's Thesis, Institute of General Chemistry of the USSR Academy of Sciences, Moscow, 1952.
12. M.A.Popov and N.I.Shuikin, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 308 (1955).
13. F.V.Bel'chev, N.I.Shuikin, and S.S.Novikov, Izv. Akad.Nauk SSSR, Otd.Khim.Nauk, 649 (1961).
14. F.V.Bel'chev, Trudy Beloruss.Sel'khozakad., **31**, 83 (1959).
15. Yu.B.Kryukov, N.S.Zakirov, F.I.Novak, A.N.Bashkirov, and E.I.Bogolepova, Neftekhimiya, 7, 124 (1967).
16. A.N.Bashkirov, R.A.Fridman, E.I.Bogolepova, R.M.Smirnova, and Yu.B.Kryukov, Dokl.Akad. Nauk SSSR, **201**, 847 (1971).
17. R.A.Fridman, E.I.Bogolepova, R.M.Smirnova, Yu.B.Kryukov, G.A.Zhukova, and A.N.Bashkirov, Neftekhimiya, **12**, 91 (1972).
18. R.A.Fridman, E.I.Bogolepova, Yu.B.Kryukov, and A.N.Bashkirov, Neftekhimiya, **15**, 426 (1975).
19. G.A.Kliger, L.F.Lazutina, R.A.Fridman, Yu.B.Kryukov, and A.N.Bashkirov, Neftekhimiya, **16**, 660 (1975).
20. G.A.Kliger, L.F.Lazutina, Yu.B.Kryukov, R.A.Fridman, A.N.Bashkirov, and Yu.S.Snagovskii, Neftekhimiya, **16**, 665 (1975).
21. N.S.Kozlov, "Kataliz v Vysshei Shkole, Trudy I Mezhvuzovskogo Soveshchaniya po Katalizu, 1958" (Catalysis in Colleges. Proceedings of the Ist Intercollegiate Conference on Catalysis, 1958), Izv. Moskov.Gos.Univ., Moscow, 1962, Vol.1, Part 2, p.307.
22. N.S.Kozlov and N.I.Panova, Zhur.Obshch.Khim., **26**, 2602 (1956).
23. A.F.Plate, M.E.Vol'pin, E.A.Reformatskaya, and S.V.Zotova, Zhur.Obshch.Khim., **26**, 687 (1956).
24. USSR P.170517 (1965); Ref.Zhur.Khim., 23N, 133 (1966).
25. N.S.Kozlov and N.I.Panova, Zhur.Obshch.Khim., **28**, 2384 (1958).
26. E.Dutkai, Rev.Chim., **22**, 263 (1971).
27. N.S.Kozlov and I.P.Kirichenko, Uch.Zap.Perm. Pedinst., **32**, 27 (1965).
28. N.S.Kozlov and N.I.Panova, Trudy Perm.Pedinst., **24**, 185 (1959).
29. N.S.Kozlov, Uch.Zap.Perm.Pedinst., **20**, 180 (1959).
30. N.S.Kozlov, V.Sh.Pasternak, N.I.Panova, and V.N.Gudz', Uch.Zap.Perm.Pedinst., **32**, 33 (1965).
31. US P.2389500 (1945); Chem.Abs., **40**, 898 (1946).
32. US P.2394515 (1946); Chem.Abs., **40**, 2455 (1946).
33. US P.2394516 (1946); Chem.Abs., **40**, 2455 (1946).
34. F.V.Bel'chev and V.I.Shuikin, Zhur.Obshch.Khim., **26**, 2218 (1956).
35. F.V.Bel'chev, Trudy Beloruss.Sel'khozakad., **28**, 87 (1958).
36. F.V.Bel'chev, N.I.Shuikin, and S.S.Novikov, Izv. Akad.Nauk SSSR, Otd.Khim.Nauk., 710 (1959).
37. V.Yu.Sak, Trudy Beloruss.Sel'khozakad., **31**, 89 (1959).
38. Y.Takita, Y.Nishida, and T.Seiyama, Bull.Chem. Soc.Japan, **49**, 3699 (1976).
39. H.Heinemann, R.W.Wert, and W.S.W.McCarter, Ind. Eng.Chem., **41**, 2928 (1949).
40. US P.3384667 (1968); Chem.Abs., **69**, P86340 (1968).
41. Kh.I.Areshidze and E.K.Tavartkiladze, Trudy Tbilissk.Univ., 143 (1972).
42. Kh.I.Areshidze and E.K.Tavartkiladze, Soobshch. Akad.Nauk Gruz.SSR, **39**, 569 (1965).
43. Kh.I.Areshidze and E.K.Tavartkiladze, Soobshch. Akad.Nauk Gruz.SSR, **52**, 63 (1968).
44. DDR P.108275 (1974); Chem.Abs., **83**, 9169 (1975).
45. W.Richarz, M.Zutz, and A.Guyer, Helv.Chim.Acta, 42, 2212 (1959).
46. W.Richarz, M.Zutz, and A.Guyer, Helv.Chim.Acta, 45, 2154 (1962).
47. US P.246599 (1948); Chem.Abs., **43**, 3440 (1949).
48. K.Patnak and B.Rao, J.Sci.Ind.Res., India, **20**, 142 (1961).
49. R.S.Egly and E.F.Smith, Chem.Eng.Progr., 44, 387 (1948).
50. S.Berkman, D.Morrel, and G.Egloff, "Catalysis in Inorganic and Organic Chemistry" (Translated into Russian), Gostoptekhizdat, Moscow, 1950, Vol.2, p.70.
51. USSR P.170997 (1965); Ref.Zhur.Khim., 23N132P (1966).
52. French P.2168716 (1973); Chem.Abs., 80, 70298 (1974).
53. US P.3723311 (1973); Chem.Abs., **79**, 4992 (1973).
54. B.P.586470 (1947); Chem.Abs., **41**, 6894 (1947).
55. BRD P.949565 (1956).
56. R.G.Rice, E.I.Kohr, and S.W.Daasch, J.Org.Chem., **23**, 1352 (1958).
57. G.N.Kao, B.D.Tilak, and K.Venkataraman, J.Sci. Ind.Res., India, **14B**, 624 (1955).
58. Japanese P.75116408 (1975); Chem.Abs., **84**, 58611 (1976).
59. US P.2782237 (1957); Chem.Abs., **51**, 1076 (1957).
60. US P.2953601 (1961); Chem.Abs., **55**, 6043 (1961).
61. BRD P.2114614 (1972); Chem.Abs., **77**, 164013 (1972).
62. BRD P.890646 (1958); Chem.Abs., **53**, 2342 (1959).
63. US P.2636902 (1953); Chem.Abs., **48**, 3991 (1954).
64. Canadian P.495013 (1953).
65. B.P.1074603 (1967); Chem.Abs., **67**, 99626 (1967).
66. French P.2180462 (1974); Chem.Abs., **80**, 120229 (1974).
67. US P.3137730 (1964).
68. BRD P.1172268 (1964).
69. French P.1483299 (1967); Chem.Abs., **69**, 10080 (1968).
70. Japanese P.7532113 (1975); Chem.Abs., **83**, 78568 (1975).
71. French P.1113411 (1956).
72. M.A.Popov, Zhur.Obshch.Khim., **18**, 438 (1948).
73. M.A.Popov, Zhur.Obshch.Khim., **18**, 1109 (1948).
74. USSR P.113889 (1960); Byul.Izobret., No.23, 17 (1960).
75. G.A.Kliger, A.N.Bashkirov, N.N.Bezinger, and Yu.B.Kagan, Neftekhimiya, **1**, 397 (1961).
76. Yu.B.Kagan, A.N.Bashkirov, and G.A.Kliger, Izv. Akad.Nauk SSSR, Otd.Khim.Nauk, 468 (1961).
77. Yu.B.Kagan, A.N.Bashkirov, G.A.Kliger, Chao-Tu Chou, and N.E.Mak, Neftekhimiya, **1**, 403 (1961).
78. G.A.Kliger, A.N.Bashkirov, O.A.Lesik, E.V.Marchevskaya, Yu.A.Koshevnik, and M.V.Shishkina, Neftekhimiya, **15**, 441 (1975).
79. Yu.B.Kagan, A.N.Bashkirov, G.A.Kliger, Chao-Tu Chou, and N.E.Mak, Neftekhimiya, **19**, 558 (1961).
80. Yu.B.Kagan, A.N.Bashkirov, G.A.Kliger, and A.Ya.Rozovskii, Neftekhimiya, **2**, 253 (1962).
81. Yu.B.Kagan, G.A.Kliger, A.N.Bashkirov, O.A.Lesik, and E.V.Marchevskaya, Neftekhimiya, 7, 619 (1967).

82. G.A.Kliger, A.N.Bashkirov, O.A.Lesik, and E.V.Marchevskaya, Neftekhimiya, **11**, 80 (1971).
83. G.A.Kliger, A.I.Bashkirov, L.S.Polak, E.N.Chervochkin, E.V.Marchevskaya, and O.A.Lesik, Neftekhimiya, **10**, 907 (1970).
84. G.A.Kliger, A.N.Bashkirov, L.S.Polak, O.A.Lesik, E.N.Chervochkin, and E.V.Marchevskaya, Neftekhimiya, **13**, 116 (1973).
85. G.A.Kliger, A.N.Bashkirov, L.S.Polak, O.A.Lesik, E.N.Chervochkin, and E.V.Marchevskaya, Neftekhimiya, **13**, 265 (1973).
86. G.A.Kliger, A.N.Bashkirov, L.S.Polak, E.V.Marchevskaya, E.N.Chervochkin, and O.A.Lesik, Neftekhimiya, **9**, 433 (1969).
87. G.A.Kliger, A.N.Bashkirov, P.Schneider, A.Ya.Rozovskii, O.A.Lesik, E.V.Marchevskaya, and Yu.B.Kagan, Neftekhimiya, **8**, 283 (1968).
88. G.A.Kliger, L.F.Lazutina, R.A.Fridman, Yu.B.Kryukov, and A.N.Bashkirov, Article Deposited at the All-Union Institute of Scientific and Technical Information (VINITI)(6347, 1973).
89. G.A.Kliger, A.N.Bashkirov, Kuan-Yü Lü, and Yu.B.Kagan, Neftekhimiya, **2**, 384 (1962).
90. R.A.Fridman, G.A.Kliger, E.P.Bogolepova, Yu.V.Maksimov, and I.P.Suzdalev, Izv.Akad.Nauk SSSR, Ser.Khim., 744 (1976).
91. N.S.Kozlov and L.F.Akhmetshina, Dokl.Akad.Nauk SSSR, **85**, 91 (1952).
92. N.S.Kozlov, G.I.Lomako, and L.G.Gurskaya, Vestsi Akad.Nauk Beloruss.SSR, Ser.Khim.Navuk, 68(1974).
93. E.Klingsberg, "Pyridine and Its Derivatives", Interscience, New York, 1966, Part I, p.152.
94. Dutch P.6401010 (1964); Chem.Abs., **62**, 3953 (1965).
95. USSR P.287956 (1970); Byul Izobret., No.36, 33 (1970).
96. Kh.I.Areshidze and B.S.Tsereteli, Soobshch.Akad. Nauk Gruz.SSR, **61**, 69 (1971).
97. Kh.I.Areshidze and B.S.Tsereteli, Soobshch.Akad. Nauk Gruz.SSR, **72**, 365 (1973).
98. BRD P.830047 (1952); Chem.Abs., **47**, 2204 (1953).
99. G.A.Kliger, A.N.Bashkirov, L.A.Lesik, and Yu.B.Kagan, Neftekhimiya, **5**, 569 (1965).
100. Y.Omote, K.Iwase, and J.Nakamura, Kogyo Kagaku Zasshi, **70**, 1508 (1967).
101. J.T.Richardson and Wei-Chu Lu, J.Catalysis, **42**, 275 (1976).
102. US P.3442950 (1969), Chem.Abs., **71**, 12780 (1969).
103. US P.3347921 (1967); Chem.Abs., **68**, 118224 (1967).
104. M.A.Popov and N.I.Shuikin, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 370 (1950).
105. N.S.Koslov and L.F.Akhmetshina, Zhur.Obshch. Khim., **25**, 485 (1955).
106. Japanese P.7414737 (1974); Chem.Abs., **81**, 135685 (1974).
107. Japanese P.7414738 (1974); Chem.Abs., **81**, 135688 (1974).
108. Japanese P.7429176 (1974); Chem.Abs., **82**, 139624 (1975).
109. Japanese P.7123053 (1971); Chem.Abs., **75**, 76390 (1971).
110. Japanese P.7123052 (1971); Chem.Abs., **75**, 76391 (1971).
111. BRD P.2003842 (1970); Chem.Abs., **73**, 66245 (1970).
112. BRD P.2026053 (1970); Chem.Abs., **74**, 42125 (1971).
113. Belg.P.635927 (1964); Chem.Abs., **61**, 13237 (1964).
114. US P.3275567 (1966); Chem.Abs., **65**, 20055 (1966).
115. BRD P.1954274 (1970); Chem.Abs., **73**, 35024 (1970).
116. K.Tanabe, M.Itch, and M.Sato, Chem.Comm., 676 (1973).
117. M.Itoh, H.Hattori, and K.Tanabe, J.Catal., **35**, 225 (1974).
118. Japanese P.7396475 (1973); Chem.Abs., **80**, 137568 (1974).
119. Y.Watanabe and N.Nojiri, Nippon Kagaku Zasshi, 540 (1974).
120. M.Yamamoto, N.Takamiya, and S.Murai, Nippon Kagaku Zasshi, 2135 (1974).
121. G.A.Kliger, A.N.Bashkirov, O.A.Lesik, E.V.Marchevskaya, and Yu.B.Kagan, Neftekhimiya, 6, 769 (1966).
122. D.Claude, Ann.Mines, 1101 (1975).
123. US P.3931298 (1976); Chem.Abs., **84**, 89799 (1976).
124. US P.3355490 (1967).
125. US P.3364261 (1968).
126. Japanese P.7434677 (1974); Chem.Abs., **82**, 124897 (1975).
127. US P 3351661 (1967); Chem.Abs., **68**, 95388 (1968).
128. T.H.Evans and A.N.Bours, Canad.J.Technol., **29**, 1 (1950).
129. A.A.Balandin and N.P.Sokolova, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 1543 (1961).
130. N.S.Kozlov and G.I.Lomako, Vestsi Akad.Nauk Beloruss.SSR, Ser.Khim.Navuk, 83 (1972).
131. N.S.Kozlov and G.I.Lomako, Vestsi Akad.Nauk Beloruss.SSR, Ser.Khim.Navuk, 29 (1972).
132. N.S.Kozlov, G.I.Lomako, and A.G.Zezyulya, Dokl. Akad.Nauk Beloruss.SSR, 522 (1973).
133. G.I.Lomako and A.P.Zezyulya, Vestsi Akad.Nauk Beloruss.SSR, Ser.Khim.Navuk, 116 (1974).
134. R.N.Shreve, G.N.Vriens, and D.A.Vogel, Ind.Eng. Chem., **42**, 791 (1950).
135. Japanese P.76101929 (1976); Chem.Abs., **86**, 29469 (1977).
136. BRD P.2348738 (1973); Chem.Abs., **81**, 34125 (1974).
137. R.G.Rice and E.I.Kohn, J.Amer.Chem.Soc., 77, 4052 (1955).
138. C.Ainworth, J.Amer.Chem.Soc., **78**, 1635 (1956).
139. J.Horyna and O.Cerny, Chem.Listy, **50**, 381 (1956).
140. J.Horyna and O.Cerny, Coll.Czech.Comm., **21**, 906 (1956).
141. J.Weichet, J.Hodrova, and L.Blaha, Coll.Czech. Comm., **26**, 2040 (1961).
142. J.C.Jungers and L.Sajus, Rev.Inst.Franc.petrole, **20**, 1899 (1965).
143. A.Le Bris, G.Lefebvre, and F.Goussemant, Bull.Soc. chim.France, **6**, 1366 (1964).
144. A.Le Bris, G.Lefebvre, and F.Goussemant, Bull.Soc. chim.France, **6**, 1375 (1964).
145. A.Le Bris, G.Lefebvre, and F.Goussemant, Bull.Soc. chim.France, **7**, 1584 (1964).
146. A.Le Bris, G.Lefebvre, and F.Goussemant, Bull.Soc. chim.France, **7**, 1595 (1964).
147. H.Wilms, "Methoden der organischen Chemie", Verlag, Stuttgart, 1957, Vol.11/1, p.611.
148. E.R.Alexander and A.Misegades, J.Amer.Chem.Soc., **70**, 1315 (1948).
149. V.L.Mirzoyan, Yu.A.Matveev, and V.N.Lopastinskaya, Trudy Khim.Metallurg.Inst., Akad.Nauk Kazakh.SSR, **20**, 75 (1973).
150. P.Richter and J.Pasek, Chem.prumysl, **20**, 426 (1970).

151. R.L.Augustine, Catal.Rev.Sci.Eng., **13**, 285 (1976).
152. E.T.Borrows, B.M.Hargreaves, J.E.Page, J.S.Resuggen, and F.A.Robinson, J.Chem.Soc., 197 (1947).
153. L.Haskelberg, J.Amer.Chem.Soc., **70**, 2811 (1948).
154. Y.Omote, K.Masuda, and J.Nakamura, J.Chem. Soc.Japan, Ind.Chem.Sect., **70**, 1339 (1967).
155. Y.Omote, K.Masuda, and J.Nakamura, Kagaku Zasshi, 70, 1343 (1967).
156. Japanese P.6920322 (1969); Chem.Abs., 71, 112397 (1969).
157. Japanese P.62217 (1962); Ref.Zhur.Khim., 21L37 (1963).
158. T.Sasaki, J.Soc.Org.Synth.Chem.Japan, **17**, 131 (1959).
159. H.L.Bami, B.H.Iyer, and P.C.Guba, Current Sci. (India), 16, 253 (1947).
160. A.M.Grigorovskii and R.S.Margolina, Zhur.Prikl. Khim., 18, 644 (1945).
161. French P.1590871 (1970); Chem.Abs., **74**, 76004 (1971).
162. Czech.P.131353 (1969); Chem.Abs., **72**, 132022 (1970).
163. J.Pasek and P.Richter, Chem.prumysl, **19**, 63 (1969).
164. P.Richter and J.Pasek, Chem.prumysl, 17, 353 (1967).
165. S.Serban, D.Goidea, I.Duldner, M.Biro, and E.Dutkai, Rev.Chim., **17**, 519 (1966).
166. B.P.632219 (1949); Chem.Abs., **44**, 4023 (1950).
167. USSR P.455944 (1975); Byul.Izobret., No.52, 51 (1975).
168. M.A.Popov and N.I.Shuikin, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 1082 (1962).
169. DDR P.12870 (1957); Chem.Abs., **53**, 6080 (1959).
170. Czech.P. 88273 (1959); Ref.Zhur.Khim., 6L77 (1961).
171. DDR P.14768 (1958).
172. E.Treszczanovicz, I.Jaworska, and W.Kazmierowicz, Przemysl Chem., **34**, 36 (1955).
173. Polish P.42199 (1959); Chem.Abs., **55**, 4361 (1961).
174. Polish P.41732 (1959); Ref.Zhur.Khim., 6L75 (1961).
175. Japanese P.7436608 (1974); Chem.Abs., 81, 77456 (1974).
176. BRD P.2535725 (1976); Chem.Abs., **85**, 62629 (1976).
177. US P.3976697 (1976); Chem.Abs., **85**, 73138 (1976).
178. French P.1468354 (1967); Chem.Abs., **67**, 81798 (1967).
179. BRD P.2219475 (1973); Chem.Abs., **80**, 26739 (1974).
180. Japanese P.7424905 (1974); Chem.Abs., **80**, 145377 (1974).
181. B.P.701228 (1953).
182. US P.2828343 (1958).
183. N.S.Kozlov, S.I.Kozintsev, L.V.Naumova, and T.K.Efimova, Vestsi Akad.Nauk Beloruss.SSR, Ser. Khim.Navuk, 50 (1976).
184. BRD P.1049853 (1959).
185. M.A.Popov and N.I.Shuikin, Izv.Akad.Nauk SSSR, Ser.Khim., 140 (1951).
186. M.A.Popov, N.I.Shuikin, and O.L.Baranovskaya, Izv.Akad.Nauk SSSR, Ser.Khim., 91 (1953).
187. A.Bonvicini, G.Cantatore, and E.Ildos, Chimica e Industria, **47**, 641 (1965).
188. J.Volf, J.Pasek, and P.Krans, Sb.Vys.Sk.Chem.-Technol.Praze, Org.Chem.Technol., C19, 27 (1973).
189. Czech.P.162257 (1976); Chem.Abs., **85**, 176815 (1976).
190. US P.3597439 (1971); Chem.Abs., **75**, 110046 (1971).
191. I.V.Kirilyus, V.L.Mirzoyan, and D.V.Sokol'skii, Elektrokhimiya, **10**, 859 (1974).
192. USSR P.482436 (1975); Byul.Izobret., No.52, 63 (1975).
193. H.Muto, E.Ichikawa, and K.Odo, Denki Kagaku, **36**, 363 (1968).
194. Japanese P.7019898 (1970); Chem.Abs., **73**, 98470 (1970).
195. Japanese P.7019897 (1970); Chem.Abs., **73**, 98471 (1970).
196. Y.Omote, K.Iwase, and J.Nakamura, Kogyo Kagaku Zasshi, **70**, 1335 (1967).
197. A.N.Kost, Nauch.Dokl.Vys.Shkoly, Khim.i Khim. Tekhnol., No.1, 125 (1958).
198. P.M.Adrov, V.N.Yanovskii, V.N.Borodin, M.I.Komendantov, and N.N.Shenberg, Zhur.Org. Khim., **12**, 1827 (1976).
199. M.Freifelder, W.D.Smart, and G.R.Stone, J.Org. Chem., **27**, 2209 (1962).
200. D.V.Sokol'skii, V.L.Mirzoyan, and Yu.N.Matveev, Trudy Khim.Metallurg.Inst.Akad.Nauk Kazakh.SSR, 18, 111 (1972).
201. Japanese P.667575 (1966); Ref.Zhur.Khim., 4N187 (1968).
202. Japanese P.683606 (1968); Ref.Zhur.Khim., 9N170 (1969).
203. French P.1492098 (1967).
204. Japanese P.669416 (1966); Ref.Zhur.Khim., 8N201 (1968).
205. M.A.Popov and N.I.Shuikin, Dokl.Akad.Nauk SSSR, 101, 273 (1955).
206. N.S.Kozlov, S.I.Kozintsev, and D.I.Burakova, Vestsi Akad.Nauk Beloruss.SSR, Ser.Khim.Navuk, 70 (1974).
207. N.S.Kozlov and S.I.Kozintsev, Vestsi Akad.Nauk Beloruss.SSR, Ser.Khim.Navuk, 108 (1975).
208. BRD P.956754 (1957).
209. BRD P.2546192 (1976); Chem.Abs., **85**, 33036 (1976)
210. Czech.P.154133 (1974); Chem.Abs., **82**, 16401(1975).
211. B.Dvorak and J.Pasek, Sb.Vys.Sk.Chem.-Technol. Praze, Org.Chem.Technol., C19, 35 (1973).
212. BRD P.2118283 (1972); Chem.Abs., **78**, 29217 (1972).
213. US P.3154580 (1964).
214. US P.3347921 (1967).
215. DDR P.49611 (1966); Chem.Abs., **66**, 18576 (1967).
216. DDR P.42124 (1965).
217. P.Mastagli, M.Metayer, and A.Bricarg, Bull.Soc.chim France, 1045 (1950).
218. US P.3187047 (1965); Chem.Abs., **63**, 9873 (1965).
219. F.Randvere, Anales Farm.Bioquim, **19**, 81 (1948).
220. French P.2228484 (1974); Chem.Abs., **83**, 9457 (1975).
221. D.E.Pearson and J.D.Bruton, J.Amer.Chem.Soc., 73, 864 (1951).
222. M.Munk-Weinert and M.Prostenik, Arkiv Kemi, **26**, 89 (1954).
223. US P.3078229 (1963).
224. US P.3234281 (1966).
225. US P.3402201 (1968).
226. US P.3271452 (1966).
227. S.I.Murahashi, T.Shimamura, and I.Moritani, Chem. Comm., 931 (1974).
228. N.Yoshimura, I.Moritani, T.Simamura, and S.I.Murahashi, J.Amer.Chem.Soc., **95**, 3038 (1973).
229. B.P.1117332 (1968).
230. F.S.Dovell, J.Amer.Chem.Soc., **87**, 2767 (1965).

231. US P.3275567 (1966).
232. M.A.Ryashentseva, Kh.M.Minachev, and L.S.Geidysh, Izv.Akad.Nauk SSSR, Ser.Khim., 1601 (1968)(and references quoted therein).
233. H.Greenfield and F.S.Dovell, J.Org.Chem., **31**, 3053 (1966).
234. B.P.1098236 (1968).
235. US P.3384664 (1968).
236. M.E.Ryashentseva, Kh.M.Minachev, O.A.Kalinovskii, and Ya.L.Gol'dfarb, Zhur.Org.Khim., 1, 1104 (1965).
237. F.S.Dovell and H.Greenfield, J.Org.Chem., **29**, 1265 (1964).
238. Japanese P.6815601 (1968); Ref.Zhur.Khim., 22N208 (1969).
239. F.S.Dovell and H.Greenfield, Ind.Eng.Chem.Prod. Res.Develop., 1, 179 (1962).
240. C.F.Lane, Synthesis, 135 (1975).
241. R.F.Borch and H.D.Durst, J.Amer.Chem.Soc., **91**, 3996 (1969).
242. R.F.Borch, M.D.Bernstein, and H.D.Durst, J.Amer. Chem.Soc., 93, 2897 (1971).
243. R.F.Borch, J.Org.Synth., 52, 124 (1972).
244. US P.3873621 (1975); Chem.Abs., **83**, 43014 (1975).
245. R.F.Borch and A.I.Hassid, J.Org.Chem., **37**, 1673 (1972).
246. R.A.Crochet and C.D.Blanton, Synthesis, **55** (1974).
247. Y.Watanabe, M.Yamashita, T.Mitsudo, M.Tanaka, and Y.Takegami, Tetrahedron Letters, 1879 (1974).
248. Y.Watanabe, T.Mitsudo, M.Yamashita, S.C.Shim, and Y.Takegami, Chem.Letters, 1265 (1974).
249. Y.Watanabe, S.C.Shim, T.Mitsudo, M.Yamashita, and Y.Takegami, Chem.Letters, 699 (1975).
250. Y.Watanabe, S.C.Shim, T.Mitsudo, M.Yamashita, and Y.Takegami, Chem.Letters, 995 (1975).
251. Y.Watanabe, S.C.Shim, T.Mitsudo, M.Yamashita, and Y.Takegami, Bull.Chem.Soc.Japan, **49**, 1378 (1976).
252. G.P.Boldrini, M.Panunzio, and A.Umani-Ronchi, Synthesis, 733 (1974).
253. L.Marko and J.Bakos, J.Organometallic Chem., **81**, 411 (1974).
254. M.Murakami, K.Suzuki, and J.-W.Kang, Nippon Kagaku Zasshi, **83**, 1226 (1962).
255. M.Murakami, K.Suzuki, M.Fujishige, and J.-W.Kang, Nippon Kagaku Zasshi, **85**, 235 (1964).
256. M.Murakami and J.-W.Kang, Bull.Chem.Soc.Japan, **35**, 1243 (1962).
257. Japanese P.6321058 (1963); Chem.Abs., **60**, 3093 (1964).
258. Japanese P.6317306 (1963); Chem.Abs., **60**, 3092 (1964).
259. M.Sund, H.Dieter, R.Koberstein, and J.Rasched, J.Mol.Catalysis, **2**, 1 (1977).
260. G.N.Schrauzer and R.H.Windgassen, Nature, **214**, 492 (1967).
261. M.V.Klyuev, M.V.Gapeeva, and M.L.Khidekel', Izv. Akad.Nauk SSSR, Ser.Khim., 2140 (1978).
262. B.G.Rogachev and M.L.Khidekel', Izc.Akad.Nauk SSSR, Ser.Khim., 141 (1969)(and references quoted therein).
263. M.Becker and J.Russel, Chem.Eng., **80**, 42 (1973).
264. K.A.Alekseeva, M.P.Vysotskii, N.S.Imyanitov, and V.A.Rybakov, Zhur.Vses.Khim.Obshch.im.Mendeleeva **22**, 45 (1977).
265. B.A.Brunshtein, V.L.Klimenko, M.L.Kolesov, and E.B.Tsyrkin, Symposium, "Gidroformilirovanie" (Hydroformylation), Izd.Khimiya, Leningrad, 1972, p.240.
266. M.L.Khidekel' and V.E.Vasserberg, Zhur.Vses.Khim. Obshch.im.Mendeleeva, **22**, 73 (1977).

Institute of Chemical Physics,
USSR Academy of Sciences, Moscow

Ivanovo State University

Translated from *Uspekhi Khimii*, 49, 54-91 (1980) U.D.C. 547.793

The Chemistry of Sydnone Imines

V.G.Yashunskii and L.E.Kholodov

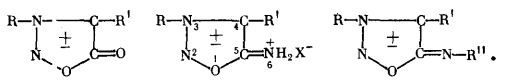
All the available data on the structures, physicochemical properties, reactivities, reactions, and biological activities of sydnone imines—representatives of the class of the so-called mesoionic heterocycles—are surveyed and described systematically.
The bibliography includes 166 references.

CONTENTS

I. Introduction 28
II. The synthesis of sydnone imines 28
III. Physicochemical properties and electronic structure 31
IV. Chemical properties 34
V. Biological properties of sydnone imines 42

I. INTRODUCTION

Among the so-called mesoionic heterocyclic compounds[1-4], sydnones (I), which are derivatives of anhydro-1,2,3-oxadiazol-5-one, are best known and have been most thoroughly investigated. Their exocyclic nitrogen analogues—the sydnone imines (II) and (III)—were discovered only 20 years ago, but during these years many interesting data have been obtained on the structures, reactivities, physicochemical properties and biological activities of these compounds.



(I) (II) (III)

Certain representatives of sydnone imines have found application as medicinal drugs. Soviet and Japanese investigators have made the greatest contribution to the development of this interesting field of the chemistry of heterocycles.

While the chemistry of sydnones has been fairly widely described in the review literature[2,3], only brief information is available concerning their nitrogen analogues—sydnone imines. This article is the first attempt at a survey and systematic account of data on the synthesis, structures, and chemical, physical, and biological properties of sydnone imines available in the periodical and patent literature (up to 1978 inclusive).

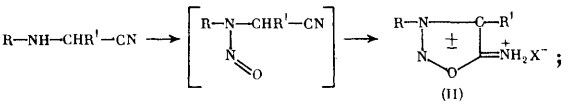
II. THE SYNTHESIS OF SYDNONE IMINES

Sydnone imines exist in the form of salts, as a rule hydrochlorides (II, X = Cl), or exocyclic derivatives ($N_{(6)}$-derivatives) (III), where R" are the residues of various organic acids (carboxylic, carbamic, arenesulphonic etc.) or inorganic acids (nitrous, nitric etc.). With the exception of special cases (see below), sydnone imines have not been isolated in the form of the free base.

1. Sydnone Imine Salts

Although the possibility of the existence of nitrogen analogues of sydnones was predicted as early as 1949,[5] the first sydnone imines were synthesised in 1957 independently by Japanese[6] and English[7] chemists.

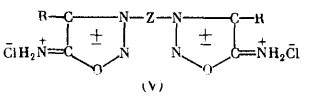
Having treated *N*-nitroso-*N*-phenylaminoacetonitrile (IVa) and its *C*-phenyl analogues (IVb) with hydrogen chloride, Kato et al.[6] obtained the hydrochlorides of 3-phenylsydnoneimine (IIa) and 3,4-diphenylsydnoneimine (IIb). When the *N*-methyl derivatives of isobutyronitrile and isovaleronitrile were treated with nitrogen oxides, the corresponding sydnone imines (II, c and d) were isolated in the form of the hydrogen nitrates (X = NO_3), which were then converted into the hydrochlorides (X = Cl):[7]



(II)

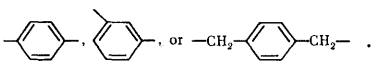
(a) R = C_6H_5, R' = H; (b) R = R' = C_6H_5;
(c) R = CH_3, R' = iso-C_4H_9; (d) R = CH_3, R' = iso-C_5H_{11}.

A large number of sydnone imine salts with various substituents in the 3- and 4-positions in the ring have been synthesised by the cyclisation of *N*-substituted *N*-nitroso-α-aminonitriles (IV) in an acid medium (the only known method hitherto). Derivatives of sydnones themselves and their exocyclic hydrogen analogues with an unsubstituted third nitrogen atom do not exist. The majority of the known sydnone imines contain hydrocarbon substituents in the 3-position: alkyl,[7,8-18] cycloalkyl,[9,10,19,20] arylalkyl,[9,11-15,17,21-23,25,26] and aryl.[6,9,11,17,27] Polymethylene-3,3'-bis-sydnone imines[9,28,29] and phenylene-3,3'-bis-sydnone imines (V)[9,16,30] have been described:



(V)

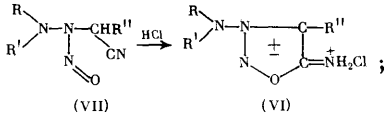
Z = $(CH_2)_n$ (*n* = 2-10), $(CH_2)_2$—O—$(CH_2)_2$,



Sydnone imines containing various functional and other groups in the hydrocarbon substituent have been synthesised, for example: 3-hydroxyethyl[14], 3-chloroethyl[14], 3-carboxylalkyl[31,32], 3-alkoxycarbonylalkyl[33], 3-dialkylaminoalkyl[34], and dinitromethyl-3,3'-bisethyl[35] derivatives. The presence of powerful electronegative substituents (for example, three nitro-groups[35]) in the β-position of the hydrocarbon chain attached to the nitrogen atom prevents cyclisation with formation of a mesoionic heterocycle.

N-nitrosoaminoacetonitriles with an arylacetyl or sulphogroup at the amino-nitrogen atom do not enter into the cyclisation reaction[6].

In recent years much attention has been devoted to the synthesis of sydnone imine salts (VI) with a dialkylaminogroup in the 3-position, which are obtained by the cyclisation of *N*-nitroso-derivatives of various *N*,*N*'-dialkyl and *N*,*N*'-cycloalkyl-hydrazinoacetonitriles (VII) under the influence of hydrogen chloride[36–47]:

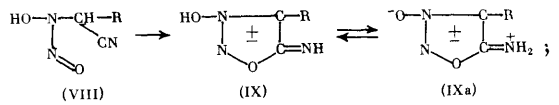


(VII) (VI)

R, R' = alkyls or X, where X = CH_2, O, or NH.

Among sydnone imines of this type, compounds containing the morpholino-,[36–38,44,45] piperidino-,[36,37,40,41,45] piperazino-,[36,45] and *N*'-substituted piperazino-groups[36,38,39,46,47] have attracted most attention.

It has recently proved possible to cyclise derivatives of *N*-nitrosohydroxylaminoacetonitrile (VIII),[48] which yielded 4-alkyl-substituted 3-hydroxysydnoneimines (IX), to which the betaine structure (IXa) was ascribed:

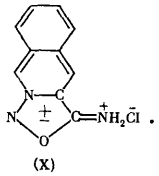


(VIII) (IX) (IXa)

R=C_3H_7, $PhCH_2$, or $PhCH_2CH_2$.

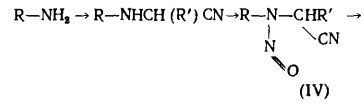
The cyclisation of *N*-nitrosoaminoacetonitriles can give rise to sydnone imine salts containing, apart from hydrogen, hydrocarbon substituents in the 4-position of the ring, namely alkyl[7,9,11–13,16,18,26,31,36,39], arylalkyl and aryl[9,11,12,16,17,25,36], chloromethyl[18,44], and dialkylaminomethyl[44] groups in the 4-position of the ring.

The synthesis of a single representative of the tricyclic series—3,4-dihydroisoquinolinyl[1,2-*c*]sydnone imine hydrochloride—has been described:



(X)

The synthesis of sydnone imine salts is fairly simple and consists in general of three stages: (1) the formation of an *N*-substituted α-aminonitrile having at least one hydrogen atom at the α-carbon atom; (2) the nitrosation of the α-aminonitrile; (3) the cyclisation of the resulting *N*-nitroso-derivative to the sydnone imine:



(IV)

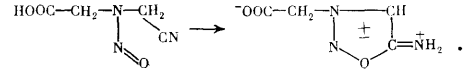
Sometimes the isolation of one or both intermediates is difficult and the synthesis of sydnone imines is converted into a single-stage process; this requires a more careful purification of the final product.

α-Aminoacetonitriles are usually obtained by the cyanomethylation of primary amines. The use of glycolonitrile as the cyanomethylating agent has been described[8]. Acetone cyanohydrin can be conveniently used as the cyanating agent under laboratory and industrial conditions[11,22–24]. Cyanomethyl derivatives of aminoacids can be obtained smoothly in an alkaline medium[14,31–33].

The nitrosation of aminoacetonitriles is carried out in most instances with sodium nitrite in the presence of inorganic acids. When an excess of sodium nitrite in an acid is used, cyclisation can take place in the course of the nitrosation with formation of sydnone imine nitrite or nitrate salts[7,14]. The *N*-nitroso-derivatives (IV) are sometimes obtained in a non-aqueous medium by treating aminotriles with nitrogen oxides.

Other inorganic acids, for example sulphuric, as well as organic carboxylic acids, such as succinic and picric, can be used for the cyclisation of nitrosoaminonitriles (IV) to sydnone imine salts, in addition to hydrogen chloride in varous organic solvents (lower alcohols, ether, tetrahydrofuran, dichloroethane, methylene chloride, chloroform, ethyl acetate, and acetone)[37].

Nitrosoaminoacetonitriles can also be cyclised in an aqueous medium[9,45]. The cyclisation in acetic acid has recently been described[49] and it has been possible for the first time to demonstrate, in relation to *N*-nitroso-*N*-carboxymethylaminoacetonitrile, the feasibility of self-cyclisation catalysed by the protons of the carboxy-group[50]:

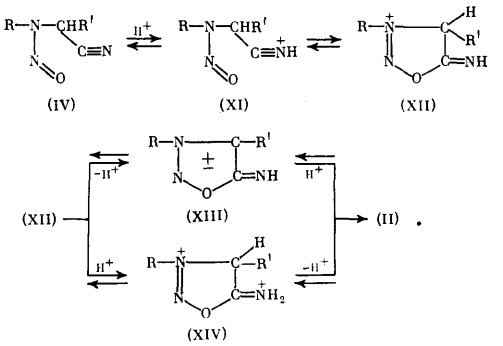


The formation of sydnone imines under the influence of HCl can be accompanied by a side reaction—the denitrosation of *N*-nitrosoaminoacetonitriles with elimination of nitrosyl chloride[14,15,18,26,29]. Thus, despite the variation of the conditions[14], it has not been possible to cyclise *N*-nitroso-*N*-t-butylaminoacetonitrile[14]. The low yields of sydnone imine in the cyclisation of *N*-nitroso-*N*-methylaminoacetonitrile in the presence of an excess of HCl have been noted[18].

It has been suggested[26] that the denitrosation can be avoided by carrying out the cyclisation in solvents without oxygen, for example in methylene chloride; however, it has been shown[15] that the cleavage of nitroso-derivatives and the low yield of sydnone imines are due to the use of an excess of HCl and the increase of temperature above 10 °C rather than the choice of a particular solvent.

A spectrophotometric study of the kinetics of the acid cyclisation of *N*-nitrosoaminoacetonitriles[5] showed that in the case of non-aromatic substituents at the nitrogen atom their reaction is of first order with respect to the nitroso-derivative and of second order with respect to protons. The rate of cyclisation depends significantly on the nature of the substituents at the nitrogen atom of the nitrosoaminoacetonitrile and increases with increasing inductive effect and bulk of the radical. Thus, one passing from the methyl to the cyclohexyl substituent, the rate of cyclisation increases by more than two orders of magnitude. Analysis with the aid of correlation equations made it possible to estimate the electronic and steric effects of the substituents. The equation obtained ($\lg k = -3.2 - 3.6\sigma^* - 1.2E_S^C$) agrees satisfactorily with the experimental cyclisation rate constants. It has been suggested that in the course of this reaction "steric acceleration" takes place with increasing bulk of the substituent at the amino-nitrogen and after the introduction of substituents at the α-carbon atom in the nitrosoaminoacetonitrile. The cyclisation takes place most readily for *N*-nitrosoadamantylaminoacetonitrile: the rate of formation of the sydnone imine ring is in this case more than 1500 times higher compared with the methyl analogue.

From these results, a mechanism of the formation of the sydnone imine ring, illustrated in the scheme below, has been put forward[51]:

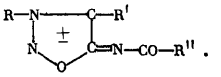


The first stage of the process is in all probability the protonation of the nitrile group in (IV) which is followed by the conversion of the protonated product (XI) into the cyclic iminoester diazotate (XII), which can give rise to the cation of the sydnone imine (II) either via the stage of the sydnone imine base (XIII) or via the dication (XIV).

2. *N*-Exocylic ($N_{(6)}$) Derivatives of Sydnone Imines

The exocyclic *N*-derivatives of the heterocycles, which are synthesised from the corresponding salts, have perhaps attracted no less attention than the sydnone imine salts.

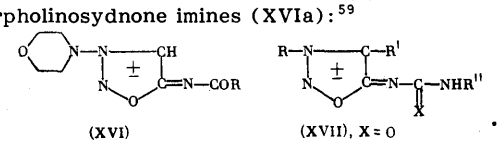
While manifesting properties typical for strong amines, sydnone imine salts interact with carboxylic acid anhydrides and chlorides in the presence of basic agents under mild conditions to form the corresponding $N_{(6)}$-acylsydnone imines (XV):



(XV)

Apart from the $N_{(6)}$-acetyl derivatives (XV, $R = CH_3$),[6,7,10,11,14,21,25,30,32,36,41,48,52-57] which can be prepared by treatment with acetic anhydride in the absence of a base[52], compounds have been synthesised with other alkanoyl[15,53-55] and aroyl[6,10,11,14-16,21,25,36,52,56-58] substituents as well as halogenoacetyl,[53-56] isonicotonyl[15,59], and alkoxycarbonyl[10,11,15,27,36,52,56] groups.

$N_{(6)}$-Acyl derivatives have been obtained not only for sydnone imines with hydrocarbon substituents in the 3- and 4-positions in the ring, but also for 3-hydroxy-,[48] 3-carboxyalkyl-,[32-58] and 3-dialkylamino-derivatives[36,40,41,44,59-63]. By treatment with formic anhydride or *p*-nitrophenyl formate, it has been possible to synthesise the $N_{(6)}$-formyl derivative of 3-morpholinosydnone imines (XVIa):[59]



(XVI) (a) R = H

(XVII), X = O

(XVIII), X = S

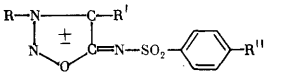
Apart from compound (XVIa), mono-, di-, and tri-chloroacetyl, trifluoroacetyl, phenoxyacetyl, trimethoxybenzoyl, benzyloxycarbonylalanyl, nicotinoyl, and other $N_{(6)}$-acyl derivatives of this sydnone imine have been obtained[59]. The interaction of sydnone imine hydrochlorides with diketen in the presence of sodium dicarbonate yielded $N_{(6)}$-acetoacetylsydnone imines (XV, $R'' = CH_3COCH_2$).[52,54,59]

Sydnone imine salts react smoothly with aliphatic and aromatic isocyanates in the presence of bases—pyridine and sodium acetate or bicarbonate—in aqueous and alcoholic media, forming $N_{(6)}$-carbamoyl derivatives (XVII).[13,15,16,21,32,53-55,58,64-70] Among these, compounds containing carboxy-substituents in the 3-position of the ring have been described[32,58,64].

When the reaction is carried out in an aqueous medium, the corresponding diarylureas are formed by a side reaction in the case of aryl isocyanates. Di-(*o*-chlorophenyl)urea proved to be the only reaction product for *o*-chlorophenyl isocyanate[15]. The reaction takes place most smoothly in alcohols[53,54]. Unsubstituted carbamoyl derivatives (XVII, $R'' = H$) have been synthesised by treating sydnone imine hydrochlorides with sodium cyanate[15,32,64,71,74].

Sydnone imine isothiocyanates react similarly to the isocyanates, giving rise to the corresponding $N_{(6)}$-thiocarbamoylsydnone imines (XVIII).[11,15,52,65] The reaction proceeds under the same conditions as with the oxygen analogues. Unsubstituted thiocarbamoyl derivatives could not be synthesised by treating sydnone imine hydrochlorides with ammonium thiocyanate[15,25,71]. The corresponding sydnone imine hydrogen thiocyanates proved to be the only reaction product.

Several studies have been devoted to the synthesis of $N_{(6)}$-arenesulphonyl derivatives (XIX), which are formed under fairly severe conditions (heating in the presence of aqueous alkali) when sydnone imine salts are acted upon by the corresponding arenesulphonyl chlorides[10,11,59,72,75]:

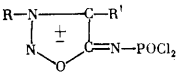


(XIX)

$R'' = H$, $NHCOCH_3$, or NH_2.

The sydnonyl analogues of sulphonamide preparations with the amino-group in the *p*-position in the benzene ring (XIXa, $R'' = NH_2$) have been synthesised in this way[10,72].

When the hydrochlorides of 3-isopropyl-, and 3-phenyl-4-methylsydnone imines were heated cautiously with phosphoryl chloride in dichloroethane solution, the corresponding $N_{(6)}$-dichlorophosphino-derivatives (XX) were synthesised[14]:

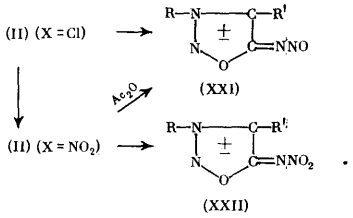


(XX)

$R = C_3H_7$, $R' = H$; $R = Ph$, $R' = CH_3$.

The presence of the exocyclic imino-group is confirmed by the ready formation of $N_{(6)}$-nitroso-derivatives (XXI) when sydnone imine salts are acted upon by sodium nitrite[6,25,32,33,53,73]. A number of $N_{(6)}$-nitroso-derivatives with alkyl, arylalkyl, and aryl substituents in the ring have been synthesised in this way. It has been observed that in certain cases the formation of $N_{(6)}$-nitroso-derivatives requires an acid medium and the introduction of an excess of sodium nitrite in order to avoid the formation of the nitrite of the corresponding sydnone imine[73]. The latter can be converted into $N_{(6)}$-nitrososydnone imine by treatment with acetic

anhydride[73]. The $N_{(6)}$-nitro-derivative (XXII) can be obtained analogously from the sydnone imine nitrite[7]:



(II) (X = Cl) → (XXI)

(II) (X = NO_2) → (XXII)

III. PHYSICOCHEMICAL PROPERTIES AND ELECTRONIC STRUCTURE

Numerous studies have been made on the physicochemical properties of sydnone imines. Investigation of the ultraviolet, infrared, NMR, and mass spectra, polarographic studies, etc. yielded data which can be used to explain the characteristics of the structures and a number of chemical and physical properties of these heterocyclic compounds. On the other hand, effective methods for the investigation of the kinetics and mechanisms of the chemical reactions of sydnone imines and for the identification of the resulting products have been developed on the basis of the study of certain physicochemical properties.

1. Electronic Spectra

Sydnone imines absorb intensely in the ultraviolet[9,15,27,32,48,52,56,72,73,76-79] and their $N_{(6)}$-nitroso-derivatives have absorption maxima also in the visible part of the spectrum[73]. Alkylsydnone imine salts have two intense absorption maxima in the region of 270–306 and 200–208 nm; the latter has been observed and described quite recently[78].

The bands have been assigned[80] on the basis of quantum-mechanical calculation by the Pariser–Parr–Pople (PPP) method and it has been shown that the long-wavelength maximum is a $\pi-\pi^*$ band corresponding to the $S_0 \rightarrow S_1^*$ transition, while the short-wavelength band corresponds to the $S_0 \rightarrow S_3^*$ transition. Calculations predict[80] the existence of yet another band corresponding to the $S_0 \rightarrow S_2^*$ transition, but, owing to its low intensity, it has not been possible to observe it. The absorption bands of $N_{(6)}$-exonitroso-derivatives of sydnone imines in the visible region have been assigned[73] to the $n \rightarrow \pi^*$ transition.

The nature of the substituents in the 3- and 4-positions in the ring and of the exocyclic group has almost no influence on the position of the short-wavelength maximum, in contrast to the long-wavlenegth absorption, whose shifts reach considerable magnitudes[78]. Thus the introduction of an aryl substituent in the 3- or 4-position in the sydnone imine ring[27] or the substitution of the hydrogen at the exocyclic nitrogen by an aryl residue[27,56] lead to a bathochromic shift of the absorption band and to the appearance of a new band at 222–260 nm. On protonation of $N_{(6)}$-acylsydnone imines, the opposite hypsochromic shift of the long-wavelength band from 308–342 nm to 278–306 nm was observed, which made it possible to measure the pK_a spectrophotometrically[56].

The great similarity of the ultraviolet spectra of sydnone imine salts and correspondingly substituted sydnones, indicating the similarity of the strctures of the electronic shells in these compounds, is striking[76]. A satisfactory correlation of the frequencies of the long-wavelength $\pi \rightarrow \pi^*$ transition with the energy difference between the highest occupied and lowest vacant molecular orbitals (calculation by the Hückel molecular orbital method) has been demonstrated[81] for the series of sydnone imines:

$$\nu_{\pi\rightarrow\pi^*} = 23\,241 + 8366\,(m_{m+1} - m_m)\,(r = 0.938)\,.$$

On passing from non-polar to polar solvents, the long-wavelength absorption of sydnone imines, like that of sydnones, shifts towards shorter wavelengths, in full agreement with calculations[80]. Owing to the formation of hydrogen bonds, in hydroxylated solvents a pronounced hypsochromic shift of the absorption bands of $N_{(6)}$-nitrososydnone imines is observed in the visible region[73].

The $N_{(6)}$-nitrosoaminoacetonitriles, formed by the opening of the sydnone imine ring, absorb at much shorter wavelengths (approximately 230 nm for the 3-alkyl-substituted derivatives); on the basis of this difference, the kinetics of the ring opening process[82] and the reverse cyclisation reaction[51] of sydnone imine have been investigated spectrophotometrically.

A weak pale-yellow luminescence (with a maximum at approximately 510 nm) has been observed recently[82] for solid solutions of sydnone imine salts in water; a pronounced bathochromic shift of the luminescence bands relative to the corresponding absorption bands has been noted.

2. Vibrational Spectra

Characteristic intense bands due to the stretching vibrations of the exocyclic $\rangle C{=}N-$ bond (1671–1700 cm^{-1}) and deformation vibrations of the immonium group $=\overset{+}{N}H_2-$ (1588 to 1606 cm^{-1}) have been observed in the infrared spectra of sydnone imine salts[83,84]. These bands were assigned by comparing the spectra with those of the salts of iminoesters and deuterated derivatives of sydnone imines[83,84].

A low-intensity band due to the stretching vibrations of the $C_{(4)}-H$ bond has been observed in the region of 3110 to 3205 cm^{-1} in the spectra of sydnone imines unsubstituted in the 4-position[32,68]. Other systematically observed absorption bands (at 742–810 and 1160–1216 cm^{-1}) are probably associated with the deformation vibrations of the sydnone imine ring[83,84]. The positions of the characteristic frequencies depend little on the type of substituents in the 3- and 4-positions in the ring. It has been noted that the presence of a substituent at a ring carbon atom diminishes somewhat the intensity of the vibrations of the $\overset{+}{N}H_2$ group.

The band due to the stretching vibrations of the carbonyl group in $N_{(6)}$-acylsydnone imines (1620–1670 cm^{-1})[84] is displaced towards lower frequencies, compared with acyclic *N*-acylamines (1660–1680 cm^{-1}). This shift can be accounted for by the electron-donating properties of the sydnone imine ring relative to the imino-group[56]. Owing to its conjugation with the carbonyl group, the C=N bond in the $N_{(6)}$-acylsydnone imines has a stretching vibration band in the region of lower frequencies (1546–1608 cm^{-1})[56,69] than the C=N bond in the corresponding $N_{(6)}$-unsubstituted sydnone imine salts. As a result of the exclusion from conjugation of the electron pair of the exocyclic nitrogen atom, the spectra of the salts of $N_{(6)}$-acylsydnone imines[32,56,69] exhibit an appreciable shift of the carbonyl band to the $\nu(C{=}O) = 1722$–1739 cm^{-1} and of the C=N bond stretching vibration band to $\nu(C{=}N) = 1615$–1635 cm^{-1}. The study of the infrared spectra showed that in $N_{(6)}$-acylsydnone imines the proton adds to

the exocyclic nitrogen and not to the oxygen of the carbonyl group[56].

The vibration frequencies of the carbonyl groups in $N_{(6)}$-acylsydnone imines are weakly correlated with the calculated C=O bond orders[85] (the calculation was performed[86] by the Hückel molecular orbital method with parameters obtained by the PPP method).

The infrared and Raman spectra of $N_{(6)}$-carbamoylsydnone imines have been studied in detail[69] in the region of the characteristic vibrations of the $>C{=}N{-}\overset{\overset{O}{\|}}{C}{-}NHR$ group; the following assignments have been made: $\nu(C{=}O) = 1640–1660\ cm^{-1}$; $\nu(C{=}N) = 1580–1600\ cm^{-1}$; $\delta(NH) = 1510–1540\ cm^{-1}$. The bands were found[69] to have high integral intensities ($A_{C=O} = 3.1 \times 10^{4}–5.0 \times 10^{-4}$ cm^2 litre mole^{-1} and $A_{C=N} = 2.4 \times 10^{-4}–3.1 \times 10^{-4}$ cm^2 litre mole^{-1}); comparison with the spectroscopic characteristics of other $N_{(6)}$-acyl derivatives indicates an effective electronic interaction of the atoms in the group investigated. It has been shown by infrared spectroscopy[69] that the proton adds to the exocyclic nitrogen atom in the $N_{(6)}$-carbamoyl derivatives.

The value of $\nu(C{=}N)$ in the spectra of 3-hydroxysydnone imines (1680 cm^{-1}) led to the conclusion that these compounds have the zwitter-ionic (*N*-oxide) structure (IXa).[48]

Two intense bands at 1335–1355 and 1408–1421 cm^{-1}, assigned to the stretching vibrations of the N=O bond in the associated and non-associated molecules respectively, are characteristic[73] of $N_{(6)}$-nitrososydnone imines; the band at 1503–1599 cm^{-1} corresponds[73] to the exocyclic C=N bond and that at 1090–1111 cm^{-1} corresponds to the N–N bond in the $>C{=}N{-}N{=}O$ group.

The characteristic vibration frequencies of various groups attached to substituents in the 3- and 4-positions in the sydnone imine ring have been quoted in a number of investigations, namely carboxy-,[32] ester, hydroxy-, and other groups[84,87]. When the groups are close to the ring, the characteristic frequencies undergo a shift due to the electronegative properties of the mesoionic ring.

3. Nuclear Magnetic Resonance Spectra

There can be only one hydrogen atom at the carbon atom in the 4-position in the sydnone imine ring. The chemical shifts of this proton have been quoted in a number of reports as a function of the substituents at the $N_{(3)}$ and $N_{(6)}$ atoms[9,33,52,68,88]. The chemical shifts of the protons in the sydnone imine salts ($\delta = 7.4–8.1$ p.p.m.†) are located in a lower field[9,23] than for sydnones ($\delta = 6.2–6.8$ p.p.m.).[33] In $N_{(6)}$-acylsydnone imine salts the signal due to the proton at $C_{(4)}$ is displaced downfield even more ($\delta = 8.3–8.8$ p.p.m.).[52] Owing to the combination of the anisotropic effects of the two rings in the 3-aryl derivatives of sydnone imines, the signal due to the proton at $C_{(4)}$ is displaced downfield[88].

The signal due to the protons of the methyl group in 3-methyl-substituted sydnone imines is located in a very low field (5.5–5.9 p.p.m.), which indicates an appreciable positive charge on the $N_{(3)}$ atom.

† Here and henceforth the chemical shifts are relative to tetramethylsilane.

The positions of the substituents entering the molecule in electrophilic substitution (nitration and bromination) reactions involving certain $N_{(6)}$-arylcarbamolysydnone imines have been determined with the aid of the analysis of the ^{1}H NMR spectra[68].

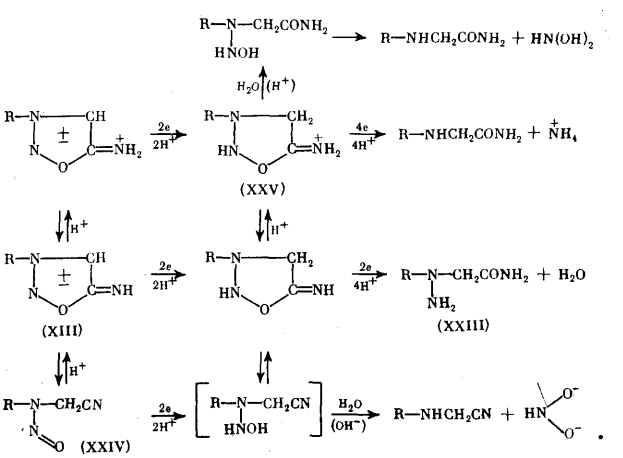
The ^{13}C NMR spectrum of 3-methylsydnone imine hydrochloride has been recently investigated and it has been shown that the $C_{(4)}$, $C_{(5)}$, and $C_{(CH_3)}$ atoms have chemical shifts of 97.3 170.4 and 40.1 p.p.m. respectively. Thus the signals due to the ring carbon atoms are located in a very high field compared with those of the carbon atoms in many other heterocycles, which in general agrees[89] with the higher effective charges on the carbon atoms in the sydnone imine ring (calculation by the CNDO/2 method).

4. Polarography

Like the sydnone ring, the sydnone imine ring is polarographically active; sydnone imine derivatives are very readily reduced at a dropping mercury electrode[27,90–98]. The influence of pH, temperature, drop period, and the addition of alcohol and the surfactants on the polarographic behaviour of sydnone imines has been investigated[90,92,94,95]. Coulometric measurements have been made to determine the number of electrons consumed at the anode[90,94,95] and it has been found that in an acid medium sydnone imine salts give rise to a single six-electron reduction wave[90,94], while in an alkaline medium $N_{(6)}$-acylsydnone imines give a four-electron wave[90,93].

Two waves are characteristic of $N_{(6)}$-acyl derivatives in the pH range 8–11: one corresponds to the reduction of the cation and the other, at more negative potentials, corresponds to the reduction of the base[92,95]. Two waves have been observed in the polarography of 3,3′-dimethylene-, trimethylene, and *p*-phenylene-3,3′-bis-sydnone imines—the reduction of the first heterocycle is facilitated under the influence of the second[98].

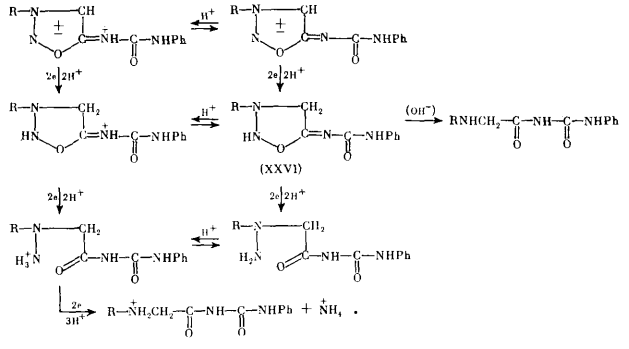
A mechanism has been proposed for the polarographic reduction of the sydnone imine cation[90]. For 3-alkyl derivatives, this mechanism has been revised[94] and can be represented schematically as follows#:



The vertical arrows in the above scheme indicate the chemical processes accompanying the reduction reactions represented horizontally.

After the electrolysis of sydnone imines in a neutral medium (four electrons are consumed), the polarogram shows the anodic wave due to the oxidation of the hydrazine (XXIII); the anodic peak due to the oxidation of (XXIII) is observed likewise in cyclic voltamperometric measurements[92]. In unbuffered solutions the sydnone imine ring is partly cleaved to the *N*-nitroso-derivative (XXIV) in the region near the electrode. In the reduction of the sydnone imine ring ($c = 0.86 \times 10^{-3}$ M) in 0.1 M KCl with added 0.5×10^{-3} M HCl the splitting of the wave was observed—as a result of the increase in the alkalinity of the space near the electrode, the sydnone imine base (XIII) is formed and is involved in the production of the second wave at more negative potentials[94].

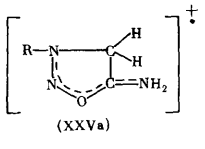
A similar mechanism has been proposed[92] for the reduction of $N_{(6)}$-carbonyl derivatives of sydnone imines and was subsequently revised and extended[95]. For example, for $N_{(6)}$-phenylcarbamoyl derivatives, it can be represented by the following scheme:



(XXVI)

In solutions with insufficient buffer capacity it was possible to observe the reduction wave of the dihydrosydnone imine (XXVI).

The proposed mechanisms agree with quantum-chemical calculations on certain possible intermediates[96]. From the standpoint of these calculations, the capture of the first potential-determing electron followed by the addition of a proton to the $C_{(4)}$ atom with formation of the radical-cation (XXVa)



(XXVa)

is most probable. The addition of a second electron and a proton to the $N_{(2)}$ atom of this radical-cation leads to the dihydro-compound (XXV).

3-Aryl derivatives of sydnone imines have a number of characteristic features in their polarographic behaviour and their reduction mechanism is somewhat different[88].

On the basis of calculations, it has been suggested[94] that the reduction of the sydnone imine cation is greatly facilitated as a result of the gain of hydration energy on passing from the cation to the corresponding radical-cation (XXVa), which is formed following the addition of the first electron.

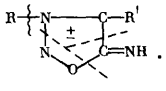
The values of $E_{1/2}$ for sydnone imines are proportional to the energies of the lowest vacant molecular orbitals calculated by the Hückel method with the parameters of Pullman and Pullman[81]. When the energies of the lowest vacant molecular orbitals calculated by the Hückel molecular orbital method are used together with the parameters obtained by the PPP method, such proportionality is observed simultaneously for sydnones and sydnone imines[86].

The validity of the Hammett and Taft equations for the sydnone imines reduction half-wave potentials $E_{1/2}$ has been demonstrated: $E_{1/2} = -0.93 + 0.37\sigma^*$ for 3-alkyl-substituted derivatives (pH 7.4);[90] $E_{1/2} = -0.63 + 0.17\sigma$ for 3-aryl-substituted derivatives[27,77] (pH 7.4);[27,93] $E_{1/2} = -0.305 \pm 0.14\sigma$ for $N_{(6)}$-methoxycarbonyl-3-aryl-substituted derivatives[27,93] (0.1 *N* HCl).

The polarographic method has been used to investigate the kinetics and equilibria in the alkaline opening of the sydnone imine ring[97,99,100]. The dynamics of the changes in the concentration of $N_{(6)}$-phenylcarbamoyl-3-phenylisopropylsydnone imine (the medicinal drug sydnocarb) in the blood of experimental animals has been followed with the aid of oscillographic polarography[101].

5. Mass Spectrometry

The most intense peak in the mass spectra of sydnone imine hydrochlorides corresponded[102] to the base (M–HCl). The heterocyclic ring of the base is cleaved preferentially into three fragments (NO, C=NH, and NCR') in accordance with the scheme



The mass spectra confirmed[48] the mode of methylation of 3-hydroxysydnone imine—both methyl groups are directed to the $N_{(6)}$ atom.

Table 1. The effective atomic charges in the sydnone imine base (XIII) and in the sydnone imine cation (II).

Method of calcn.*	Compound	$O_{(1)}$	$N_{(2)}$	$N_{(3)}$	$C_{(4)}$	$C_{(5)}$	$N_{(6)}$	Refs.
1	(XIII)	+0.242	−0.039	+0.666	−0.245	+0.068	−0.683	103
1	(II)	+0.289	+0.052	+0.653	−0.081	−0.012	+0.099	103
2	(XIII)	+0.076	−0.440	+0.536	−0.031	+0.146	−0.290	85
3	(XIII)	+0.098	−0.325	+0.476	−0.044	+0.128	−0.333	108,109
3	(II)	+0.156	−0.600	+0.531	−0.016	+0.183	+0.206	108,109
4	(XIII)	+0.157	−0.575	+0.846	−0.198	+0.125	−0.358	110
4	(II)	+0.276	−0.300	+0.847	−0.207	+0.178	+0.179	110
5	(XIII)	−0.178	−0.149	+0.234	−0.076	+0.295	−0.332	110
5	(II)	−0.063	+0.063	+0.240	−0.068	+0.346	−0.214	110

*Notation: 1) Hückel molecular orbital method, parameters of Pullman and Pullman; 2) Hückel molecular orbital method, parameters calculated by the PPP method; 3) PPP; 4) CNDO/2, π electrons (for the 3-methyl-substituted derivative); 5) CNDO/2, σ and π electrons (for the 3-methyl substituted derivative).

6. Quantum-Chemical Calculations of the Electronic Structure of Sydnone Imines

Quantum-chemical calculations on sydnone imines (and sydnones) have been carried out by various methods (see Tables 1 and 2).

The calculations were performed by the Hückel method using the parameters of Pullman and Pullman[81,103] and a self-consistent system of parameters computed from data evaluated by the PPP method[85]. The electron density distributions obtained were qualitatively independent (as regards the signs of the effective charges) of the parametrisation, but the quantitative differences between them were fairly marked. The most equalised charges were obtained using parameters calculated by the PPP method[85]. The influence of substituents in the 3-, 4-, and 5-positions has been calculated[81,85,104]. Analysis of the results shows that the sydnone imine ring (like the sydnone ring) is a weak "transmitter" of π-electronic effects from the 3-position to the 1- and 5-positions and to the exocyclic nitrogen atom and also from the 4-position to the 1- and 5-positions and from the 5-position to the 3-position; the charges on the $N_{(2)}$ and $C_{(4)}$ atoms are most sensitive to the influence of substituents in sydnone imine[85,105].

Table 2. Bond orders in the sydnone imine base (XIII) and in the sydnone imine cation (II).

Method of calcn.*	Compound	$O_{(1)}$-$N_{(2)}$	$N_{(2)}$-$N_{(3)}$	$N_{(3)}$-$C_{(4)}$	$C_{(4)}$-$C_{(5)}$	$C_{(5)}$-$O_{(1)}$	$C_{(5)}$-$N_{(6)}$	Refs.
1	(XIII)	0.411	0.752	0.498	0.670	0.373	0.576	103
1	(II)	0.447	0.758	0.485	0.786	0.408	0.312	103
2	(XIII)	0.162	0.529	0.658	0.419	0.225	0.853	85
3	(XIII)	0.212	0.532	0.609	0.485	0.240	0.821	108,109
3	(II)	0.339	0.667	0.536	0.672	0.339	0.486	108,109

*Notation: 1) Hückel molecular orbital method, parameters of Pullman and Pullman; 2) Hückel molecular orbital method, parameters calculated by the PPP method; 3) PPP.

Calculations have been made by the Hückel method on sydnone imines, sydnones, and certain other mesoionic heterocycles using the ω-technique[88,106].

The first calculation on sydnone imine in terms of the π-electron approximation by the LCAO-MO SCF method was performed[107] using a modified PPP method. Calculations have been made[108,109] on sydnone imine and sydnone by the PPP method and the influence of the initial system of parameters was analysed. In contrast to the results obtained by the simple Hückel molecular orbital method, the PPP method predicts a much higher effective charge on the $N_{(2)}$ atom than on the $C_{(4)}$ atom.

Calculations have been carried out[110] on the 3-methylsydnone imine cation and its base by the LCAO-MO SCF method in terms of the CNDO/2 valence approximation and the dipole moment of the hypothetical 3-methylsydnone imine base has been calculated ($\mu = 6.39$ *D*). A comparative calculation has been performed recently by the same method[111] on sydnone imine in which protons have been added to different atoms. Comparison of the total energies of the resulting cations showed that protonation at the exocyclic nitrogen atom is energetically most favourable. Calculations have been made in the same study[111] on certain possible intermediates in the acid cyclisation of *N*-nitrosaminoacetonitrile and the reverse reaction involving the alkaline opening of the sydnone imine ring. The calculations permitted certain hypotheses concerning the mechanisms of these reactions.

A number of studies demonstrated a fair agreement of the results of the calculations with experimental physicochemical characteristics[86,96,105,109] and the fundamental chemical properties, which will be dealt with below.

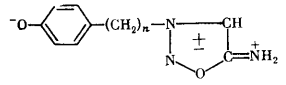
IV. CHEMICAL PROPERTIES

Like sydnone, sydnone imines are extremely reactive; reactions occurring with both retention and opening of the heterocyclic ring are characteristic of these compounds and the majority of reactions take place under fairly mild conditions.

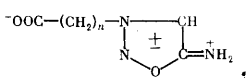
1. Reactions with Retention of the Ring

(a) *Reactions involving the exocyclic group.* The synthesis of $N_{(6)}$-exocyclic derivatives of sydnone imines, obtained by the electrophilic substitution of the hydrogen at the exocyclic nitrogen atom, was examined in detail above. These reactions take place readily and smoothly, which makes it possible to characterise the exocyclic imino-group as highly basic.

Frequent attempts to isolate the free sydnone imine bases have been unsuccessful, except for 3-hydroxy-derivatives (IX),[48] which exist as a result of betaine stabilisation. The strong base formed on neutralisation apparently undergoes autocatalytic tautomerisation to the initial nitrosoaminoacetonitrile (for further details, see below). The high basicity of the hypothetical sydnone imine base is also indicated by other facts, such as the ability to form salts with weak acids (carbonic or thiocyanic) and to form inner salts as a result of the involvement in the betaine structure of the phenolic hydroxyl of (XXVII) [9] and (XXVIII) [21] or the carboxy-group in a series of free-carboxyalkyl-substituted sydnone imines (XXIX):[32]



(XXVII) $n = 0$
(XXVIII) $n = 2$



(XXIX) $n = 1, 2$

The pK_a values have been determined for certain 3-dialkylaminosydnone imines (VI) and were found to be ~8.15–8.85,[36] i.e. are similar to, for example, the pK_a for morpholine (8.7). According to Gotz and Grozinger[36], this shows that the exocyclic nitrogen atom is protonated in these compounds, since its acylation leads to a decrease of pK_a by 4–5 orders of magnitude.

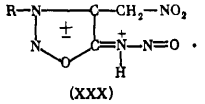
The capacity of $N_{(6)}$-acyl derivatives for protonation, which likewise confirms the high basicity of the sydnone imine "base", has been observed not only for 3-dialkylaminosydnone imines but also for compounds with hydrocarbon substituents in the 3-position[15,27,52,56]. $N_{(6)}$-Carbamoylsydnone imines possess similar properties[52]. The hydrochlorides, sulphates, and nitrates of a series of compounds of this type has been isolated in the solid state.

The basicity of $N_{(6)}$-acyl- and $N_{(6)}$-carbamoyl-sydnone imines depends significantly on the nature of the substituent in the 3- and 4-positions and in the acyl residue. The pK_a values for $N_{(6)}$-acyl derivatives vary in the range 2.5–4.6. Compounds with alkyl substituents in the 3-poisition are more basic than their aryl analogues. The substitution of the hydrogen atom at the carbon atom in the 4-position of the ring by the methyl or phenyl group leads to a decrease of capacity for salt formation.

Comparison of the pK_a values for compounds with the same exocyclic substituent, for example, the methoxycarbonyl group, reveals an increase in the basicity of the exocyclic nitrogen following the enhancement of the electron-donating properties of the substituent in the 3-position[27]. As was to be expected, in compounds with the same substituent in the 3-position, a decrease of the electronegativity of the substituent at the $N_{(6)}$ atom increases significantly the basicity for the following series of substituents: $CCl_3CO < C_6H_5CO < CH_3OCO < CH_3CO$.[56]

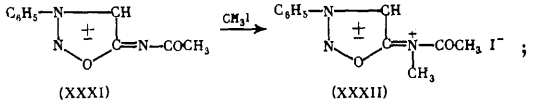
The carbamoyl analogues of $N_{(6)}$-acylsydnone imines are somewhat less basic than the latter compounds[52,101]. Benzenesulphonyl and thiocarbamoyl derivatives exhibit weak basic properties; the pK_a of the latter compounds cannot even be measured[52].

A single instance of the protonation of $N_{(6)}$-nitroso-derivatives has been described, namely of compound (XXX) having in the 4-position the nitromethyl group, which apparently stabilises the molecule[49]:

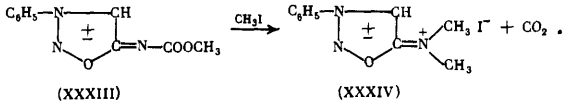


(XXX)

Evidence additional to the spectroscopic data quoted above, confirming that the protonation of $N_{(6)}$-acylsydnone imines proceeds at the exocyclic nitrogen atom, comes from the ability of these compounds to form quaternary salts[56]. Thus, when $N_{(6)}$-acetyl-3-phenylsydnone imine (XXXI) was heated with methyl iodide in acetone, the methiodide (XXXII) was obtained:



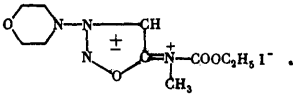
(XXXI) (XXXII)



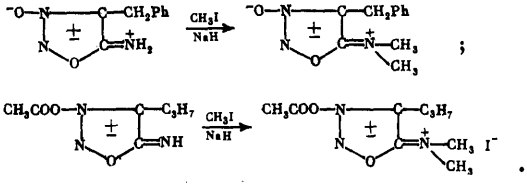
(XXXIII) (XXXIV)

Under analogous conditions, the $N_{(6)}$-methoxycarbonyl derivative (XXXIII) is converted into the quaternary salt (XXXIV).[56] Evidently the methiodide of type (XXXII) formed in the latter reaction is readily decarboxylated.

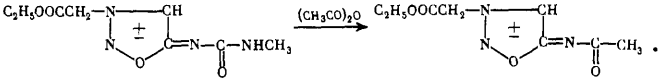
Decarboxylation was not observed in the methylation of $N_{(6)}$-ethoxycarbonyl-3-morpholinosydnone imine[59] and the final product had a structure similar to that of (XXXII):



Quaternary salts of type (XXXIV) have been obtained from 4-benzyl-3-hydroxysydnone imine and 3-acetoxy-4-propylsydnone imine by treatment with methyl iodide in the presence of sodium hydride[48]:



Other types of reactions of the exocyclic group in $N_{(6)}$-substituted sydnone imines have also been described. Thus, in the presence of boron trifluoride etherate, the $N_{(6)}$-methylcarbamoyl derivative (XXXV) is smoothly converted under the influence of acetic anhydride into the corresponding acetyl derivatives (XXXVI):[112]

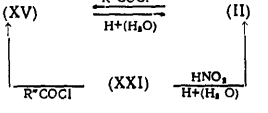


(XXXV) (XXXVI)

Certain $N_{(6)}$-acyl-3-arylsydnone imines split off the acyl group under the influence of 1 *N* HCl even at room temperature, giving rise to sydnone imine salts[41,48,52,59]. On the other hand, this reaction for the majority of other acyl derivatives requires fairly severe conditions (for example, 1 *N* HCl, 1 h, 100 °C).[52] The phenylcarbamoyl group is not eliminated under analogous conditions[52].

The acid elimination of the acyl group could be used to obtain other $N_{(6)}$-derivatives of 4-substituted sydnone imines when a sydnone imine salt cannot be used. For example, on heating the $N_{(6)}$-methoxycarbamoyl-4-bromo-3-phenylsydnone imine (XV, $R = C_6H_5$, $R' = Br$, $R'' = OCH_3$) with 2.7 *N* H_2SO_4 and subsequent nitrosation of the reaction mixture, the $N_{(6)}$-nitroso-derivative of this sydnone imine (XXI, $R = C_6H_5$, $R' = Br$) was synthesised[73].

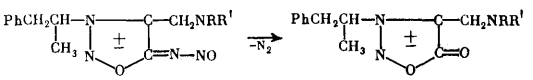
$N_{(6)}$-Nitrososydnone imines (XXI) exhibit a high reactivity. Under the influence of carboxylic acid chlorides, they are converted smoothly into the corresponding $N_{(6)}$-acylsydnone imines (XV):[25]



When the $N_{(6)}$-nitroso-derivative is treated with hydrogen chloride in alcohol, the nitroso-group is eliminated as nitrosyl chloride with formation of the sydnone imine hydrochloride[25]. This reaction also proceeds smoothly with sulphuric or hydrochloric acid, giving an almost quantitative yield. Its detailed kinetic study established[25] that the nitroso-group in compound (XXI) hydrolyses extremely readily. The reaction is catalysed by acids and proceeds via the S_N2 mechanism. Under identical conditions, $N_{(6)}$-nitrososydnone imines hydrolyse at a rate faster by several orders of magnitude than the usual *N*-nitrosoamines[25].

When $N_{(6)}$-nitroso-derivatives are heated in inert solvents, they are converted into the corresponding sydnones (I) with evolution of nitrogen[25,73]. It has been observed[25] that in alcohols and dichloroethane the reaction is slow and the yield of sydnones is frequently 25–50%; in boiling dimethylformamide (DMF) the process also proceeds partly with liberation of nitrogen oxides. On moderate heating in DMF (at approximately 90 °C), the reaction proceeds rapidly and sydnone is formed almost quantitatively[113]. This transformation is observed for compounds with aliphatic, alicyclic, and aliphatic-aromatic substituents in the 3-position and also for 4-benzylsydnone imines. The kinetic studies have led to the conclusion that the reaction is a unimolecular process, which can be classified as an S_Ni intramolecular substitution reaction.

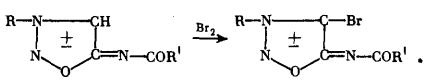
A new method of synthesising sydnones[114] can be more convenient in some cases than the usual procedure; it leads to higher yields and makes it possible to synthesise sydnones which cannot be obtained by the cyclisation of the corresponding *N*-nitrosoaminoacids. Thus the $N_{(6)}$-nitroso-derivative of 4-dimethylamino-3-phenylisopropylsydnone imine (XXXVIIa) and 3-phenylisopropyl-4-piperidinosydnone imine (XXXVIIb) are converted in almost quantitative yields into the corresponding sydnones (XXXVIIIa) and (XXXVIIIb) on heating in DMF:[49]



(XXXVII) (XXXVIII)

(a) R, $R^1 = CH_3$, (b) $RR^1 = -(CH_2)_5-$.

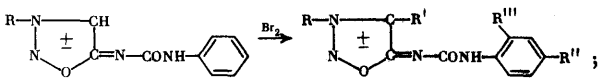
(b) Reactions involving substitution in the 4-position and transformation of side groups. By analogy with sydnones, $N_{(6)}$-acyl derivatives of sydnone imines enter into electrophilic substitution reactions involving the fourth carbon atom. Under mild conditions, the hydrogen at the $C_{(4)}$ atom is replaced by the mercuriacetate group[6]. The bromination of $N_{(6)}$-acylsydnone imines proceeds smoothly[6,9,20,42,76,115] and the reaction takes place most readily in ether in the presence of an excess of sodium bicarbonate[9,20]; the use of dibromodioxan and bromosuccinimide[20,41] leads to much lower yields:



It has been noted that substitution of 3-alkyl derivatives takes place much more readily than that of their aryl analogue[20]. Like the $N_{(6)}$-acylsydnone imines, their $N_{(6)}$-sulphonyl derivatives undergo the bromination reaction[75].

On bromination of $N_{(6)}$-carbamoylsydnone imines containing alkyl substituents in the exocyclic group, substitution by bromine, as in the $N_{(6)}$-acyl analogues, takes place at the $C_{(4)}$ atom of the sydnone imine ring[68].

In the course of the bromination of $N_{(6)}$-phenylcarbamoyl-3-butylsydnone imine (XXXIX, $R = C_4H_9$), it was observed[41] that bromine enters the benzene ring and not the sydnone imine ring and it was postulated that this leads to the formation of the *p*-bromo-derivative (XL, $R = C_4H_9$):



(XXXIX)

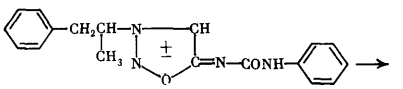
(XL): $R^1 = R''' = H$, $R'' = Br$;
(XLI): $R''' = H$, $R^1 = R'' = Br$;
(XLII): $R^1 = R'' = R''' = Br$.

A detailed study of the bromination of $N_{(6)}$-phenylcarbamoylsydnone imines showed[68] that, when equimolar amounts of bromine are used, *p*-bromophenyl derivatives (XL) are indeed formed. An increase of the amount of bromine to 2 moles leads to the substitution of both the benzene and sydnone imine rings in (XLI). When the reaction was carried out in the presence of a large excess of bromine, the tribromo-derivative (XLII) was obtained.

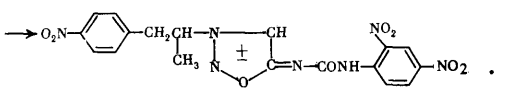
The introduction of chlorine and iodine atoms into the 4-position of $N_{(6)}$-acyl-3-morpholinylsydnone imines with the aid of chloro- and iodo-succinimide has been described[41,115].

The attempt to substitute at the $C_{(4)}$ atom by treatment with chlorine or sulphuryl chloride led only to the cleavage of the sydnone imine ring[116]. In contrast to sydnones, the bromine in $N_{(6)}$-acyl-4-bromosydnone imines could not be substituted by lithium[75].

Nitration of $N_{(6)}$-phenylcarbamoyl-3-arylalkylsydnone imines with a mixture of nitric and acetic acid at room temperature gives rise, in contrast to sydnones, to the corresponding nitrate salts only[68]. Under more severe conditions (treatment with a mixture of nitric and sulphuric acid), $N_{(6)}$-phenylcarbamoyl-3-phenylisopropylsydnone imine (XLIII) is converted into a trinitro-derivative, to which structure (XLIV) was attributed:

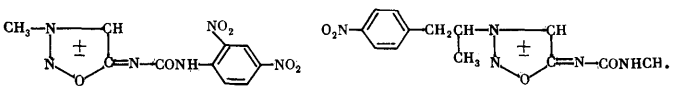


(XLIII)



(XLIV)

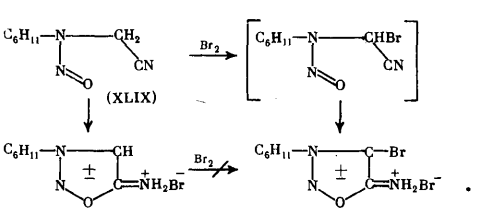
$N_{(6)}$-Phenylcarbamoyl-3-methyl- and $N_{(6)}$-methylcarbamoyl-3-phenylisopropyl-sydnone imines give rise under these conditions, to the nitro-derivatives (XLV) and (XLVI) respectively without a nitro-group in the sydnone imine ring:



(XLV) (XLVI)

In the bromination and nitration reactions a decrease of the nucleophilic activity of the $C_{(4)}$ atom of the sydnone imine ring is observed relative to the phenylcarbamoyl group.

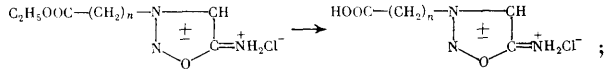
The impossibility of introducing the nitro-group into the sydnone imine ring is apparently due to the sharp decrease of the nucleophilic activity of the entire molecule and in the first place of the carbon atom in a strongly acid medium owing to the protonation of the exocyclic nitrogen atom. For the same reason, it is impossible to brominate 3-cyclohexylsydnone imine hydrobromide (XLVII) by treatment with bromine in chloroform[20]. The expected product (XLVIII) was obtained by allowing a solution of *N*-nitroso-*N*-cyclohexylaminoacetonitrile (XLIX) in bromine-containing methylene chloride to stand for a long time, whereupon compound (XLVII) was isolated together with compound (XLVIII). Apparently there is initially substitution of the hydrogen at the α-carbon atom by bromine, which results in the evolution of hydrogen bromide, under the influence of which both nitrosonitriles cyclise;



(XLVII) (XLVIII)

Thus exocyclic derivatives of sydnone imines can enter into electrophilic substitution reactions involving a ring carbon atom, provided that the formation of the cationic form of the molecule is excluded during the process.

Apart from the examples of the involvement of the side groups of sydnone imines in bromination and nitration reaction quoted above, a number of other instances are also known were side groups react, while the mesoionic ring remains unaffected. Thus 3-carboxymethylsydnone imine hydrochloride (La), which could not be obtained by direct synthesis, has been prepared by the hydrolysis of the corresponding ethyl ester (LIa) (which is available) with hydrochloric acid at room temperature[64]:

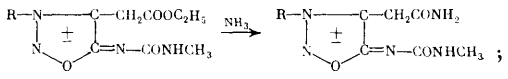


(LI) (a) $n = 1$. (L)

The hydrochlorides of other carboxylalkylsydnone imines (L) [33] have been synthesised analogously and the esters of $N_{(6)}$-carbamoyl and $N_{(6)}$-thiocarbamoyl-3-carboxymethylsydnone imines have been converted into the corresponding acids[64].

Under the influence of aqueous ammonia at room temperature, the ester group in the 3- or 4-positions in $N_{(6)}$-methylcarbamoylsydnone imines is smoothly converted into the amide group[58,117].

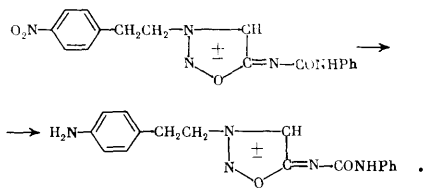
In contrast to the compound with the methyl substituent in the 3-position (LIIa), its phenyl analogue (LIIb) undergoes ring cleavage with further rearrangement under these conditions, in addition to the formation of the amide:



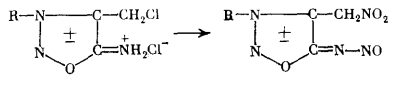
(LII)

(a) R = CH_3, (b) R = Ph.

By virtue of the considerable stability of the $N_{(6)}$-carbamoyl derivatives, it was possible to reduce the nitro-group in the benzene ring of the substituent with the aid of iron in acetic acid[68]:



Interesting reactions are observed for 4-chloromethylsydnone imines (LIII).[49] On treatment with sodium nitrite in water or methanol, a reaction involving both the exocyclic group and the side chain takes place. The reaction products were found to be $N_{(6)}$-nitroso-derivatives of 4-nitromethylsydnone imines (LIV):

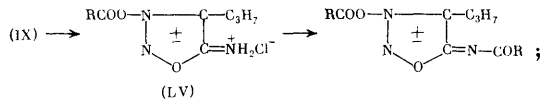


(LIII) (LIV)

This indicates a high mobility of the chlorine atom in the chloromethyl group.

Incidentally, attempts to obtain 4-chloro- or 4-bromomethyl derivatives of sydnone imines by substituting the hydrogen atom by a halogen in *N*-acyl-4-methylsydnone imines under various conditions were unsuccessful[49].

The simultaneous involvement in the reaction of the exocyclic nitrogen atom and the side chain was observed also in the acetylation or carbamoylation of 3-hydroxy-4-propylsydnone imine[33] (IX). In the first place the reaction involves the oxygen atom, as shown by the formation of the monosubstituted product (LV):



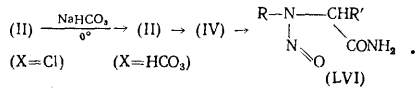
(LV)

R = CH_3, or NHPh.

2. Reactions with Opening of the Ring

The high reactivity of sydnone imines is manifested particularly strikingly in reactions leading to the opening of the heterocyclic ring. Ring cleavage can take place at different bonds under the influence of various reagents.

(*a*) *The action of alkalis and bases.* When sydnone imine hydrochlorides are treated cautiously with sodium bicarbonate at 0 °C, it is possible to isolate acid carbonate salts, but even at room temperature the ring opens under these conditions with formation of the initial *N*-nitrosoaminonitrile[9]:

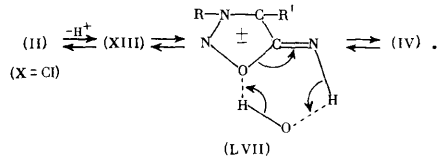


(LVI)

When sydnone imine salts are treated with a solution of sodium carbonate or caustic alkalis and also on being passed through an anion-exchanger, saturated with hydroxide ions, the reaction products are the corresponding *N*-nitrosoaminoacetamides (LVI), probably obtained as a result of the hydrolysis of the nitriles produced initially[7,9,97,118].

The formation of *N*-nitrosoacetamide has been observed also on treating sydnone imine hydrochloride with piperidine[119]. It has been shown by a polarographic procedure for a series of 3-alkylsydnone imine hydrochlorides[99] that they are rapidly converted in a weakly alkaline medium (pH 11) into *N*-nitrosoaminoacetonitriles (IV), which give rise to the corresponding amides (LVI) at higher pH values.

The kinetics of the alkaline opening of the ring in 3-isopropylsydnone imine hydrochloride has been studied spectrophotometrically[120] and it has been established that the process is reversible in the pH range 7.15–8.60 and is of first order with respect to the sydnone imine and of second order with respect to hydroxide ions. The authors[120] suggest that the first stage involves the elimination of a proton from the salt, leading to the formation of the base (XIII), which is a cyclic tautomer of the final cleavage product—*N*-nitrosoaminoacetonitrile (IV). The rate-limiting stage of the process is a bimolecular reaction involving the attack on the base (XIII) by a hydroxide ion. The resulting reaction complex, which may have the bicyclic structure (LVII), is converted into (IV) either directly with elimination of a hydroxyl or via an intermediate:

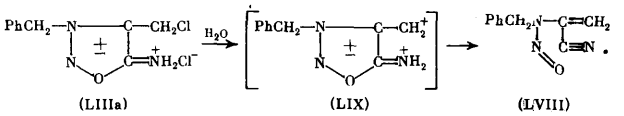


(LVII)

It has been observed that in the case of 3-arylsydnone imines the reaction is of first order with respect to both the heterocycle and the hydroxide ion[97]. Apparently here too

the first stage involves the elimination of a proton from the sydnone imine cation with formation of a base, which undergoes spontaneous ring opening to give compound (IV) without the involvement of the OH^- ion or an activated complex. This difference in the mechanism can probably be accounted for by the conjugation between the sydnone imine and benzene rings in the 3-arylsydnone imine base.

In the series of 3-arylalkylsydnone imines there is also a possibility of ring opening not catalysed by hydroxide ions. Thus, it has been noted that the hydrochloride of 3-benzyl-4-chloromethylsydnone imine (LIIIa, $R = C_6H_5CH_2$) undergoes ring cleavage even under the influence of water[49]. α-(*N*-Nitrosobenzylamino)acrylonitrile (LVIII) was isolated as the final product:



(LIIIa) (LIX) (LVIII)

The process probably involves the initial elimination of a chloride ion from the chloromethyl group with formation of the unstable dication (LIX), which is stabilised with elimination of two protons and the opening of the ring to give the unsaturated nitrile (LVIII).

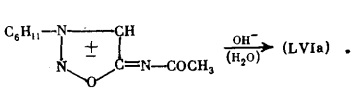
The determination of the rate and equilibrium constants made it possible to elucidate the effect of substituents on the stability of the sydnone imine ring in an alkaline medium[90,107]. Electron-donating substituents in the 3- and 4-positions, which lower the electrophilic activity of the entire molecule and of the reaction centre in relation to the reaction catalysed by hydroxide ions, increase the stability of the ring. It has been shown recently[121] that even the carboxy-group in 3-carboxyalkylsydnone imines promotes an increase of the stability of the ring compared with the 3-methyl derivative.

A detailed study of the alkaline opening of the ring in the hydrochloride of 3-morpholinosydnone imine[122] showed that this process has the general characteristic observed for sydnone imines with hydrocarbon substituents in the 3-position.

All the available data permit the conclusion that the opening of the ring in sydnone imine salts is not a result of hydrolysis but constitutes a tautomeric ring–chain reversible transformation: sydnone imine base ⇋ *N*-nitrosoaminoacetonitrile.

N-Exocyclic derivatives of sydnone imines are much more stable in relation to alkalis and bases, like sydnones[46].

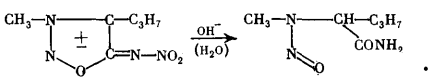
While the majority of $N_{(6)}$-acylsydnone imines are resistant to the action of alkalis at room temperature, they are cleaved on raising the temperature. Thus heating of $N_{(6)}$-acetyl-3-cyclohexylsydnone imiine for 10 min with a 10% solution of sodium hydroxide gives an almost quantitative yield of *N*-cyclohexyl-*N*-nitrosoaminoacetamide (LVIa):[52]



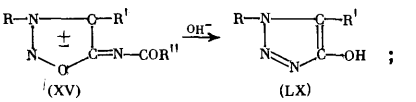
(LVIa).

It has been shown in relation to $N_{(6)}$-ethoxycarbonyl-3-morpholinosydnone imine[122] that the first stage of the alkaline cleavage of $N_{(6)}$-acylsydnone imines involves the formation of the "base", as for sydnone imine salts, which is subsequently converted into a nitrosonitrile and a nitrosoamide.

$N_{(6)}$-Nitro-derivatives undergo an alkaline decomposition analogously for $N_{(6)}$-acylsydnone imines[7]:



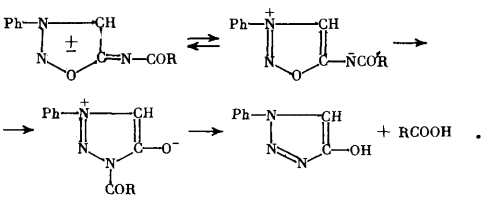
When $N_{(6)}$-acylsydnone imines are treated with a methanol solution of potassium hydroxide, the formation of *N*-nitrosoaminoacetamides, which are obtained also in an aqueous medium, can be accompanied by other reactions[52]. Thus $N_{(6)}$-acyl-3-butyl- and $N_{(6)}$-acyl-3-phenyl-sydnone imines (XV, a and b) give rise to the corresponding nitrosoamides (LVI) even at room temperature. In the latter case the main reaction product proved to be 4-hydroxy-3-phenyl-1,2,3-triazole (LXb), which is obtained with a high yield on heating (XVb) with a 10% potassium hydroxide solution in methanol:



(XV) (LX)

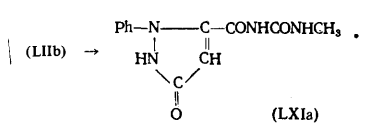
(a) $R = C_4H_9$, $R' = H$, $R'' = CH_3$, C_2H_2Ph;
(b) $R = Ph$, $R' = H$, $R'' = CH_3$, C_2H_5, or Ph;
(c) $R = R' = Ph$, $R'' = C_2H_5$.

The reaction involving $N_{(6)}$-propionyl-3,4-diphenylsydnone imine (XVc) also proceeds analogously. It is believed[52] that under these conditions ring opening is accompanied by a rearrangement which can be represented by the following scheme:



$N_{(6)}$-Carbamoylsydnone imines are more resistant to alkalis than the corresponding acyl derivatives, but, on heating with an alcoholic solution of potassium hydroxide, their heterocyclic ring is opened[52]. Urea derivatives were isolated among the cleavage products.

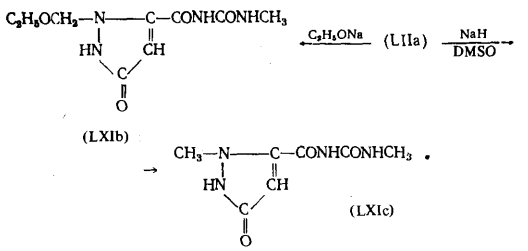
It was mentioned above[117] that, in contrast to the 3-methyl analogue, $N_{(6)}$-methylcarbamoyl-4-ethoxycarbonylmethyl-3-phenylsydnone imine (LIIb) undergoes preferential cleavage on treatment with aqueous ammonia at room temperature, forming a rearrangement product—5-pyrazolinone (LXIa):



(LXIa)

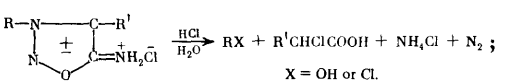
Derivatives of 5-pyrazolinone (LXI, b and c) have been isolated and identified after treating $N_{(6)}$-methylcarbamoyl-4-ethoxycarbonylmethyl-3-methylsydnone imine (LXIIa) with

sodium ethoxide[117] or hydride[123]:



These reactions apparently involve the simultaneous or successive rupture of the $N_{(2)}-O_{(1)}$ bond in the ring and the intramolecular acylation of the unsubstituted nitrogen atom by the carboxymethyl group.

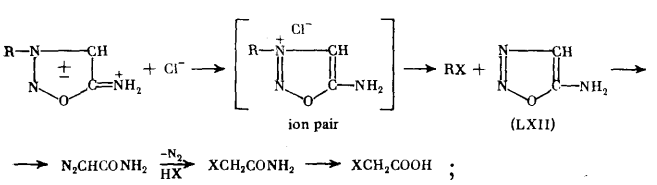
(*b*) *The action of acids*. It was believed initially that, in contrast to sydnones, sydnone imine salts are resistant to the action of acids even on raising the temperature[6,11]. However, a detailed study showed that, on heating with hydrochloric acid, sydnone imines are cleaved with liberation of nitrogen and formation of the corresponding halogeno- or hydroxy-derivatives, substituted chloroacetic acids, and ammonium chlorides[9,123,125]:



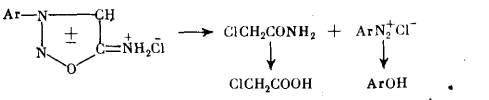
The study of the kinetics of the cleavage of sydnone imine hydrochlorides with aryl substituents in the 3-position showed[125,126] that nitrogen is evolved via a first-order reaction and that the pseudo-unimolecular rate constant is directly proportional to the HCl concentration but is independent of that of H_2SO_4. This confirms that the reaction is catalysed by chloride ions and not protons.

The rate of hydrolysis of sydnone imine salts increases with enhancement of the electron-donating properties of the substituents or with increase of their bulk[125,127]. It has been suggested[125] that the acid hydrolysis of 3-alkylsydnone imine salts is an S_N1 reaction, the first rate-limiting stage of which involves dissociation of the $R-N_{(3)}$ bond with formation of the carbonium ion R^+ and the unstable 5-amino-1,2,3-oxadiazole molecule (LXII). The latter decomposes with evolution of nitrogen and the formation of the amide of glycolic acid. In hydrochloric acid the hydroxy-group is replaced by chlorine and the amide group is converted into a carboxy-group. The R^+ cation reacts instantaneously with water to form the alcohol ROH, while in the presence of chloride ions the chloride RCl is formed.

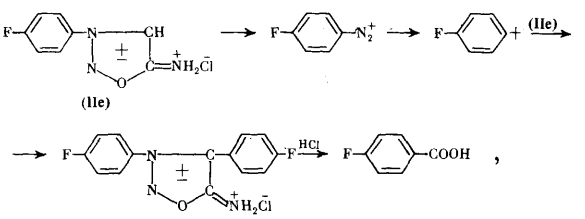
The specific effect of HCl can apparently be explained by the ability of the sydnone imine cation to form ion pairs with Cl^-:



Another mechanism of the acid cleavage has been established for 3-arylsydnone imines[128]. In this case an arenediazonium chloride and chloroacetamide are formed and are subsequently converted into phenol and chloroacetic acid:

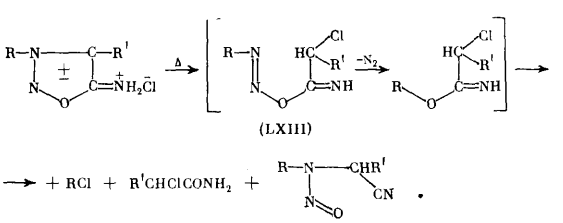


Direct confirmation of the intermediate formation of an arenediazonium compound in this reaction has been obtained[119] by employing the hydrochloride of 3-(4′-fluorophenyl)sydnone imine (IIe). *p*-Fluorobenzoic acid, whose formation has been explained[120] by the mechanism



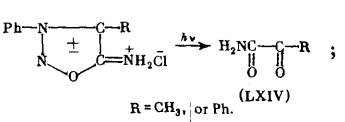
was then detected in the reaction mass.

(*c*) *Thermal and photochemical cleavage*. Sydnone imine salts with non-aryl substituents have been found to undergo thermal as well as hydrolytic cleavage, the former beginning to predominate at high chloride ion concentrations[125,127]. A detailed study of this process led to the hypothesis that in the given instance, when the concentration of the ion pair is high, the first reaction stage involves the dissociation of the $N_{(3)}-C_{(4)}$ bond with formation of the unstable diazoiminoester (LXIII), which is subsequently converted into the corresponding alkyl chloride and amide via the iminoester[125,127]:

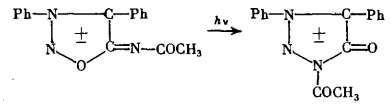


The thermal cleavage of the sydnone imine ring can occur on heating sydnone imine salts in non-aqueous solvents, for example in DMF and in butyl alcohol[127]. Together with the products formed on thermal decomposition of the salts in water, the corresponding *N*-nitrosoaminoacetonitrile is obtained. An exception is 3-benzyl derivative, from which benzyl chloride is apparently initially split off, as in an aqueous medium, while 5-amino-1,2,3-oxadiazole (LXII) is cleaved further with participation of yet another sydnone imine molecule to give the final products[128].

Examples of the photochemical cleavage of the sydnone imine ring have been described. Thus, on irradiation of aqueous solutions of the hydrochlorides of 4-methyl-3-phenyl- and 3,4-diphenyl-sydnone imines with light from a mercury lamp for 20–40 h, the corresponding dicarbonyl compounds (LXIV) are formed in 8–9% yield[129]:



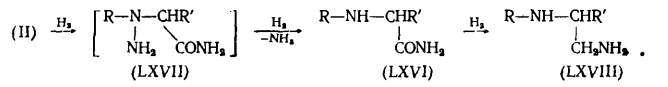
Morpholine, glycolic acid, and nitrogen were identified among the products of the photochemical decomposition of the hydrochloride of 3-morpholinosydnone imine[122]. After ultraviolet irradiation of $N_{(6)}$-acetyl-3,4-diphenylsydnone imine, it was possible to detect the mesoionic triazolone (LXV) among the decomposition products[130]:



(LXV)

Morpholine, chloroacetic acid, ethyl alcohol, and carbon dioxide were found among the products of the photolysis of $N_{(6)}$-ethoxycarbonyl-3-morpholinosydnone imine in 0.1 *N* HCl solution[122].

(d) Other ring cleavage reactions. The sydnone imine ring is opened also in catalytic hydrogenation. In an early study Brookes and Walker[7] observed that, when the hydrochlorides of 4-isopropyl-3-methyl- and 4-isobutyl-3-methylsydnone imines are reduced over a platinum catalyst, the corresponding aminoacetamides (LXVI) are formed and ammonia is evolved;

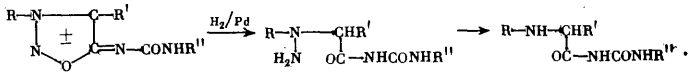


(LXVII) (LXVI) (LXVIII)

Since in the reduction of a sydnone imine salt over a palladium catalyst the first two moles of hydrogen are absorbed rapidly, the authors[9] suggested that a hydrazinoamide (LXVII) is formed initially and is then deaminated on further reduction to give (LXVI). They showed that, in the reaction of the hydrochloride of 3,4-diphenylsydnone imine (IIb), the formation of an amide of type (LXVI) is accompanied under these conditions by the formation of a product of further hydrogenation—*N*,*C*-diphenylethylenediamine.

It was mentioned above that, when $N_{(6)}$-phenylcarbamoylsydnone imines are reduced with iron, ring cleavage is not observed[68], but hydrogenation over palladium black leads to ring opening in these compounds[52].

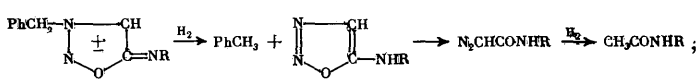
The main product of the reductive cleavage of $N_{(6)}$-carbamoylsydnone imines is the hydrazine derivative (LXIX):



(LXIX) (LXX)

In an acid medium or on hydrogenation of the hydrochlorides of $N_{(6)}$-carbamoyl derivatives, the deamination product (LXX) is formed preferentially.

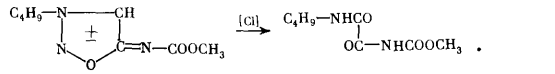
As in thermal cleavage, hydrogenolysis of sydnone imines with a benzyl substituent in the 3-position (LXXI) takes place differently. It has been shown[131] that under these conditions the primary step is debenzylation with successive formation of unstable oxadiazoles (LXXII) and acetyldiazoacetamides (LXXIII). The latter can be partly hydrogenated to the corresponding acetamides:



(LXXI) (LXXII) (LXXIII)

R = H · HCl, $COCH_3$ or CONHPh.

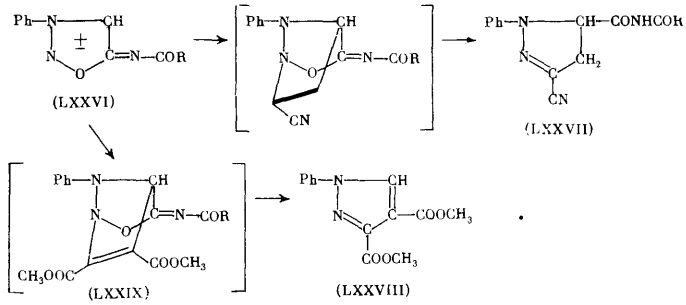
Yet another example of the oxidative cleavage of the sydnone imine ring has been described[116]. In contrast to sydnones, which are chlorinated fairly smoothly in the 4-position in the ring, when sydnone imine salts were acted upon by chlorine their decomposition was observed and the individual products could not be isolated. On treatment of $N_{(6)}$-methoxycarbonyl-3-butylsydnone imine (LXXIV) with chlorine in dichloroethane in the presence of sodium dicarbonate or with sulphuryl chloride in dichloroethane and subsequent treatment of the reaction mixture with water, the cleavage product was isolated to which the structure (LXXV) was attributed:



(LXXIV) (LXXV)

Like sydnones, $N_{(6)}$-acylsydnone imines enter into 1,3-dipolar addition reactions with unsaturated compounds[132]. Thus, when $N_{(6)}$-methoxycarbonyl- and $N_{(6)}$-benzoyl derivatives of 3-phenylsydnone imines (LXXXVI, a and b) are heated with an excess of acrylonitrile, the sydnone imine ring is opened with formation of a new ring (the pyrazoline ring). In contrast to sydnones, the ring oxygen and the exocyclic group are not then eliminated and the final reaction product is a derivative of 1-phenylpyrazoline-5-carboxylic acid (LXXVII, a and b), i.e. 1,3-addition with a subsequent rearrangement takes place.

On the other hand, the reaction with dimethyl acetylenedicarboxylate proceeds via a "sydnone" type mechanism[133]: on prolonged heating with $N_{(6)}$-benzoyl-3-phenylsydnone imine (LXXVIb), the main reaction products isolated were dimethyl 1-phenylpyrazole-3,4-dicarboxylate (LXXVIII) and dibenzoylurea:



(LXXVI) (LXXVII) (LXXIX) (LXXVIII)

The authors[133] suggest that the latter is formed as a result of the elimination of benzoyl isocyanate from the intermediate (LXXIX), analogous to the elimination of CO_2 when the similar reaction is carried out with sydnones.

3. Characteristics of the Reactivity of Sydnone Imines

It follows from the examination of the chemical behaviour of sydnone imines that these compounds exhibit a high and many-faceted reactivity due to a number of their structural features, primarily the unusual distribution of electron density in the unsaturated heterocyclic system, including the exocyclic group.

The relative reactivities of sydnone imines are on the whole consistent with the calculations of the distribution of electron density. The ease of their hydrolytic and thermal decomposition is consistent with the presence of a large positive charge on the $N_{(3)}$ atom in sydnone imine salts. The enhanced electron density at the exocyclic nitrogen atom in

$N_{(6)}$-acyl and $N_{(6)}$-carbamoyl derivatives is confirmed by the high basicity of these compounds. The excess electron density at the $C_{(4)}$ atom in $N_{(6)}$-acylsydnone imines determines the mode of the electrophilic substitution reaction. The large negative charge on the exocyclic nitrogen atom in the sydnone imine base is consistent with the ease of the electrophilic substitution at and addition to this atom. As already mentioned above, calculations indicate a fair agreement with the values of $E_{1/2}$ for the polarographic reduction of sydnone imines[81,86].

Quantitative analysis of the reactivity of sydnone imines with the aid of equations based on the principle of the linearity of free energies (LFE), namely in terms of the influence of substituents on the kinetics and equilibria in certain reactions, made it possible to deduce the properties of the sydnone imine ring as a transmitter of the electronic effects of both the reaction centre and the substituent[58,87,97,99,100].

Substituents in the 3-position exhibit an inductive effect in relation to reactions involving the exocyclic group and the influence of these substituents is correlated satisfactorily with the Taft inductive constants (σ^*) of non-aryl substituents and the σ^0 constants of aryl substituents.

In view of the identical order of magnitude of the constants σ^* and σ^0 ($\sigma^* = 0.600 + \sigma^0$), the data for 3-substituted derivatives can be combined into a single reaction series. Thus a single straight line has been obtained for the basicities of $N_{(6)}$-methoxycarbonyl-3(R)-sydnone imines[100]:

$$pK_a = 3.50 - 0.65\,\sigma^* \quad (r = 0.990),$$

and two virtually parallel straight lines have been obtained for the kinetics of the acid hydrolysis of the nitroso-group in $N_{(6)}$-nitroso-3(R)-sydnone imines[87,135]:

$$\lg k = -3.84 + 0.39\,\sigma^* \quad \text{(for non-aromatic R)},$$
$$\lg k = -4.06 + 0.39\,\sigma^* \quad \text{(for aromatic R)}.$$

The distance between these straight lines along the ordinate axis ($\psi = -0.22$) is determined by the non-polar conjugation of the exocyclic N=O group with the benzene ring in the 3-position; the calculated energy of this conjugation is low[87,135]: $E_\psi = 2.3RT\psi = 0.3$ kcal.

Reactions involving the exocyclic group are also satisfactorily correlated with the σ^0 constants of 4-aryl substituents, as shown in the conversion of $N_{(6)}$-nitroso-4-aryl-3-benzylsydnone imines into the corresponding sydnones ($\rho^0 = 0.18$) and in the acid hydrolysis ($\rho^0 = 0.24$) and polarographic reduction of the nitroso-group ($\rho^0 = 0.025$) in these compounds[87].

The sydnone imine ring is a reaction centre in polarographic reduction[90,93]; the correlation analysis of the half-wave potentials $E_{1/2}$ in accordance with the LFE principle has already been described. For the alkaline opening of the sydnone imine ring[82,97,100], which in this case also behaves as a reaction centre, the equilibrium constant for derivatives with non-aromatic substituents in the 3-position is described satisfactorily by the equation[99,100]

$$\lg K = -6.63 + 2.44\sigma^* + 0.46E_S^c, \qquad (1)$$

where E_S^c is the steric constant of the substituents. The steric hindrance in the ring opening reaction can apparently be accounted for by the "expansion" of the substituents at the $N_{(3)}$ atom on passing from the sp^2 hybridisation of this atom in the sydnone imine to the p^3 state in *N*-nitrosoaminoacetonitrile. The equilibrium constant for this reaction involving 3-(R)-aryl derivatives is described by the equation[27,99,100]

$$\lg K = -6.16 + 2.44\,\sigma^0. \qquad (2)$$

Comparison of Eqns.(1) and (2), taking into account the fact that $\sigma^* = 0.600 + \sigma^0$ and $E_S^c \cong 0.25$ for R = aryl, led to the calculation[99,100] of the effect of the non-polar conjugation of the benzene and sydnone imine rings ($\psi = -1.2$) and of the energy of this conjugation: $E_\psi = 1.6$ kcal. The energy of the non-polar conjugation with the sydnone imine ring for the phenyl substituent in the 4-position is[87] $E_\psi \cong -2.0$ kcal. These values of E_ψ are smaller by a factor of approximately four than the energy of the conjugation of the two benzene rings in biphenyl.

The following equations have been obtained for the kinetics of the alkaline ring opening (pH 8.75):

$$\lg k = -2.374 + 1.00\,\sigma^0 \quad (3(R) = Ar)^{27,100},$$
$$\lg k = -3.19 + 1.86\,\sigma^* \quad (3(R) = Alk)^{91}.$$

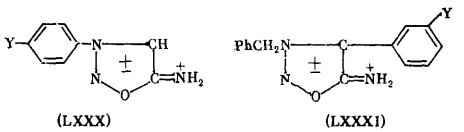
The absence of a steric effect in the latter case can serve as evidence in support of the view that the activated complex in this reaction has a geometry closer to that of the initial sydnone imine than that of *N*-nitrosoaminoacetonitrile[97]. On the other hand, as stated above, a considerqble "steric acceleration" effect was observed in the acid cyclisation reaction[51].

The rate-limiting stage in the thermal cleavage of the hydrochlorides of 3-alkyl- and 3-aryl-sydnone imines (except 3-benzylsydnone imine) involves the interaction of the chloride ion with the $C_{(4)}$ atom and subsequent rupture of the $N_{(3)}-C_{(4)}$ bond. The substituent at $N_{(3)}$ is in the *ortho*-position with respect to the ring $C_{(4)}$ atom and therefore exhibits a considerable steric as well as electronic effect[127]:

$$\lg k = -3.21 + 0.90\sigma^* + 1.00E_S^c \text{ (DMF, 89°)}.$$

The retardation of the reaction as the bulk of the substituent increases and its electron-donating capacity is diminished supports an S_N2 mechanism for this reaction, since a steric acceleration of the reaction might have been expected for an S_N1 mechanism[127].

The Hammett constants σ for the sydnone imine ring have been calculated from the half-wave potentials $E_{1/2}$ for the polarographic reduction of the Y group in compounds of the type (LXXX) and (LXXXI):[98]



(LXXX) (LXXXI)

The results are presented below; the σ constants of the sydnone ring and of the *N*-nitrosoaminoacetonitrile group, from which sydnone imine groups are synthesised, are included for comparison:

Substituent	σ
p-(3-sydnone iminyl)	+1.1
m-(3-benzyl-4-sydnone iminyl)	+0.40
p-[N(N=O)CH$_2$CN]	+0.5
p-(3-sydnonyl)	+1.0
p-(3-benzyl-4-sydnonyl)	+0.3

The values of σ indicate strong electron-accepting properties of the 3-sydnone iminyl substituent; the addition of a heterocycle to the 4-position entails an appreciable weakening of these properties. Sydnones and sydnone imine cations proved to have similiar σ constants, while the opening of the sydnone imine ring leads to a decrease of the electronegativity by a factor greater than two.

V. BIOLOGICAL PROPERTIES OF SYDNONE IMINES

Like sydnones, sydnone imines are not found in nature and have no analogues among the known natural and synthetic biologically active substances. However, the high and varied reactivity of sydnone imines as well as the possibility of converting them under mild conditions into *N*-nitroso-compounds and aminoacid derivatives led investigators to study their biological activity. Data have now been obtained on the antibacterial, antitumour, pharmacological, and biological activities of a number of sydnone imine derivatives[88,135]. By analogy with sulphonamide preparations, incorporating a five-membered nitrogen-containing heterocycle with an exocyclic amino-group (ethazole, norsulphazole, etc.), a study was made of the antimicrobial activity of $N_{(6)}$-*p*-aminobenzenesulphonyl derivatives of sydnone imines (XIX, $R'' = NH_2$).[10,72] However, like the hydrochlorides of 4-alkyl-3-methylsydnone imines[7], these compounds proved to be relatively inactive in relation to various experimental infections. Among 3-piperonylsydnone imines, substances with antimalarial activity were discovered[26].

The antiblastic activity of a number of mono- and bis-sydnone imines has been investigated on small laboratory animals[8,136]. Among the lower alkyl derivatives, compounds with antitumour activity were not discovered[8]. On the other hand, it has been shown that[136] 3-isopropyl-, 3-cyclohexyl-, 3-piperidinylethyl-, and a number of alkylene-bis-sydnone imines are able to inhibit at least one of the five grafted tumours employed. The dichloride of ethylenebis-3,3'-sydnone imine [V, $Z = (CH_2)_2$] and its $N_{(6)}$-bismethoxycarbonyl derivative proved to be the most active in relation to sarcoma 45 and M-1 in rats and sarcoma 180 in mice. In one of the experiments 80% inhibition of the growth of sarcoma 45 was noted. It has been observed that in the general case the salt form of sydnone imines has a favourable influence on the antiblastic activity and that, with increase of the length of the hydrocarbon chain in polymethylenebis-3-sydnone imines, the antiblastic activity falls. It has been suggested that the antitumour activity of sydnone imines is associated with their conversion into *N*-nitrosoaminoacid derivatives, some of which have an inhibiting effect on tumour growth.

Interesting results have been obtained in the study of the pharmacological activity of sydnone imine derivatives. As a result of extensive research by Soviet and Japanese scientists, substances which have found applications as medicinal drugs have been found among compounds of this series. It has been discovered that many salts of 3-aryl-,[9] 3-benzyl-,[16] and 3-ethoxycarbonylmethyl-sydnone imines[17] as well as their $N_{(6)}$-acyl[53-55,57] and $N_{(6)}$-carbamoyl[53-55,58,64,65,74,112] derivatives exhibit analgesic and antipyretic activities. Together with the analgesic and antipyretic activities, certain hydrochlorides of 3-arylsydnone imines show an anti-inflammatory action[17,64,65,74,112]. It has been stated[53-55] that certain 3-aryl- and 3-benzyl-sydnone imines can be used in the treatment of rheumatism.

It has been found[137] that, among the series of sydnone imine salts with hydrocarbon substituents investigated, only the 3,4-diaryl derivative shows a spasmolytic activity. An analogous activity is also exhibited by certain 3-amino-sydnone imines[45].

Pharmacological studies have shown that many sydnone imine salts and their exocyclic derivatives exhibit a hypotensive activity. A fairly prolonged effect has been observed for compounds containing the benzyl group in the 3-position[16]. In experiments on cats the hydrochloride of 3-phenoxyethyl-sydnone imine reduced the arterial pressure by 30–50 mm for 1–2 h.[13] The hydrochlorides of 3-cyclobutyl- and 3-cyclopentyl-sydnone imines have been patented as vasodilators[49]. Sydnone imine salts containing 4-benzyl, 4-*o*-methoxyphenyl-, 4-piperonyl-, and 4-α-pyridylpiperazinoalkyl substituents in the 3-position show antianginal and hypotensive activities.

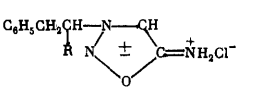
However the hypotensive activity is exhibited most strikingly by 3-amino-derivatives[138]. In small doses, the hydrochlorides of 3-dimethylamino-,[37,38,44] 3-dibutylamino-,[37,45] 3-piperidino-,[37,38,43,45] 3-(α-pipecolinyl)-,[38,43,45] 3-pyrrolidino-,[37,38,43,45] 3-morpholino-,[37,38,43,45,118,139,140] and 3-(4'-methylpiperazino)-sydnone imines[38,45] reduce blood pressure for a long time.

The salts of 3-aminosydnone imines containing in the 4-position chlorine or bromine atoms[41,42,45] or alkyl substituents[43] as well as the dihydrochloride of 3,3'-(1'',4''-piperazino)bis-sydnone imine[37,38,45] have a dilating effect on the coronary artery. The $N_{(6)}$-acyl derivatives of 3-aminosydnone imines containing the benzoyl[44,61], cyclohexanecarbonyl[44,115], and ethoxycarbonyl[62,63] residues at the exocyclic nitrogen atom proved to be still more effective.

From compounds of this type, Japanese investigators selected one substance—$N_{(6)}$-ethoxycarbonyl-3-morpholinosydnone imine—which was subjected to an extensive pharmacological study[141-143]. Under the names SIN-10, morsydomine, or morial[144], this sydnone imine has found application as a hypotensive drug. The use of a specimen labelled at the $C_{(5)}$ atom[145] made it possible to investigate in detail the pharmacokinetics and metabolism of this preparation[146]. It has been suggested[143] that the mechanism of its hypotensive action based on its ability to block α-adrenergic receptors.

In the series of sydnone imines substances acting on the central and peripheral nervous systems have been discovered: these are the salts of certain 3-aminosydnone imines[39] and their $N_{(6)}$-acyl derivatives[60] as well as various 3-phenylalkylsydnone imines[12,13,21,147]. It has been shown that the salts of a number of sydnone imines exhibit an adrenopositive peripheral activity and exert a stimulating influence on the central nervous system[12,147]. The inhibiting effect of these compounds on the enzyme monoamine oxidase has been studied in detail[12,33,147]. It has been shown the sydnone imine salts inhibit the oxidative deamination of a number of biogenic amines and that the majority of the compounds cause reversible competitive inhibition of enzymes. Among a whole series of the sydnone imine salts investigated with different substituents in the 3- and 4-positions, the most effective inhibitors in relation to tyramine and serotonine as substrates *in vitro* proved to be the hydrochlorides of 3-phenylethylsydnone imine (LXXXII) and 3-phenylisopropylsydnone imine (LXXXIII), whose activity [$I_{50} = (1.8–6.6) \times 10^{-5}$ M] is comparable to that of iproniazid. An increase of the bulk of the group in the 3-position [$(C_6H_5)_2CHCH_2$ and $(C_6H_5CH_2)_2CH$] and the replacement of hydrogen in the 4-position by the CH_3 or C_6H_5 group lowers the inhibiting effect[12,148].

The hydrochloride of 3-phenylisopropylsydnone imine showed a high activity also in *in vivo* experiments on rats and it was demonstrated that the inhibiting effect is exhibited by the sydnone imine itself and not by products of its metabolism:



(LXXXII), R = H
(LXXXIII), R = CH_3

The results of biochemical studies permitted a specific investigation of the pharmacological activities of the compounds which enhance the activity of biogenic amines[12,147]. It was found that the intensity of pharmacological effects in this series of compounds is more notable the higher the ability of the sydnone imine salts to inhibit the oxidation of biogenic imines, which serve in the organism as chemical mediators in nervous excitation.

Among alkyl- and aryl-sydnone imines, substances were discovered which influence the central nervous system and exhibit a peripheral sympathomimetic activity[147-149]. They diminish somewhat the sedative and hypothermal activity of reserpine, enhance the convulsant effect of tryptamine and 5-hydroxytryptophan, and intensify the motor activity of animals. Among them, the highest pharmacological activity was shown by the hydrochloride of 3-phenylisopropylsydnone imine (LXXXIII), which under the name sydnophen has found applications in psychiatric practice as a medicinal drug acting both as a psychostimulator and antidepressant[22,23,24,150-153].

An interesting pharmacological activity is manifested by $N_{(6)}$-phenylcarbamoyl-3-phenylazopropylsydnone imine (XLIII), which is an effective psychostimulator. In experiments on animals this compound increases motor activity, shortens the latent period in conditioned reflexes, has an activating effect on the bioelectric processes in the cortex and subcortical structures of the brain, weakens the effect of hypnotic substances, and increases the body temperature. This relatively non-toxic substances has found applications as a medicinal drug (under the name sydnocarb) stimulating the central nervous system in the treatment of various mental illnesses and in other cases, and it has many advantages over other preparations with similar activities[67,154-160]. A similar study of the pharmacokinetics of sydnocarb by chromatographic[161] and polarographic[101] methods and a procedure using synthetic [^{14}C]sydnocarb specimens labelled in different sites within the molecule[162] made it possible to establish clearly the characteristics of the action of this preparation, its metabolism, its distribution in the organism[163], and its elimination from the latter.

During the preparation of the manuscript for the press, several reports on the chemistry of sydnone imines were published. It has been shown[163] that the sydnone imine ring can be formed not only under the conditions of acid catalysis but also under the conditions of base catalysis; the intermediate cyclisation product, formerly regarded as the hypothetical base of the sydnone imine (XIII), has been detected spectroscopically.

Infrared spectroscopic data have led to the conclusion that the side chain in $N_{(6)}$-carbamoylsydnone imines has a planar structure and an inference has been drawn about its conformation[164]. A number of $N_{(6)}$-aminoalkylacyl derivatives of sydnone imines have been synthesised by the method of polymeric activated esters[165].

REFERENCES

1. W.Baker and W.D.Ollis, Quart.Rev., **11**, 15 (1951).
2. F.H.C.Stewart, Chem.Rev., **64**, 129 (1964).
3. M.Ohta and H.Kato, In "Nonbenzoid Aromatics" (Edited by I.P.Snyder), Acad.Press, New York, 1969, p.117.
4. W.D.Ollis and C.A.Ramsden, Advances in Heterocyclic Chemistry, **19**, 3 (1976).
5. W.Baker, W.D.Ollis, and V.D.Poole, J.Chem.Soc., 311 (1948).
6. H.Kato, M.Hasimoto, and M.Ohta, Nippon Kagaku Zasshi, **78**, 707 (1957).
7. P.Brookes and J.Walker, J.Chem.Soc., 4409 (1957).
8. C.W.Greco, W.H.Nyberg, and C.C.Cheng, J.Medicin.Chem., **5**, 861 (1962).
9. H.U.Daeniker and J.Druey, Helv.Chim.Acta, **45**, 2426 (1962).
10. V.G.Yashunskii and V.G.Ermolaeva, Zhur.Obshch. Khim., **32**, 186 (1962).
11. V.F.Vasil'eva and V.G.Yashunskii, Khim.Nauka i Prom., **4**, 678 (1959).
12. W.G.Jashunskii, W.Z.Gorkin, M.D.Mashkovskii, R.A.Altshuler, I.W.Veryovkina, and L.E.Kholodov, J.Medicin.Chem., **14**, 1013 (1971).
13. L.E.Kholodov, I.F.Tishchenkova, R.A.Al'tshuler, V.G.Yashunskii, and M.D.Mashkovskii, Khim.-Farm. Zhur., No.5, 3 (1968).
14. V.G.Yashunskii, L.E.Kholodov, and S.A.Zotova, Zhur.Vses.Khim.Obshch.im.Mendeleeva, **10**, 105 (1965).
15. L.E.Kholodov, I.F.Tishchenkova, Z.A.Pankina, and V.G.Yashunskii, Zhur.Org.Khim., **3**, 1513 (1967).
16. B.P.962 293 (1963); Chem.Abs., **61**, 9504 (1964).
17. Japanese P.7026089 (1970); Chem.Abs., **74**, 13 166 (1971).
18. V.G.Yashunskii, V.F.Fedorovich, and S.E.Kholodov, Zhur.Vses.Khim.Obshch.im.Mendeleeva, **8**, 583 (1963).
19. Japanese P.6342 (1967); Chem.Abs., **68**, 29702 (1964).
20. V.G.Yashunskii and V.S.Fedorovich, Zhur.Obshch. Khim., **34**, 3075 (1964).
21. Z.A.Olovyanishnikova, V.V.Ogorodnikova, V.I.Mamonov, V.G.Yashunskii, R.A.Al'tshuler, and M.D.Mashkovskii, Khim.-Farm.Zhur., No.6, 20 (1972).
22. R.A.Al'tshuler, O.N.Volzhina, F.Ya.Leibel'man, M.D.Mashkovskii, I.S.Slyusarenko, and V.G.Yashunskii, Khim.-Farm.Zhur., No.4, 59 (1971).
23. USSR P.437 762 (1974); Byul.Izobret., No.51 (1974).
24. French P.1 589 783 (1970); Chem.Abs., **74**, 13 131 (1971).
25. L.E.Kholodov and V.G.Yashunskii, Zhur.Org.Khim., 1, 2063 (1965).
26. W.H.Nyberg and C.C.Cheng, J.Medicin.Chem., **30**, 4257 (1965).
27. V.G.Yashunskii, L.E.Kholodov, and O.I.Samoilova, Chem.Comm., **30**, 4257 (1965).
28. V.G.Yashunskii, V.F.Vasil'eva, L.E.Kholodov, and M.N.Shchukina, Zhur.Obshch.Khim., **32**, 192 (1962).
29. L.E.Kholodov and V.G.Yashunskii, Zhur.Obshch. Khim., **32**, 865 (1962).
30. L.E.Kholodov and V.G.Yashunskii, Zhur.Obshch. Khim., **32**, 3661 (1962).
31. I.S.Slyusarenko, Z.M.Kol'tsova, V.I.Mamonov, and V.G.Yashunskii, Khim.-Farm.Zhur., No.8, 12 (1971).
32. I.S.Slyusarenko, V.V.Ogorodnikova, V.I.Mamonov, and V.G.Yashunskii, Khim.Geterotsikl.Soed., 1469 (1973).
33. I.S.Slyusarenko, I.V.Verevkina, B.I.Bryantsev, V.Z.Gorkin, and V.G.Yashunskii, Khim.-Farm.Zhur., No.3, 19 (1975).
34. V.G.Yashunskii, Zhur.Obshch.Khim., **33**, 192 (1963).
35. F.M.Mukhametshin, A.L.Fridman, and A.D.Nikolaeva, Khim.Geterotsikl.Soed., 125 (1970).
36. M.Gotz and K.Grozinger, J.Heterocycl.Chem., **7**, 123 (1970).

37. K.Masuda, Y.Imashiro, and T.Kaneko, Chem.Pharm. Bull.Japan, **18**, 128 (1970).
38. US P.3 312 690 (1967); Chem.Abs., **67**, 108 662 (1967).
39. Japanese P.6 918 302 (1969); Chem.Abs., **72**, 3502 (1970).
40. French Appl., 2 004 770 (1969); Chem.Abs., **72**, 111 479 (1970).
41. French P.1 551 013 (1969); Chem.Abs., **72**, 12 732 (1970).
42. BRD P.1 942 854 (1970); Chem.Abs., **73**, 131 005 (1970).
43. B.P.1 116 692, 1 116 693 (1966); Chem.Abs., **67**, 108 662 (1967).
44. BRD P.1 813 752 (1970); Chem.Abs., 73, 66 584 (1970).
45. Dutch P.145 547 (1974).
46. BRD P.2 241 991 (1973); Chem.Abs., **78**, 159 672 (1973).
47. B.P.1 358 413 (1974).
48. M.Gotz and K.Grozingen, Tetrahedron, **27**, 4449 (1971).
49. S.A.Zotova and V.G.Yashunskii, Zhur.Org.Khim., **3**, 1889 (1967).
50. I.S.Slyusarenko, Candidate's Thesis, Lomonosov Moscow Institute of Fine Chemical Engineering, Moscow, 1973.
51. V.V.Ogorodnikova, L.E.Kholodov, and V.I.Yashunskii, Khim.Geterotsikl.Soed., 39 (1977).
52. H.U.Daeniker and J.Druey, Helv.Chim.Acta, **45**, 2441 (1962).
53. Belg.P.618 822 (1962); Chem.Abs., **59**, 2840 (1963).
54. Belg.P.618 823 (1962); Chem.Abs., **59**, 2838 (1963).
55. Belg.P.618 824 (1962); Chem.Abs., **59**, 2839 (1963).
56. V.G.Yashunskii, O.I.Samoilova, and L.E.Kholodov, Zhur.Obshch.Khim., **34**, 2050 (1964).
57. Japanese P.7 026 265 (1970); Chem.Abs., **74**, 13 165 (1971).
58. Japanese P.7 026 088 (1970); Chem.Abs., **74**, 13 161 (1971).
59. K.Masuda, T.Kamiya, I.Imashira, and T.Kaneko, Chem.Pharm.Bull.Japan, **19**, 72 (1971).
60. Japanese P.7 006 265 (1969); Chem.Abs., **73**, 25 485 (1970).
61. US P.3 833 589 (1974); Chem.Abs., 81, 152 276 (1974).
62. US P.3 769 283 (1973).
63. US P.3 812 128 (1974).
64. Japanese P.7 026 086 (1970); Chem.Abs., **74**, 13 164 (1971).
65. Japanese P.7 026 090 (1970); Chem.Abs., **74**, 13 160 (1971).
66. USSR P.222 370; Byul.Izobret., No.21 (1973).
67. L.E.Kholodov, V.G.Yashunskii, R.A.Al'tshuler, M.D.Mashkovskii, L.F.Roshchina, et al., Khim.-Farm. Zhur., No.1, 50 (1973).
68. Z.A.Olovyanishnikova, B.I.Bryantsev, I.S.Slyusarenko, and V.G.Yashunskii, Khim.Geterotsikl.Soed., 1198 (1975).
69. Z.A.Olovanishnikova, T.M.Ivanova, V.W.Sviridova, and V.G.Yashunskii, Khim.Geterotsikl.Soed., 170 (1978).
70. French P.1 337 878 (1966); Chem.Abs., **67**, 10 765 (1967).
71. M.Ohta, K.Yoshida, and S.Sato, Bull.Chem.Soc. Japan, **39**, 1269 (1966).
72. H.U.Daeniker and J.Druey, Helv.Chim.Acta, **45**, 2446 (1962).
73. L.E.Kholodov and V.G.Yashunskii, Zhur.Org.Khim., **3**, 2047 (1967).
74. Japanese P. 7 006 015 (1970); Chem.Abs., **73**, 3918 (1970).
75. S.A.Zotova and V.G.Yashunskii, Zhur.Org.Khim., 1, 2218 (1965).
76. V.G.Yashunskii, E.M.Peresleni, and Yu.N.Sheinker, Izv.Akad.Nauk SSSR, Ser.Fiz., **26**, 1295 (1962).
77. V.G.Yashunskii and E.M.Peresleni, Zhur.Obshch. Khim., **32**, 1687 (1962).
78. V.V.Ogorodnikova, I.S.Slyusarenko, and V.G.Yashunskii, Khim.Geterotsikl.Soed., 464 (1972).
79. V.P.Buryak and N.M.Turkevich, Farmatsiya, 25, 41 (1976).
80. E.V.Borisov, V.V.Ogorodnikova, N.D.Lebedeva, and V.G.Yashunskii, Khim.Geterotsikl.Soed., 53 (1976).
81. E.V.Borisov, L.E.Kholodov, A.A.Bagatur'yants, O.A.Subbotina, and V.G.Yashunskii, Khim.Geterotsikl.Soed., 1456 (1970).
82. L.E.Kholodov, E.M.Peresleni, and V.G.Yashunskii, Zhur.Obshch.Khim., **33**, 3685 (1963).
83. V.G.Yashunskii and Yu.N.Sheinker, Zhur.Obshch. Khim., **32**, 1681 (1962).
84. V.G.Yashunskii, Doctoral Thesis, Moscow State University, 1963,
85. D.A.Bochvar, A.A.Bagatur'yants, and E.V.Borisov, Zhur.Fiz.Khim., **46**, 523 (1972) [Russ.J.Phys.Chem., No.2 (1972)].
86. E.V.Borisov, L.E.Kholodov, A.A.Bagatur'yants, and V.G.Yashunskii, Khim.Geterotsikl.Soed., 1407 (1971).
87. L.E.Kholodov, Candidate's Thesis, VNIKhFI, Moscow, 1965.
88. L.B.Kier and E.B.Roche, J.Pharm.Sci., **56**, 149 (1967).
89. E.V.Borisov, N.V.Gorskaya, V.G.Yashunskii, and L.K.Vasyanina, Khim.Geterotsikl.Soed., 1049 (1975).
90. V.G.Mairanovskii, L.E.Kholodov, and V.G.Yashunskii, Zhur.Org.Khim., **33**, 347 (1963).
91. L.E.Kholodov, V.V.Alekseev, and V.G.Yashunskii, Zhur.Fiz.Khim., **39**, 1566 (1965) [Russ.J.Phys.Chem., No.7 (1965)].
92. L.E.Kholodov and V.G.Yashunskii, Reakts.Sposobn. Org.Soed., **1**, 67 (1964).
93. L.E.Kholodov and V.G.Yashunskii, Zhur.Fiz.Khim., **42**, 206 (1968) [Russ.J.Phys.Chem., No.1 (1968)].
94. L.E.Kholodov, T.A.Kovalenko, and M.K.Polievktov, Khim.Geterotsikl.Soed., 1042 (1975).
95. M.K.Polievktov, T.A.Motoricheva, and L.E.Kholodov, Khim.Geterotsikl.Soed., 33 (1977).
96. E.V.Borisov and V.G.Yashunskii, Zhur.Fiz.Khim., **48**, 455 (1974) [Russ.J.Phys.Chem., No.2 (1974)].
97. L.E.Kholodov, E.V.Borisov, and V.G.Yashunskii, Khim.Geterotsikl.Soed., 702 (1968).
98. L.E.Kholodov, E.V.Borisov, and V.G.Yashunskii, Reakts.Sposobn.Org.Soed., 7, 704 (1970).
99. L.E.Kholodov and V.G.Yashunskii, Khim.Geterotsikl. Soed., 328 (1965).
100. L.E.Kholodov and V.G.Yashunskii, Reakts.Sposobn. Org.Soed., 1, 77 (1964).
101. R.A.Al'tshuler, T.A.Kovalenko, L.E.Kholodov, and M.K.Polievktov, Khim.-Farm.Zhur., No.2, 20 (1976).
102. A.Shima, A.Ouchida, and G.Asahi, Shitsuryo Bunseki, 17, 661 (1969); Chem.Abs., **78**, 87 149 (1970).
103. D.A.Bochvar and A.A.Bagatur'yants, Zhur.Fiz.Khim., **39**, 1631 (1965) [Russ.J.Phys.Chem., No.7 (1965)].
104. D.A.Bochvar, A.A.Bagatur'yants, and A.V.Turkevich, Zhur.Fiz.Khim., **40**, 1366 (1966) [Russ.J.Phys.Chem., No.6 (1966)].

105. E.V.Borisov, Candidate's Thesis, Moscow State Pedagogic Institute, Moscow, 1974.
106. L.B.Kier and E.B.Roche, J.Pharm.Sci., **55**, 807 (1966).
107. K.Sundaram and W.P.Purall, Int.J.Quantum.Chem., **2**, 148 (1968).
108. D.A.Bochvar and A.A.Bagatur'yants, Teor.Eksper. Khim., **5**, 19 (1969).
109. A.A.Bagatur'yants, Candidate's Thesis, Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow, 1968.
110. E.V.Borisov and V.G.Yashunskii, Zhur.Strukt. Khim., **16**, 123 (1975).
111. E.V.Borisov, V.L.Lebedev, and V.G.Yashunskii, Zhur.Fiz.Khim., **49**, 769 (1975) [Russ.J.Phys. Chem., No.3 (1975)].
112. Japanese P.7375 (1972); Ref.Zhur.Khim., 6N371 (1973).
113. L.E.Kholodov and V.G.Yashunskii, Dokl.Akad.Nauk SSSR, **179**, 366 (1968).
114. USSR P.173 872 (1965); Byul.Izobret., No.16 (1965).
115. M.Gotz, K.Grosinger, and Y.T.Oliver, J.Medicin. Chem., **16**, 671 (1973).
116. V.G.Yashunskii, Zhur.Vses.Khim.Obshch.im. Mendeleeva, **8**, 705 (1963).
117. Y.Saito, T.Teraji, and T.Kamiya, Tetrahedron Letters, **30**, 2893 (1971).
118. US P.3 950 332 (1973).
119. G.S.Puranik and H.Suschitzky, J.Chem.Soc.C, 1006 (1967).
120. V.G.Yashunskii and E.M.Peresleni, Zhur.Obshch. Khim., **33**, 3699 (1963).
121. I.S.Slyusarenko, V.V.Ogorodnikova, and V.G.Yashunskii, Khim.Geterotsikl.Soed., 450 (1976).
122. Y.Asahi, K.Shinozaki, M.Nagaoka, Chem.Pharm.Bull., **19**, 1079 (1971).
123. Japanese P.7 327 312 (1973); Chem.Abs., 78, 14 276 (1973).
124. L.E.Kholodov and V.G.Yashunskii, Zhur.Obshch. Khim., **33**, 3409 (1963).
125. L.E.Kholodov and V.G.Yashunskii, Zhur.Obshch. Khim., **35**, 1551 (1965).
126. L.E.Kholodov and V.G.Yashunskii, Zhur.Obshch. Khim., **37**, 670 (1967).
127. L.E.Kholodov, A.M.Khelem, and V.G.Yashunskii, Zhur.Org.Khim., **3**, 1870 (1967).
128. H.U.Daeniker, Helv.Chim.Acta, **47**, 2421 (1964).
129. A.Chinone, Y.Huseya, and M.Ohta, Bull.Chem.Soc. Japan, **43**, 2650 (1970).
130. A.Chinone and M.Ohta, Chem.Heft., 969 (1972).
131. H.Daeniker and J.Druey, Helv.Chim.Acta, **46**, 805 (1963).
132. V.F.Vasil'eva and V.G.Yashunskii, Zhur.Obshch. Khim., **34**, 702 (1964).
133. K.T.Potts, S.Syeda, and S.Husain, J.Chem.Soc.D, 1360 (1970).
134. L.E.Kholodov, Reakts.Sposobn.Org.Soed., **5**, 246 (1968).
135. E.Ackermann, Pharmazie, **22**, 537 (1967).
136. V.A.Chernov and V.G.Yashunskii, Dokl.Akad.Nauk SSSR, **155**, 216 (1964).
137. P.Oehme, E.Göes, K.Schwarz, G.Petsch, et al., Acta Biol.Med.Ger., **14**, 368 (1965).
138. K.Kikushi, K.Kenzo, Y.Aramaki, et al., Japan J. Pharmacol., **20**, 23 (1970); Chem.Abs., **73**, 2429 (1970).
139. K.Kikushi, M.Hirdta, A.Nagaoka, and Y.Aramaki, Japan J.Pharmacol., **20**, 44 (1970); Chem.Abs., **73**, 2429 (1970).
140. K.Hasimoto, N.Taira, and M.Hiata, Arzneim.Forsch., **21**, 1329 (1971).
141. F.Makenaka, S.Norihide, M.Ishihara, et al., Japan J.Pharmacol., **20**, 253 (1970); Chem.Abs., **73**, 6478 (1970).
142. H.Minori and K.Kenzo, Japan J.Pharmacol., **20**, 187 (1970); Chem.Abs., **73**, 64 778 (1970).
143. K.Kikushi and K.Kenzo, Japan J.Pharmacol., 20, 102 (1970); Chem.Abs., **73**, 2430 (1970).
144. Japan Med.Gaz., **8**, No.9, 10 (1971).
145. K.Masuda, T.Toga, and N.Hayashi, J.Labelled Compounds, 11, 301 (1975).
146. S.Tanayama, T.Fujita, J.Shirakawa, and Z.Suzuoki, Japan.J.Pharmacol., 20, 413 (1970); Chem.Abs., **74**, 40 769 (1971).
147. V.G.Yashunskii, M.D.Mashkovskii, V.Z.Gorkin, L.E.Kholodov, et al., Farm.i Toksikol., 33, 1297 (1970).
148. V.G.Yashunskii, L.E.Kholodov, M.D.Mashkovskii, G.A.Al'tshuler, and V.Z.Gorkin, "Tezisy Doklada na Vsesoyuznoi Konferentsii" (Abstracts of Reports at the All-Union Conference), Leningrad, 1966, p.76.
149. M.D.Mashkovskii, R.A.Al'tshuler, V.Z.Gorkin, V.G.Yashunskii, I.V.Verevkina, and L.E.Kholodov, "Tezisy Doklada na Mezhdunarodnom Kongresse Farmakologov, Bazel', 1969" (Abstracts of Reports at the International Congress of Pharmacologists, Basel, 1969), p.101.
150. R.A.Al'tshuler, M.D.Mashkovskii, and L.F.Roshchina, Farm.i Toksikol., **35**, 406 (1972).
151. B.P.1 242 742 (1971); Chem.Abs., **75**, 129 816 (1971).
152. B.P.1 242 743 (1971); Chem.Abs., **75**, 118 321 (1971).
153. M.D.Mashkovskii, "Lekarstvennye Sredstva" (Medicinal Drugs), Izd.Meditsina, Moscow, 1977, Vol.1, p.113.
154. R.A.Al'tshuler, M.D.Mashkovskii, and L.E.Roshchina, Farm.i Toksikol., **36**, 18 (1973).
155. M.D.Mashkovskii, R.A.Al'tshuler, G.Ya.Avrutskii, Yu.A.Aleksandrovskii, and R.A.Shmulevich, Zhur. Neiropat.i Psikhiatr.im.Korsakova, **71**, 1704 (1971).
156. M.E.Shuvalova, S.A.Liberman, and E.V.Egorova, Khim.-Farm.Zhur., No.12, 70 (1976).
157. USSR P.329 890 (1972); Byul.Izobret., No.8 (1972).
158. BRD P.2 028 880 (1971); Chem.Abs., 76, 75 521 (1972).
159. French P.2 092 764 (1972); Chem.Abs., 77, 114 435 (1972).
160. M.D.Mashkovskii, see Ref.153, p.112.
161. R.A.Al'tshuler, L.E.Kholodov, D.V.Meirena, S.B.Seredenin, I.A.Sultanov, N.V.Steletskaya, and Yu.A.Blednov, Khim.-Farm.Zhur., No.1, 16 (1977).
162. A.D.Bulat, L.E.Kholodov, Yu.Ya.Usaevich, and L.N.Kivokurtseva, Khim.-Farm.Zhur., No.2, 9 (1975).
163. R.A.Al'tshuler, L.E.Kholodov, A.P.Gilev, D.V.Meirena, and A.G.Odynets, No.2, 12 (1977).
164. V.V.Ogorodnikova, Candidate's Thesis, IREA, Moscow, 1979.
165. T.M.Ivanova, Z.A.Olovyanishnikova, and V.G.Yashunskii, Khim.Geterotsikl.Soed., 1193 (1978).
166. Z.A.Olovyanishnikova, O.M.Galkin, V.G.Yashunskii, and Yu.A.Davidovich, Khim.Geterotsikl.Soed., 1335 (1978).

Translated from *Uspekhi Khimii*, **49**, 92-117 (1980) U.D.C. 547.26'118; 546.13

Phosphinates ("Hypophosphites") and Their Reactivity

V.I.Yudelevich, L.B.Sokolov, and B.I.Ionin

Results are given on the preparation, structure, and physicochemical properties of phosphinates, and their reactivity is discussed. A list of 234 references is included.

CONTENTS

I. Introduction 46
II. Structure, physicochemical properties, and methods of preparation 46
III. Chemical properties 49

I. INTRODUCTION

Simple compounds containing an active phosphorus–hydrogen bond can be used in general methods for preparing phosphines and phosphonic acids, phosphonous acids, and their derivatives. Various homolytic and heterolytic reactions yielding compounds containing a phosphorus–carbon bond have been applied to various phosphines, as well as phosphonic and phosphinic acids, derivatives, and analogues. However, the chemistry of phosphinates and their reactivity have hitherto been little studied, although research in this field was begun as early as the end of the nineteenth century[1] and various lines have been actively followed up to the present time. Esters[2] and organic ammonium salts[3,4] of phosphinic acid containing a four-coordinated phosphorus atom (phosphinates) are known already. A novel group of compounds having a three-coordinated phosphorus atom—full esters (dialkoxyphosphines)[5-7], diamides[8], and amidoesters[9] of phosphonous acid—have been obtained recently.

Table 1. Change in ^{31}P chemical shifts on the protonation of phosphoryl compounds[37].

Phosphoryl compound	Chemical shift, ppm	Phosphoryl compound	Chemical shift, ppm
Phosphinic acid	-24.0	Methylphosphonic acid	-15.0
Phosphonic acid	-13.6	Phosphonates and phosphonamides	-8.0--12.0
Phosphoric acid	-2.3	Trialkyl phosphates	0

However, only phosphinates have yet found extensive practical application, not only as initial reactants for the preparation of various organophosphorus compounds but also as reductants in the protective coating of metals[10-12], in analytical chemistry[13,14], in the chemical modification of antibiotics[15,16], as inhibitors of certain enzymes[17], and in other most diverse applications. Practical interest attaches also to many compounds obtainable from phosphinates: they possess biological activity[18-20], are surface-active agents, antioxidants, and flotation agents[21], find application in photography for the preparation of developers that do not darken with time[22], and enter into the composition of fluxes for low-temperature soldering[23].

The present Review discusses methods of preparation and the physicochemical and chemical properties of phosphinates. A considerable number of interesting papers of fundamental character have appeared in this field during recent years. However, among the reviews that have appeared[24-28] only three early publications—a short chapter in van Wazer's monograph[26] and Frank's[24] and Kosolapoff's[25] general surveys of the chemistry of organophosphorus compounds—devote an extremely modest space to the reactions of phosphinates. The present paper makes an attempt to fill in some measure the gap existing in the review literature on the chemistry and the reactivity of phosphinates.

II. STRUCTURE, PHYSICOCHEMICAL PROPERTIES, AND METHODS OF PREPARATION

1. Structure, Physicochemical Properties, and Method of Preparation of Phosphinic Acid and its Inorganic Salts

Phosphinic ("hypophosphorous") acid was first obtained in 1816 by Dulong[29], who identified it as containing a minimal number of oxygen atoms (two). This acid, in which phosphorus is in a lower oxidation state (+1) than in its other acids[30], corresponds to the formula H_3PO_2.

Physicochemical data indicate that the two hydrogen atoms are covalently bound to the phosphorus. Thus the phosphorus-31 nuclear magnetic resonance spectrum of aqueous phosphinic acid is a triplet having intensities 1:2:1, with a chemical shift of -13.0 ppm.[31-35]. The ^1H n.m.r. spectrum of the protons attached to phosphorus is a doublet: the chemical shift is 7.14 ppm, and the spin–spin coupling constant $J_{HP} = 566$ Hz (solution in perdeuteroacetone)[36]. Protonation of phosphinic acid is accompanied by an appreciable change in the phosphorus-31 chemical shift (Table 1).[37]

The vibrational infrared and Raman spectra of the free acid and its salts indicate four-coordinated phosphorus[38-40]. Comparison of experimental spectra with parameters of a calculated vibrational model showed that the phosphinate ion corresponds to a model with equalised phosphorus–oxygen bonds[40]. The phosphorus–hydrogen frequencies correspond to vibrations of the phosphino-group of characteristic frequency and form. Detailed study of the infrared spectra of phosphinic acid and several of its inorganic salts[41,42] also showed appreciable lowering of phosphorus–hydrogen stretching frequencies on passing from the acid to its inorganic salts (Table 2).

Results of X-ray structural investigations correlate with the spectroscopic data. The former indicate[43,44] that the $H_2PO_2^-$ ion is a tetrahedron having C_{2v} symmetry: one axis passes through a phosphorus–hydrogen bond, and another

through a phosphorus–oxygen bond. Comparison of interatomic distances and bond angles in ions of the free acid and of ammonium phosphinate shows (Table 3) that the state of the bonds with oxygen atoms remains unchanged within the limits of error in the measurements, whereas the phosphorus–hydrogen bonds, which determine the reactivity of phosphinates, are appreciably longer in the ammonium salt, with a smaller angle between the bonds. This indicates a diminution in the polarity of the phosphorus–hydrogen bond. Hence not only ammonium phosphinate but also other salts of phosphinic acid should be less reactive than the acid itself in heterolytic reactions.

Table 2. Infrared spectral data on phosphinic acid and its inorganic salts[41].

Compounds	ν_{P-H}, cm^{-1}	ν_{PO_2}, cm^{-1}	
		asym.	sym.
KH_2PO_2	2312, 2375	1230	1040
KH_2PO_2(aq)	2314, 2363	1180	1042
$Ba(H_2PO_2)_2$	2350	1170, 1147	1090, 1078
$La(H_2PO_2)_2$	2385, 2380	—	—
$Sm(H_2PO_2)_2$	2370, 2305	—	—
$Sr(H_2PO_2)_2$	—	1150	1082, 1054
NaH_2PO_2(aq)	—	1175	1045
H_3PO_2	2434, 2415, 2395	1225, 1135	1068

Table 3. Interatomic distances and bond angles in ammonium phosphinate and the free acid[43,44].

Bond	H_3PO_2	$NH_4H_2PO_2$
	interatomic distance, A	
P–O	1.505∓0.015	1.51∓0.01
P–H	1.39∓0.01	1.50∓0.01
	bond angle, °	
O–P–O	117.0	120
O–P–H	108.3	117
H–P–H	105.3	92

Considerable difficulties arise in obtaining pure phosphinic acid[45]; among numerous methods of preparation described in reviews[26–28] only a few, giving good yields of the pure acid, are of interest. Hitherto a method of practical value has involved treating white phosphorus with a boiling lime slurry[46] and other alkali[47]. Pure phosphinic acid can be obtained by oxidising phosphine in an aqueous suspension of iodine[48]: phosphine obtained from calcium phosphide and dilute hydrochloric acid is passed into the stirred suspension of iodine in a flask until the solution becomes colourless; hydrogen iodide and water are removed under reduced pressure (40 mmHg), after which pure phosphinic acid remains. The safest laboratory method for obtaining the acid involves passing an aqueous solution of an alkali-metal phosphinate through an ion-exchange resin, then concentrating the acid on a water-bath, and drying over phosphorus pentoxide in a high vacuum[49].

It was suggested[50] that chemically pure phosphinic acid could be isolated in crystalline form by continous extraction with diethyl ether. Quite recently three methods have been described for obtaining the crystalline acid from accessible inorganic salts[36]. Double decomposition between barium phosphinate and sulphuric acid followed by removal of water by low-temperature high-vacuum sublimation (lyophilic drying) gives a product which retains its physicochemical characteristics when kept in hermetically sealed vessels for a long time. However, prolonged storage of the contaminated liquid acid is not possible even when all precautionary measures are taken (cold, hermetic sealing, storage in an atmosphere of an inert gas).[51]

Decomposition of impure phosphinic acid by disproportionation can take place in the absence of air:

$$2H_3PO_2 \rightarrow H_3PO_4 + PH_3 .$$

In the presence of water hydrogen is evolved:

$$H_3PO_2 + H_2O \rightarrow H_3PO_3 + H_2\uparrow .$$

At elevated temperatures decomposition is more fundamental in character, with the formation of red or yellow phosphorus[45]. The instability of phosphinic acid in air is attributed to its strong reducing properties, which are used both in organic synthesis, e.g. for the reduction of acids[52], and in industry—to obtain chemical protective coatings (nickel and chromium plating) of better quality than electroplating[53,54].

Pure phosphinic acid comprises white crystals in the form of lobes, melting at 26.5 °C. It is a strong monobasic acid (pK 1.1).[55] Its monobasicity indicates that phosphorus has coordination number 4 in this structure. Phosphinates of alkali and alkaline-earth metals are obtained both by trivial processes (double decomposition)[45,56] and by specific methods involving change in the coordination of the phosphorus atoms[57–60].

Phosphinates are produced industrially by the action of hydroxides of alkali and alkaline-earth metals on white phosphorus: e.g.

$$8P + 3Ca(OH)_2 + 6H_2O \rightarrow 3Ca(H_2PO_2)_2 + 2PH_3$$
$$Ca(H_2PO_2)_2 + Na_2CO_3 \rightarrow 2NaH_2PO_2 + CaCO_3 .$$

Phosphinates of rare-earth metals $M_n(H_2PO_2)_3$ have been prepared in which M = Sc, Y, La, as well as double phosphinates $CeM'(H_2PO_2)_6$ with M' = Er, Tm, Yb, Lu.[61–65] Their physicochemical characteristics have been studied[66].

Table 4. Organic salts of phosphinic acid.

Compound	M.p., °C	Ref.
$C_6H_5\overset{+}{N}H_3\bar{O}P(O)H_2$ *	115	3
4-CH_2CONH–C_6H_4–$\overset{+}{N}H_3\bar{O}P(O)H_2$ *	178	2
C_6H_5–NH–$\overset{+}{N}H_3\bar{O}P(O)H_2$ *	—	3
$CH_3\overset{+}{N}H_3\bar{O}P(O)H_2$	—	4
$C_2H_5\overset{+}{N}H_3\bar{O}P(O)H_2$	—	4
$(CH_3)_2\overset{+}{N}H_2\bar{O}P(O)H_2$	—	4
$(C_2H_5)_3\overset{+}{N}H\bar{O}P(O)H_2$	—	68

* Dissolves readily in water.

2. Structure, Physicochemical Properties, and Methods of Preparation of Organic Derivatives of Phosphinic Acid

Organic derivatives of phosphinic acid were first obtained in 1948[3]. Very little is known about the organic salts[3,4,67,68] (Table 4), only two of which have been isolated in pure form

and characterised[3]. Dialkylmetal salts of general formula $(CH_3)_2MPH_2O_2$ (where M = Al, Ga, In) have been reported comparatively recently[69].

Many attempts to obtain phosphinic esters have proved unsuccessful[70-72]. In 1960 Kabachnik et al.[2] were the first to accomplish the direct esterification of phosphinic acid with diazoalkanes to obtain monoalkyl phosphinates (Table 5):

$$RCHN_2 + HOP(O)H_2 \rightarrow ROP(O)H_2 + N_2.$$

This reaction confirms the suggestion that the acid is monobasic. Later several alkyl phosphinates were prepared from phosphinic acid and orthocarbonyl compounds (acetals)[73]. This is less important than the previous method for preparative purposes, since it yields a difficultly separable mixture of compounds formed by interaction between the esters and carbonyl by products:

$$(RO)_2CR'R'' + HOP(O)H_2 \rightarrow ROP(O)H_2 + O{=}CR'R'' + ROH$$
$$ROP(O)H_2 + O{=}CR'R'' \rightarrow ROP(O)\underset{H}{\underset{|}{CR'R''}}\underset{OH}{\underset{|}{}}$$

Table 5. Esters of phosphinic acid*.

Compound	Yield, %	B.p., °C (mmHg)	n_D^{20}	d_4^{20}	Ref.
$CH_3OP(O)H_2$	—	25—25.5 (2.5)	1.4275	1.2177	2
$CH_3OP(O)H_2$	47	25—25.5 (2.5)	—	—	73
$C_2H_5OP(O)H_2$	—	31—32 (2)	1.4250	1.1120	2
$C_2H_5OP(O)H_2$	39	33—35 (1.3)	—	—	73
$C_2H_5OP(O)H_2$	45	30—32 (1)	1.3945	—	89
$C_3H_7OP(O)H_2$	77	90—100 (10)**	1.4222	1.0447	77
$C_3H_7OP(O)H_2$	70	29—30 (0.07)	1.4280	—	89
$C_4H_9OP(O)H_2$	82	120—125 (10)**	1.4288	1.0045	77
$C_4H_9OP(O)H_2$	84	52—60 (1.5)	—	—	78
iso-$C_4H_9OP(O)H_2$	91	110—115 (10)**	1.4275	0.9760	77
iso-$C_4H_9OP(O)H_2$	71	56—63 (3)	—	—	78
$C_5H_{11}OP(O)H_2$	92	70—80 (0.2)**	1.4332	1.0126	77
$C_6H_{13}OP(O)H_2$	85	—	1.4530	—	75
$C_6H_{13}OP(O)H_2$	83	105—110 (0.2)**	1.4355	0.9614	77
$C_7H_{15}OP(O)H_2$	93	100—110 (0.004)**	1.4390	0.9619	77
$C_8H_{17}OP(O)H_2$	85	120—130 (0.006)**	1.4430	0.9709	77
$C_9H_{19}OP(O)H_2$	89	160—165 (0.006)**	1.4460	1.9524	77
$C_{10}H_{21}OP(O)H_2$	78	130—140 (0.002)**	1.4465	—	77
$C_{12}H_{25}OP(O)H_2$	87	63—64 (m.p.)	—	—	5
$HOCH_2C(CH_2)_2CH_2OP(O)H_2$	97	—	1.4620	—	5
$H_2(O)PO(CH_2)_6OP(O)H_2$	95	—	1.4730	—	5
$CH_3CH(OH)(CH_2)_2OP(O)H_2$	98	—	1.4590	—	5
$HOCH_2CH_2OP(O)H_2$	84	—	1.4505	1.4259	77
$C_6H_5CH_2OP(O)H_2$	87	160—170 (0.05)**	1.5415	1.1496	77
$(CH_3)_3SiOP(O)H_2$	61.5	65—67 (10)	1.4219	1.0024	90
$(C_2H_5)_3SiOP(O)H_2$	56	62—64 (1)	1.4421	0.9720	90
$H_2(O)PO(CH_2)_{10}OP(O)H_2$	87	76—78 (m.p.)	—	—	75
$-CH_2-\underset{\displaystyle O-P(O)H_2}{\underset{|}{CH}}-O-P(O)H_2$	—	170—187 (m.p.)	—	—	75
$C_4H_9OP(S)H_2$	65	59—64 (1.5)	—	—	78
iso-$C_4H_9OP(S)H_2$	47	65—72 (2.5)	—	—	78

* Table 5 omits several phosphinic esters for which constants have not been given—6-hydroxyhexyl phosphinate[87], poly(allyl phosphinate)[87], and cellulose phosphinate[79].

** Temperature of bath.

Nifant'ev et al. proposed a simpler and more convenient method for obtaining alkyl phosphinates[74-76]:

$$HOP(O)H_2 + ROH \xrightarrow{-H_2O} ROP(O)H_2 .$$

The reaction is accomplished by azeotropic distillation of water using a Dean and Stark trap. It can be conducted either in the absence or in the presence of a catalyst such as zinc chloride, aluminium chloride, sodium acetate, etc.; excess of one of the reactants is used to accelerate the reaction. Several lower alkyl phosphinates are very unstable when purified by vacuum distillation. If the products are contaminated with the alcohol or phosphinic acid, however, they can be stored and are convenient for use. Many alkyl phosphinates have been obtained by this method[77] (Table 5); the products were freed from unchanged acid and excess of the alcohol by vacuum treatment in molecular distillation apparatus. However, after many redistillations they could not be isolated in analytically pure form.

An interesting process for obtaining phosphinic esters consists[78] in the hydrolysis of dialkoxyphosphines. Fundamentally novel alkyl phosphinates—alkyl phosphinothionates $ROPH_2S$ (Table 5)—have been obtained by essentially the same method, by oxidising dialkoxyphosphines with hydrogen sulphide:

$$(RO)_2PH \xrightarrow{+H_2S} ROP(S)H_2 .$$

Not only monohydric alcohols but also glycols react readily[5] with phosphinic acid, to form hydroxyalkyl phosphinates and alkylene bisphosphinates:

$$HOROH + HOP(O)H_2 \begin{cases} \xrightarrow{1:1} HOROP(O)H_2 \\ \xrightarrow{1:2} H_2(O)POROP(O)H_2 \end{cases} .$$

Alkylene bisphosphinates, like esters of phosphinic acid with monohydric alcohols, are unstable in pure form. In contrast, hydroxyalkyl phosphinates are stable on storage, probably as a consequence of their specific structure[5].

Phosphinic esters are formed also by the phosphorylation of certain high-molecular polyhydroxy-compounds, peptides, and monosaccharides[79-84]. The action of phosphinic acid on cellulose yields phosphinates[80] containing up to 14% of phosphorus:

$$Cell\text{-}OH + H_3PO_2 \xrightarrow{-H_2O} Cell\text{-}O\text{-}P(O)H_2 .$$

The degree of esterification of the cellulose increased steadily with rise in temperature from 80 to 120 °C. With further rise in temperature (under otherwise similar conditions), however, the phosphorus content of the reaction product diminished. This was attributed[80] to partial decomposition of phosphinic acid above 120 °C, to give phosphine, removed from the sphere of reaction[85], and phosphonic acid, which is also an esterifying reagent[86-88]:

$$3H_3PO_2 \xrightarrow{>120°} PH_3 + 2H_3PO_3 .$$

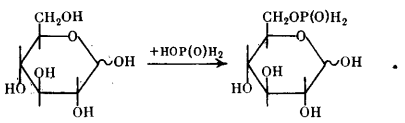
The phosphorylation of cellulose with ammonium phosphinate[79,80] showed the latter to be a more active esterifying agent than in phosphinic acid. However, the reaction products contain not only chemically bound phosphorus but also a greater or smaller quantity of nitrogen.

Research on the phosphorylation of polyols was continued with the acylation of polyvinyl alcohol by phosphinic acid[82,83]:

$$-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}- + H_3PO_2 \rightarrow -CH_2-\underset{\displaystyle O-P(O)H_2}{\underset{|}{CH}}- .$$

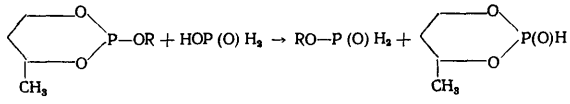
The resulting high-molecular polyphosphinate was quite stable in comparison with the unstable lower alkyl phosphinates, which break down into the initial reactants.

Study of the acylation of phosphinic acid of polyallyl alcohol and its low-molecular analogues (isobutyl alcohol and hexamethylene glycol)[84] has received a second-order reaction. Monosaccharides—glucose[76] and xylitol[81]—also react with phosphinic acid:



With xylitol the process is complicated: the formation phosphorylation products is accompanied by partial dehydration of the xylitol.

The above method of preparing phosphinic esters, though simple and convenient, is unsuitable for obtaining the simplest alkyl phosphinates. Great practical interest attaches to the dealkylation of cyclic full esters of phosphorus acid with phosphinic acid, by a modification of the Arbuzov reaction[89]:



This method gives a somewhat higher yield of ethyl phosphinate than does the process suggested by Fitch[73] (Table 5). The lower phosphinates obtained are very unstable, and can be stored only in an inert gas at temperatures below 0 °C: in air they ignite. Paper chromatography and ^{31}P n.m.r.spectra have established that the products contain the corresponding dialkyl phosphites, whose quantity increases during storage. Formation of the latter is due to disproportionation of the alkyl phosphinates, which gives also phosphine:

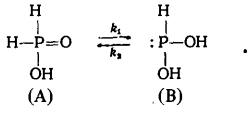
$$2RO{-}P(O)H_2 \rightarrow PH_3 + (RO)_2P(O)H_2 .$$

Organosilicon esters of phosphinic acid—trialkylsilyl phosphinates—have recently been obtained[90] by the alcoholysis of bistrialkylsilyl phosphonites:

$$(R_3SiO)_2PH + C_2H_5OH \rightarrow R_3SiOP(O)H_2 + R_3SiOC_2H_5 .$$

3. Tautomerism of Phosphinates

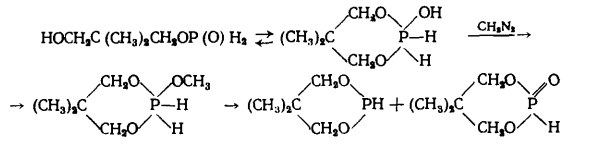
Although all the inorganic and organic phosphinates mentioned in the preceding subsections indicate that phosphinic acid is monobasic, many investigations show the occurrence of tautomerism:



Kinetic examination of the oxidation of phosphinic acid showed[91-100] that the active form is present in extraordinarily small quantities, only one-billionth (10^{-12}) part of $(HO)_2PH$ in $HOPH_2O$. As van Wazer[26] maintains, the rate-determining stage in the oxidation of phosphinic acid in acid medium by various reagents[101-105] in moderate or considerable concentrations is probably conversion of the "passive" form (A) into the "active" form (B). The rate is essentially unaffected by the nature or the concentration of the oxidant, but increases with increase in acidity. Other kinetic investigations—study of hydrogen[106,107] and oxygen[108] isotope exchange and also of the reaction mechanism[109]—confirm the tautomerism of phosphinic acid. A monograph[110] also regards the acid as tautomeric: the negative results of attempts to detect the "active" form $(HO)_2PH$ in certain spectroscopic investigations[111] are attributed to its low content in the equilibrium mixture.

The tautomerism of phosphinic acid and several other acids of phosphorus[112-114] provides an explanation of their nucleophilic reactions. The rate of conversion of "passive" into "active" form is small, so that it was difficult to count on obtaining from ordinary phosphinic acid (with the object of a final proof of tautomerism) esters of its "active" form, i.e. dialkoxyphosphines. Attempts to obtain dichlorophosphine $PHCl_2$—the initial acid chloride for the synthesis of dialkoxyphosphines—were also unsuccessful[115].

In 1969, however, appeared the first paper[5] on the preparation of a member of this class of compounds—2,2-dimethyltrimethylene phosphonite—from the phosphinic monester—3-hydroxy-2,2-dimethylpropyl phosphinate:



This was followed by the publication of several fundamental researches on this problem[6,8,9,78,116-119]. Lutsenko et al.[6] suggest obtaining dialkoxyphosphines by the reduction of dialkyl phosphorochloridites with di- and tri-alkylstannanes:

$$(RO)_2PCl + R_3SnH \rightarrow (RO)_2PH + R_3SnCl .$$

Bistrialkylsilyl phosphonites have been prepared[7,120] from ammonium phosphinate and trialkylsilylamines:

$$NH_4OP(O)H_2 + 2R_3SiNR_2 \rightarrow (R_3SiO)_2PH + NH_3 + 2HNR_2$$
$$NH_4OP(O)H_2 + (R_3Si)_2NH \rightarrow (R_3SiO)_2PH + 2NH_3 .$$

Reaction with trialkylchlorosilanes in the presence of a secondary or tertiary amine B gives the same products[121]:

$$NH_4OP(O)H_2 + 2R_3SiCl + : B \rightarrow (R_3SiO)_2PH + NH_4Cl + : B \cdot HCl .$$

The yield reaches 35–45%. High yields (80–90%) are obtained by another method[121], based on the reaction of phosphinic acid with *NN*-dialkyltrialkylsilylamines:

$$HOP(O)H_2 + 2R_3SiNR_2 \rightarrow (R_3SiO)_2PH + 2HNR_2 .$$

The formation of dialkoxyphosphines, together with the kinetic results, enables us to postulate the existence of an "active" form of phosphinic acid as the principal motive force of the nuclephilic reactions, which will be discussed in Section III.

The tautomerism of organic salts of phosphinic acid has not been studied, although its presence is suggested by studies of chemical properties.

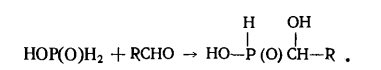
III. CHEMICAL PROPERTIES

Study of the reactivity of phosphinic acid and its inorganic salts had already begun by the end of the past century. The preparation of organic phosphinates (esters and organic salts) during recent years has given a fresh impetus to the intensive study of various reactions involving phosphinates. The present Section is devoted to a comparative analysis of the reactivity of phosphinic acid, its salts, and its esters.

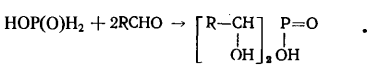
1. Reactions with Aldehydes and Ketones

Most reactions of phosphinates with aldehydes (ketones)* lead to the formation of phosphinic acids. The addition of phosphinic acid to aromatic, aliphatic, and unsaturated aldehydes (ketones) was first accomplished during 1888–1904 by Ville and by Marie[1,122,123,24-26]. Since then the reactions have aroused theoretical interest[109,124-126], and the possibility of practical utilisation of the adducts has emerged[127-131].

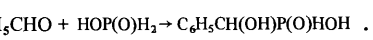
Depending on the molar proportions of phosphinic acid and aldehyde or ketone two series of derivatives may be formed[15, 124, 132–147]. Equivalent proportions give 1-hydroxyalky (or aryl) phosphinic acids:



When excess of the carbonyl compound is present, a second molecule of the latter is added:

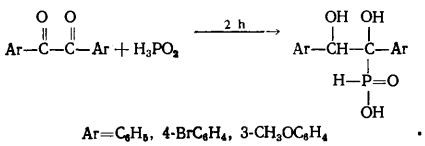


Reaction between phosphinic acid and aldehydes or ketones takes place with some difficulty, requiring heating for many hours. With benzaldehyde, for example, reaction occurs at 60–108 °C:[109]



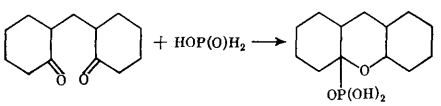
Since the equilibrium is shifted towards the initial reactants in such reactions[47], and also because of the tendency of phosphinic acid to undergo disproportionation on prolonged heating, the yields are low.

Phosphinic acid reacts considerably more rapidly with 1,2-diketones, and as a consequence the yields of condensation products—1,2-diaryl-1,2-dihydroxyethylphosphinic acids—reach 70–80%:[140]

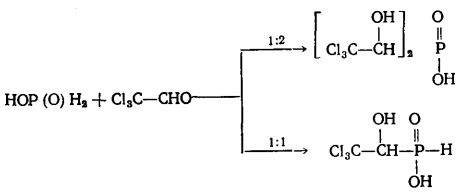


Ar=C_6H_5, 4-BrC_6H_4, 3-$CH_3OC_6H_4$

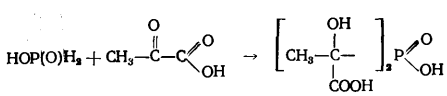
The readier addition of ketones in this case is due to the presence of two neighbouring electron-accepting (carbonyl) groups, which promote the nucleophilic addition of reactants containing phosphorus–hydrogen bonds. The action of phosphinic acid on the 1,5-diketone, methylene-2,2′-bis-cyclohexanone, is unusual[147] in that heating in acetic acid gives a 50% yield of a product regarded as a phosphonate:



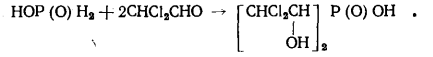
Compounds containing a polarised group react considerably more readily, i.e. at lower temperatures and with high yields. The action of anhydrous phosphinic acid on chloral in an inert solvent gives a mixture of di- and mono-substituted phosphinic acids in yields of 80% and 65% respectively[137,138]:



Pyruvic acid reacts after 2 h, to give a 46% yield of di-(1-carboxy-1-hydroxyethyl)phosphinic acid[141]:



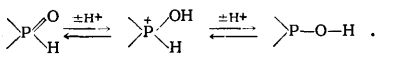
A substituted phosphinic acid is obtained also with dichloroacetaldehyde, but a period of 18 h is required and the yield is much lower (21%):[136]



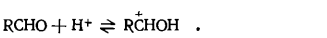
Thus reaction is hindered with less strongly electrophilic reagents (dichloroacetaldehyde), in contrast to chloral: prolonged heating is necessary, and a lower yield of the desired product is obtained.

The reaction mechanism of the condensations has been studied with the action of phosphinic acid on formaldehyde and on benzaldehyde as examples[109]. These reactions are catalysed by hydrochloric acid, but their rate is independent of the hydrogen-ion concentration. They are first order with respect to the carbonyl component and to phosphinic acid in its undissociated form.

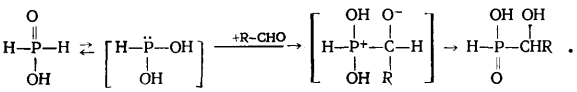
According to Kirby[110] tautomeric conversion in compounds containing a phosphinylidene group under conditions of acid catalysis corresponds to a two-stage process:



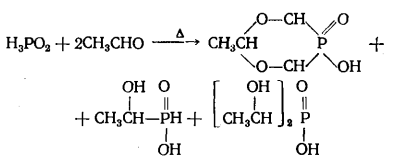
Such catalysts can apparently activate not only the phosphorus component but also the carbonyl reagent:



In view of recent studies on the mechanism of tautomeric transition of certain phosphinates into the active state with a lone pair of electrons on the phosphorus atom, and all the above considerations in relation to this problem, the addition of phosphinic acid to aldehydes can be represented by the scheme



In the cases of acetaldehyde and paraldehyde the usual adducts with phosphinic acid are accompanied by aldol condensation products, and the presence of at least two stereoisomers of the six-membered rings is postulated[125]:

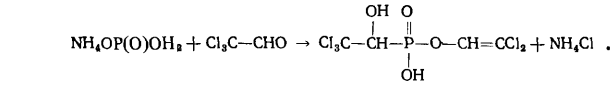


The reactivity of salts of phosphinic acid towards aldehydes has been little studied. Replacement of the acid by its potassium salt on reaction with chloral in hydrochloric acid enables the expected condensation product to be obtained[139], but the process is very slow, requiring several weeks, and gives a low yield (29%) apparently because of mutual insolubility:

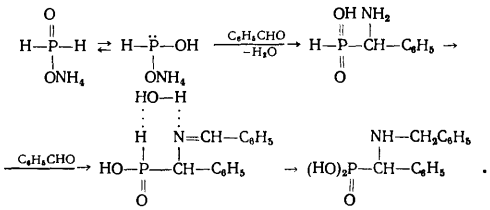
Reaction between salts of phosphinic acid and carbonyl compounds can be conducted successfully only at higher temperatures than those for the acid itself, and for a prolonged time, though in many cases the yield is high. This supports the view that the salts are more stable than phosphinic acid. Thus good yield (respectively 71% and 93%) are

obtained in the action of sodium phosphinate on 1,2,5,6-tetrahydrobenzaldehyde[135] and on paraform[148].

Unexpected results were obtained by Taube et al.[4,149], who used the little studied ammonium phosphinate as phosphorylating agent. Thus condensation of the latter with chloral gave not the expected substituted ammonium phosphinate, whatever the proportions of the reactants, but 2,2-dichlorovinyl hydrogen 2,2,2-trichloro-1-hydroxyethylphosphonate[149]:

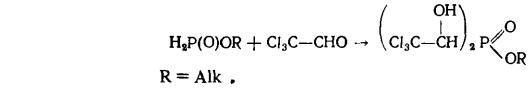


α-Benzylaminobenzylphosphonic acid was obtained by the reaction between ammonium phosphinate and benzaldehyde[4]:



The formation in the latter reaction of a phosphonic acid instead of the expected α-aminobenzylphosphinic acid is attributed to an intramolecular redox process.

The use of phosphinic esters in such reactions is of undoubted theoretical interest. It will permit comparison of the effect of replacing the acidic hydrogen by an alkyl radical: increasing the acidity of the phosphorus–hydrogen bond should favour nucleophilic addition. Indeed, the reaction of phosphinic esters with several carbonyl compounds (e.g. chloral) is exothermic and considerably more rapid than in the case of phosphinic acid[150]:



R = Alk .

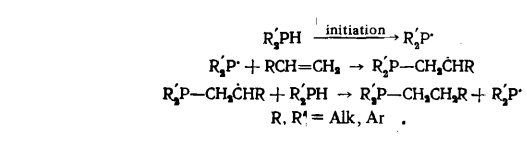
Thus the results reported in this subsection suggest the sequence of phosphinates

$$ROP(O)H_2 > HOP(O)H_2 > MOP(O)H_2,$$
R = Alk; M = Metal or NH_4

of diminishing reactivity in nucleophilic addition (to aldehydes and ketones).

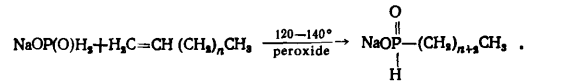
2. Reactions with Unsaturated Compounds

Free-radical addition to alkenes is a general reaction of compounds containing a phosphorus–hydrogen bond (phosphines, phosphonates, and phosphinates):

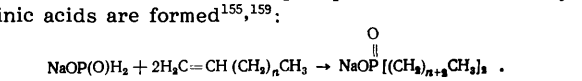


The reactions are initiated by ultraviolet irradiation or the usual sources of free radicals (organic peroxides), and take place by a radical–chain mechanism contrary to Markovnikov's rule.

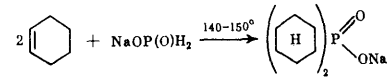
The reactions of inorganic phosphinates with unsaturated compounds usually give high yields[152–159]. For example, sodium phosphinate when heated to 120 °C with oct-1-ene in methanol in the presence of a peroxide gives a 100% yield of the salt of octylphosphonous acid[156]. Other alkylphosphonous acids have been obtained similarly from compounds having a terminal double bond:



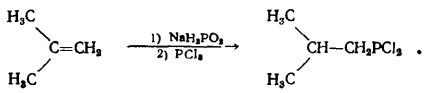
When the molar ratio of alkene to phosphinate is 2: 1, dialkylphosphinic acids are formed[155,159]:



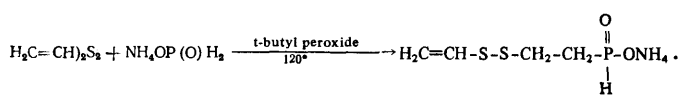
Sodium phosphinate reacts with allyl alcohol also in the presence of a peroxide[160,161]. Isolation of the reaction products presents considerable difficulties, probably owing to the occurrence of secondary processes. For the same reason individual addition products of the phosphinate to allyl cyanide and allyl acetate could not be isolated[162]. The resulting mixture was identified as the chlorides of 3-acetoxypropylphosphinic acids. The action of cyclohexene on sodium phosphinate in the presence of t-butyl peroxide gives a 77.5% yield of dicyclohexylphosphinic acid[83,163]:



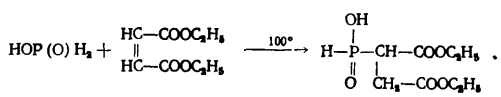
These reactions cna be used to obtain various alkyldichlorophosphines. A convenient procedure consists in initial preparation from an alkene and sodium phosphinate of the monosodium alkyl phosphinate, which is then treated with phosphorus trichloride or thionyl chloride[152]:



The above account shows clearly that all investigators have chosen sodium phosphinate to study the reactivity of salts of phosphinic acid, probably because of its better solubility in various solvents on heating. Only a British Patent[157] chose ammonium phosphinate, which on reaction with divinyl disulphide gave ammonium 3,4-dithiahex-5-enylphosphinate:

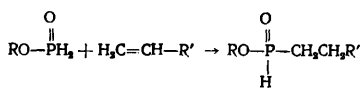


Phosphinic acid reacts with unsaturated compounds to from analogous products[164–167], but the yields are considerably lower, varying in the range 9–40%.[166,167] Reaction occurs with ethyl maleate in the absence of a catalyst to give a 65% yield[168], possibly by an ionic mechanism:



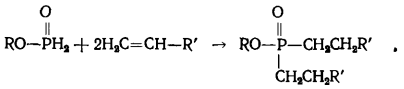
Attempts to catalyse the process with alkali-metal alkoxides or triethylamine did not increase the yield.

Alkyl phosphinates also add to alkenes in the presence of peroxides[76,169]:



R = Alk; R′ = Alk .

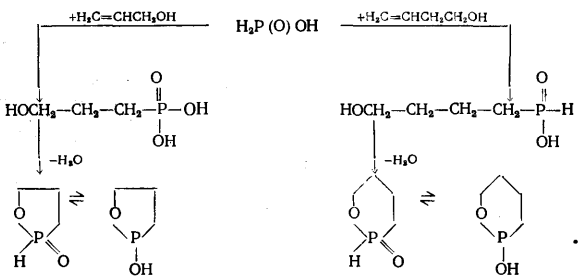
Cyclohexene reacts with greater difficulty. Phosphinic esters are formed with excess of the alkenes at a higher temperature:



The reactions of methyl phosphinate with acrylonitrile and with methyl acrylate follow a similar course; in the latter case the main product is accompanied by a dimethyl phosphonate[170]:

$$CH_3OP(O)H_2 + H_2C{=}CH\text{-}C(O)OCH_3 \rightarrow$$
$$CH_3OP(O)HCH_2CH_2C(O)OCH_3 + (CH_3O)_2P(O)CH_2CH_2C(O)OCH_3 .$$

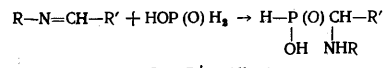
The synthetic possibilities of the reactions of phosphinic acid and its derivatives with unsaturated compounds are confirmed by a publication[161] on the action of allyl alcohols on phosphinates. Aliphatic phosphinic acids containing a hydroxy-group in position 3 or 4 of the alkyl radical, obtained from phosphinates and aliphatic alcohols having a terminal ethylenic bond, undergo cyclisation when heated to 100–150 °C, with formation of 2-oxaphospholan-1-ones and 2-oxaphosphan-1-ones (γ- and δ-phostones):



Owing to the inadequacy of published results it is fairly difficult to compare the reactivities of phosphinates in these reactions. There is no doubt, however, that the use of phosphinate salts instead of the acid itself in reactions with unsaturated compounds is entirely justified. The high yields obtainable are attributable to the greater stability of the salts under the severe conditions of addition at double bonds.

3. Reactions with Azomethines

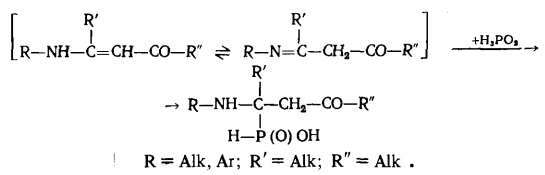
The addition to azomethines of reactants containing an active phosphorus–hydrogen bond provides a method for obtaining aminoalkyl (or aryl)phosphinic acids, interest in which is increasing in view of the physiological activity possessed by compounds of this type[171–176] and their detection in naturally occurring products of biological origin[177–180]. Substituted acids of this type were synthesised from phosphinic acid by Schmidt[3,181,182]. These reactions give good yields under mild conditions, with azomethines obtained from acetone reacting more readily:



R = Alk, Ar, Het; R′ = Alk, Ar .

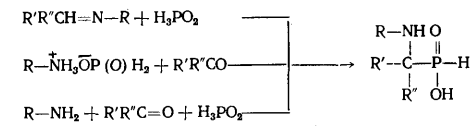
Various Schiff bases obtained from primary amines (aromatic, aliphatic, heterocyclic) and carbonyl compounds (aliphatic and aromatic aldehydes and ketones) have been used[3,182–190].

Certain enamines of β-dicarbonyl compounds react[189]:

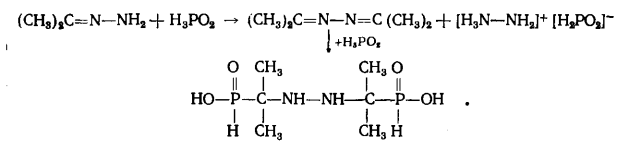


R = Alk, Ar; R′ = Alk; R″ = Alk .

Most of the investigators note[3,67,191] that 1-aminoalkyl(aryl) phosphinic acids can be obtained not only from azomethines but also by other methods, including placing all three components—amine, aldehyde (ketone), and phosphinic acid—together in the reaction vessel, but data on yields are contradictory[67,186]. A third variant—bringing a phosphinate, the amine, and the aldehyde into reaction—has been tested on several examples[3,4,185], but diminished yields of aminophosphinic acids are obtained[185]. Thus *N*-aryl(alkyl)-1-aminoaryl(alkyl)phosphinic acids can be synthesised in three ways:

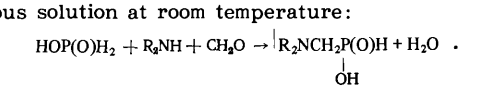


If an unsubstituted hydrazone is used as azomethine, the course of the process is anomalous[67]. Reaction between an equivalent quantity of acetone hydrazone and phosphinic acid gives a quantitative yield of acetone azine and hydrazinium phosphinate:



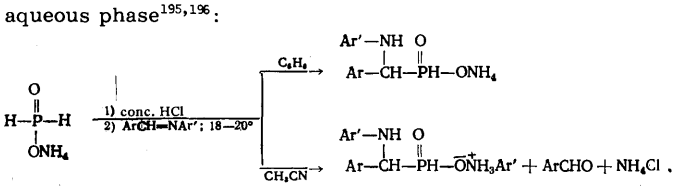
Azines can be obtained also from the hydrazones of benzaldehyde, acetophenone, and butan-2-one. Difunctional amino-acids are formed by the action of phosphinic acid on azines: a diphosphinic acid is obtained in good yield from acetone azine and two equivalents of phosphinic acid.

Secondary amines are more reactive than primary amines[192,193]. Dialkylaminomethylphosphinic acids are formed exothermally from secondary amines, formaldehyde, and phosphinic acid in aqueous solution at room temperature:

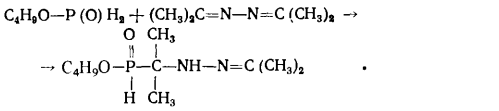


This process, which resembles formally the Mannich reaction, can be more far reaching: with excess of amine and formaldehyde bis(dialkylaminoalkyl)phosphinic acids are formed. With primary amines, however, only phosphinic acids are obtained.

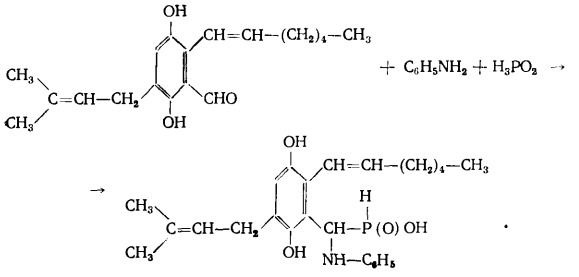
Quite recently phosphinic acid has been replaced by its salts and esters in such reactions. A series of *N*-substituted 1-aminoaralkylphosphinic acids have been obtained from ammonium phosphinate[194]. The latter reacts with azomethines in the presence of an equivalent quantity of hydrochloric acid in benzene and acetonitrile to form arylammonium 1-aryl-1-arylaminomethylphosphinates[195,196]; when benzene is used, ammonium salts of the same acids are formed in the aqueous phase[195,196]:



Treatment of alkyl phosphinates with azines[197,198] yields 1-aminoalkylphosphinic esters. The reaction studied in greatest detail is that between butyl phosphinate and acetone azine, in which heat is evolved and a 1:1 adduct is formed:

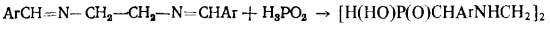


Reactions between phosphinates and azomethines (or their components) have already found practical application. Interest undoubtedly attaches to the selective modification of antibiotics by phosphorus-containing agents with the aim not only of practical application of novel semi-synthetic preparations (the possibility of obtaining forms suitable for injection) but also of their theoretical study, of the effect of introducing phosphorus grouping on the biological properties of the resulting organophosphorus antibiotics. Thus a water-soluble form of the antibacterial antibiotic aspergin has been obtained as 1-*N*-phenylaminoasperginphosphinic acid[15]:



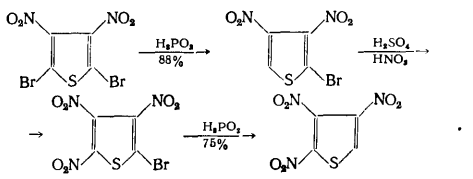
A medical form for parenteral introduction can be obtained by converting the hydrogen form into the sodium salt.

A series of phenothiazinylaminoalkylphosphinic acids have been obtained as potential medicinals[191]. Interesting complexones have been prepared by means of Schiff bases obtainable from ethylenediamine[188]:

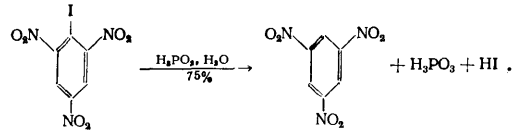


4. Other Reactions of Phosphinates

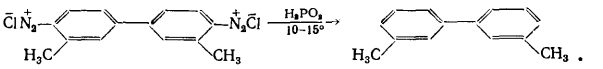
As already noted, the practical application of phosphinates is largely due to their reducing properties[10-12], which are responsible for the use of phosphinic acid in organic synthesis. 2,3,4-Trinitrothiophen can be obtained by means of this acid[199]:



The latter effects reductive elimination also in the formation of trinitrobenzene from picryl iodide[200]:

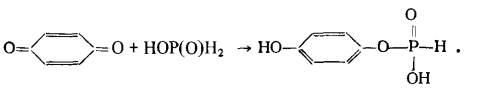


The acid was suggested also for reductive deamination by replacement of a diazonium group by hydrogen[201]:

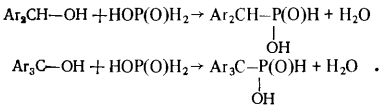


A sixfold excess of 30% phosphinic acid was used to reduce bisdiazotised o-tolidine[202]. The acid has been used also to obtain 2,4,6-tribromobenzoic from *m*-aminobenzoic acid[203].

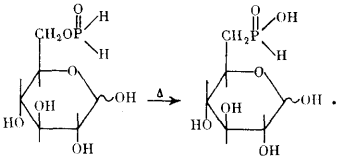
Several studies have been made of the mechanism of the reduction of organic compounds by phosphinates[204-208]. Reduction products—quinhydrone and quinol—are formed by the action of 50% phosphinic acid on *p*-benzoquinone. However, when this reaction is conducted in anhydrous medium or in the presence of a small quantity of water, an addition product—*p*-hydroxyphenyl hydrogen phosphonate—is also formed (in yields up to 46%):[209]



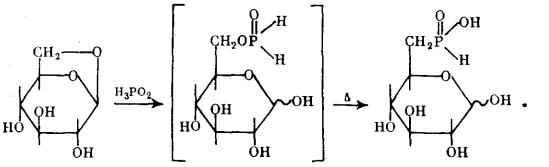
An interesting recent method for obtaining alkylphosphinic acids is the isomerisation of alkyl phosphinates. As early as 1910 Fosse[210], and later other workers[211,212], obtained alkylphosphinic acids by the action of secondary and tertiary arylcarbinols on phosphinic acid in the absence of a catalyst:



However, the mechanism of these reactions was not studied. Nifant'ev, who has detected isomerisation, considers[213] that initial esterification of phosphinic acid is followed by isomerisation of the resulting ester into the substituted phosphinic acid:



When sugars were treated with phosphinic acid, the initially formed phosphinic esters were isolated, and their structure was proved by oxidation to the corresponding phosphates or hydrolysis to the original products. The structure of glucose 6-phosphinate was proved more rigorously by the methods of carbohydrate chemistry. The same compound was obtained from phosphinic acid and levoglycosan[76,214]:



Heating levoglycosan with a mixture of phosphinic acid and sodium phosphinate gives sodium 6-glucophosphinate, whose structure has been confirmed by cross-synthesis[215]. The possibility of such intramolecular rearrangement was further postulated by Plets[216] when investigating the reactions of

sodium phosphinate with methyl iodide and with ethyl chloroacetate:

$$NaOP(O)H_2 + H_2 + CH_3I \xrightarrow{-NaI} CH_3OP(O)H_2 \rightarrow HO-\underset{\displaystyle CH_3}{\underset{|}{P(O)H}}$$

$$NaOP(O)H_2 + ClCH_2COOC_2H_5 \xrightarrow{-NaCl} \rightarrow H_2P(O)-OCH_2COOC_2H_5 \rightarrow \underset{\displaystyle OH}{\underset{|}{HP(O)}}CH_2COOC_2H_5 .$$

Phosphinate salts react vigorously with acetic anhydride. In concentrated media violent reaction occurs with formation of disproportionation products. In extremely dilute solutions (0.2M) high yields of potassium acetylphosphinate have been obtained[217,218]:

$$KOP(O)H_2 + (CH_3CO)_2O \rightarrow KO-\underset{\displaystyle H_3C-\underset{\displaystyle O}{\underset{\|}{C}}}{\underset{|}{P(O)}}H + CH_3COOH .$$

This reaction has been accomplished with various phosphinates—those of sodium, lithium, nickel, barium, and zinc—and other anhydrides of carboxylic acids react similarly. The process probably involves a Michaelis–Arbuzov reaction:

$$H-\underset{\displaystyle OH}{\underset{|}{P}}-OK + (R-\underset{\displaystyle O}{\underset{\|}{C}}-)_2O \rightarrow \left[\left(R-\underset{\displaystyle O}{\underset{\|}{C}}-\overset{\displaystyle OK}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{P^+}}}}-H\right)R-COO^-\right] \rightarrow R-\underset{\displaystyle O}{\underset{\|}{C}}-\overset{\displaystyle OK}{\overset{|}{\underset{\displaystyle O}{\underset{\|}{P}}}}-H + RCOOH .$$

The aminomethylation of alkyl phosphinates

$$ROP(O)H_2 + (C_2H_5)_2NCH_2X \begin{cases} \rightarrow [(C_2H_5)_2NCH_2]_2P(O)OR + HX \\ \rightarrow (C_2H_5)_2NCH_2P(O)(OR)_2 + HX \end{cases}$$

is of theoretical interest[77]. In the first stage the phosphorus in the phosphinates is probably electrophilic with respect to the amines[76]. The reaction was conducted at 130–160 °C, and nearly always gave a mixture of products containing aminoalkyl-phosphinic and -phosphonic esters and the corresponding amides.

The Todd–Atherton reaction has been successfully extended to phosphinates[68,76,169,219]: alkyl phosphinates react readily with alcohols and tetrachloromethane in the presence of triethylamine. Depending on the proportions of the reactants either phosphonates or phosphates are formed[76,169]:

$$ROP(O)H_2 + CCl_4 + ROH + N(C_2H_5)_3 \begin{cases} \xrightarrow{1:1:1:1} (RO)_2P(O)H \\ \xrightarrow{1:2:2:2} (RO)_3PO \end{cases} .$$

Phosphinates of glycols are converted into cyclic phosphonates:

$$HO-R-O-P(O)H_2 + CCl_4 + N(C_2H_5)_3 \rightarrow R\begin{cases} O \\ O \end{cases}P(O)H .$$

If alcohols are replaced by secondary amines, phosphorodiamidates are formed:

$$ROP(O)H_2 + 4HNR'_2 + 2CCl_4 \rightarrow ROP(O)(NR'_2)_2 .$$

The Todd–Atherton reaction has been accomplished also with phosphinic acid[68,219]: thus with tetrachloromethane, triethylamine, and water the acid is converted into phosphorous acid. With tetrachloromethane and aniline the dianilide of phosphoric acid is formed. Aliphatic secondary amines behave similarly. Phosphinic acid on treatment with alcohols, tetrachloromethane, and triethylamine is converted into dialkyl phosphates.

Thus the great activity of phosphinates has permitted their use in many heterolytic and homolytic reactions. Although the range of reactions studied has hitherto been narrowly restricted, the above results demonstrate the wide opportunities open to the use of phosphinates for the preparation of diverse organophosphorus compounds.

---o0o---

Several publications on the preparation and the chemical properties of phosphinates have appeared while this Review was being prepared for the press. The action of water and hydrogen sulphide on dialkoxyphosphines yields alkyl phosphinates and phosphinothionates respectively[220]. Several inorganic salts of phosphinic acid have been prepared and their physicochemical properties have been studied[221,222].

The thermolysis of *p*-acetylanilinium phosphinate reflects the highly reactive character of the arylammonium salts[223]. A method has been suggested for the phosphorylation of allylcellulose with alkali-metal phosphinates[224]. Ion-exchange resins of polycondensation type, containing phosphorus and nitrogen, have been obtained from various di- and poly-amines, aqueous formaldehyde, and phosphinic acid[225,226]. The condensation of oximes with phosphinic acid yields 1-aminoalkyl-phosphinic and -phosphonic acids[227]. 1,5-Diketones react with phosphinic acid to give hydroxyalkylphosphinic or tetrahydropyranylphosphonic acids and their analogues depending on the structure of the ketone and the acidity of the medium[228–231]. The structure of the reaction product reported in Ref.231 has been refined[228–230]. Several macrocycles[232] and arenediazonium compounds[233] have been reduced with phosphinic acid. Homolytic reactions of phosphinates have been described in a monograph[234].

REFERENCES

1. M.J.Ville, Compt.rend., 107, 659 (1888).
2. M.I.Kabachnik, A.E.Shipov, and T.A.Mastryukova, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 81, 477 (1948).
3. H.Schmidt, Chem.Ber., 81, 477 (1948).
4. D.O.Taube, B.A.Vovsi, and B.I.Ionin, Zhur.Obshch. Khim., 42, 351 (1972).
5. E.E.Nifant'ev and L.M.Matveeva, Zhur.Obshch. Khim., 39, 1955 (1969).
6. I.F.Lutsenko, M.V.Proskurnina, and A.A.Borisenko, Dokl.Akad.Nauk SSSR, 193, 828 (1970).
7. M.G.Voronkov and L.Z.Marmur, Zhur.Obshch. Khim., 40, 2135 (1970).
8. E.E.Nifant'ev, A.A.Borisenko, A.I.Zavalishina, and S.F.Sorokina, Dokl.Akad.Nauk SSSR, 219, 881 (1974).
9. N.B.Karlstedt, T.P.Goranskaya, M.V.Proskurnina, and I.F.Lutsenko, in "Khimiya Elementoorganicheskikh Soedinenii: Elementy III–V Grupp" (Chemistry of Hetero-organic Compounds–Elements of Groups III–V), Nauka, Leningrad, 1976, p.172.
10. S.Sebek and B.Machánová, Chem.průmysl, 15, 307 (1965).
11. W.Blum, Canad.Metals, 15, No.5, 52 (1952).
12. A.Brenner, D.E.Couch, and E.K.Williams, J.Res. Nat.Bur.Stand., 44, 109 (1950).
13. R.N.Venkteswara and D.V.V.S.Eswara, Mikrochim. Acta, 1970, 512.
14. P.K.Norkus and R.M.Markyavichene, Trudy Akad. Nauk Lit.SSR, B51, No.4, 85 (1967).

15. V.I.Yudelevich and V.M.Tikhonova, in "Izuchenie Biologicheski Aktivnykh Veshchestv—Metabolitov Mikroorganizmov" (Study of Biologically Active Substances—Metabolites of Micro-organisms), Meditsina, Leningrad, 1976, Part 2, p.37.
16. V.I.Yudelevich, in "Materialy VII Konferentsii Molodykh Uchenykh Leningradskogo NII Antibiotikov" (Proceedings of the Seventh Conference of Young Students of the Leningrad Antibiotics Scientific Research Institute), Meditsina, Leningrad, 1975, p.31.
17. W.G.Grewther, Biochim.Biophys.Acta, 21, 178(1956).
18. US P. 2648706 (1953); Chem.Abs., 48, 8252 (1954).
19. BRD P. 1005063 (1958); C.Zbl., 16095 (1959).
20. K.V.Nikonorov, E.A.Gurylev, F.F.Fakhrislamova, T.V.Raspopova, L.G.Urazaeva, M.G.Berim, K.B.Budnaya, E.K.Naumova, and T.L.Nosyreva, Dokl.Akad.Nauk SSSR, 172, 353 (1967).
21. W.Perkow, Ber., 87, 755 (1955) [sic].
22. W.Perkow, K.Ullerich, and F.Meyer, Naturwiss., 39 353 (1952).
23. N.V.Vvedenskii, G.A.Kondratovich, V.I.Yudelevich, G.S.Gusakova, and N.I.Yaskina, USSR P.449 792 (1973); Byull.Izobr., No.42, 25 (1974).
24. A.W.Frank, Chem.Rev., 61, 392 (1961).
25. G.M.Kosolapoff, "Organophosphorus Compounds", Wiley and Sons, New York 1950, chapters 7 and 8.
26. J.R.van Wazer, "Phosphorus and its Compounds" (Translated into Russian), Inostr.Lit., Moscow, 1962, Vol.1.
27. R.R.Pahud, Chimie et Industrie, 87, 759 (1962).
28. N.V.Romanova and N.V.Demidenko, Uspekhi Khim., 44, 2150 (1975) [Russ.Chem.Rev., No.12 (1975)].
29. P.L.Dulong, Ann.Chem.Phys., 2, 141 (1816).
30. S.Ohashi, Topics in Phosphorus Chemistry, 1, 113 (1964).
31. W.E.Quinn and R.M.Brown, J.Chem.Phys., 21, 1605 (1953).
32. H.S.Gutowsky, D.W.McCall, and C.P.Slichter, J.Chem.Phys., 21, 279 (1953).
33. H.S.Gutowsky and D.W.McCall, J.Chem.Phys., 22, 162 (1954).
34. J.R.Van Wazer, C.F.Callis, J.N.Shoolery, and R.C.Jones, J.Amer.Chem.Soc., 78, 5715 (1956).
35. R.A.Y.Jones and A.R.Katritzky, Angew.Chem., 74, 28 (1962).
36. V.I.Yudelevich, L.B.Sokolov, and B.I.Ionin, Zhur.Obshch.Khim., 47, 2387 (1977).
37. N.K.Skvortsov, B.I.Ionin, and A.A.Petrov, Zhur. Obshch.Khim., 44, 220 (1974).
38. M.Tsuboi, A.Amer.Chem.Soc., 79, 1351 (1957).
39. T.J.Honwick and P.O.Hoffmann, J.Chem.Phys., 19, 708 (1951).
40. L.S.Mayants and E.I.Matrosov, Izv.Akad.Nauk SSSR, Ser.Neorg.Mater., 1, 546 (1965).
41. D.E.Corbridge, Topics in Phosphorus Chemistry, 6, 235 (1969).
42. D.Chément and L.Jean, Mikrochim.Acta., 454, 1956.
43. W.H.Zachariasen and R.C.Mooney, J.Chem.Phys., 2, 34 (1934).
44. W.Dewald, Fette und Seifen, 56, 105 (1954).
45. J.W.Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Longmans Green London, 1928, Vol.8, 870.
46. J.R.Van Wazer, "Encyclopedia of Chemical Technology", Interscience Publishers, New York, 1953, Vol.10, p.488.
47. R.F.Hudson, "Organophosphorus Compounds—Structure and Reaction Mechanisms" (Translated into Russian), Mir, Moscow, 1967, p.53.
48. R.Paris and P.Tardy, Compt.rend, 223, 242 (1946).
49. G.Brauer (Editor), "Handbuch der präparativen anorganischen Chemie" (Translated into Russian), Inostr.Lit., Moscow, 1956, p.276.
50. K.V.Nikonorov and E.A.Gurylev, Izv.Akad.Nauk SSSR, Ser.Khim., 1, 683 (1967).
51. W.A.Jenkins and R.I.Jones, J.Amer.Chem.Soc., 74, 1353 (1952).
52. L.Horner and H.Röder, Chem.Ber., 103, 2984 (1970).
53. A.Brenner and G.Riddel, J.Res.Nat.Bur.Stand., 39, 385 (1947).
54. K.M.Gorbunova and A.V.Nikiforova, "Fiziko-khimicheskie Osnovy Khimicheskogo Nikelirovaniya" (Physicochemical Principles of Chemical Nickel Plating), Izd.Akad.Nauk SSSR, Moscow 1960.
55. A.Albert and E.P.Serjeant, "Ionisation Constants of Acids and Bases: A Laboratory Manual" (Translated into Russian), Izd.Khimiya, Moscow–Leningrad, 1964.
56. D.A.Everest, J.Chem.Soc., 2954, 1952.
57. Z.Uhlir, S.Schoole, and J.Benes, Chem.prumysl, 8, 891 (1958).
58. US P. 2938770 (1960); Chem.Abs., 54, 18907 (1960).
59. US P. 2977192 (1961); Chem.Abs., 55, 18039 (1961).
60. BRD P. 1029809 (1958): Chem.Abs., 54, 23223 1960).
61. A.T.Malinina, V.I.Birolina, and V.S.Serebryannikova, in "Khimicheskie Svoistva Soedinenii Redkozemel'nykh Elementov" (Chemical Properties of Compounds of the Rare-earth Metals), Nauka, Moscow, 1973, p.13.
62. L.S.Aslanov, V.M.Ionov, M.A.Porai-Koshits, V.G.Lebedev, B.N.Kulikovskii, O.N.Gilyarov, and T.L.Novoderezhkina, Izv.Akad.Nauk SSSR, Ser. Neorg.Mater., 11, 117 (1975).
63. J.Pokorný, Chem.Zvesti, 19, 628 (1965).
64. V.V.Serebryannikov, "Khimiya Redkozemel'nykh Elementov" (Chemistry of the Rare-earth Metals), Izd.Tomsk.Univ., 1969, Vol.1., p.378.
65. T.G.Shvalova, G.A.Seryakova, and A.T.Malinina, Sbornik Nauch.Trudov Kuzbassk.Politekh.Inst., 52, 34 (1973).
66. N.S.Poluektov, R.S.Lauer, and S.F.Ognichenko, Zhur.Neorg.Khim., 15, 2133 (1970) [Russ.J.Inorg. Chem., No.8 (1970)].
67. N.Kreutzkamp, K.Storck, and C.Schimpfky, Arch. Pharm., 302 554 (1969).
68. E.E.Nifant'ev, V.S.Blagoveshchenskii, A.M.Sokurenko, and L.S.Sklyarskii, Zhur.Obshch.Khim., 44, 108 (1974).
69. B.Schaible, K.Roessel, J.Weidlein, and H.D.Hansen, Z.anorg.Chem., 409, 176 (1974).
70. R.Fosse, Bull.Soc.chim.France, 7, 962 (1910).
71. V.M.Plets, Zhur.Obshch.Khim., 7, 84 (1937).
72. J.Mai, Ber., 35, 162 (1902).
73. S.T.Fitch, J.Amer.Chem.Soc., 86, 61 (1964).
74. USSR P. 166 028 (1963); Byull.Izobr., No.21 (1964).
75. E.E.Nifant'ev and L.P.Levitan, Zhur.Obshch.Khim., 35, 758 (1965).
76. E.E.Nifant'ev, L.M.Matveeva, and I.P.Gudkova, in "Trudy IV Konferentsii po Khimii i Primeneniyu Fosfororganicheskikh Soedinenii" (Proceedings of the Fourth Conference on the Chemistry and Application of Organophosphorus Compounds), Nauka, Moscow, 1972, p.391.
77. B.E.Ivanov and L.A.Kudryavtseva, Izv.Akad.Nauk SSSR, Ser.Khim., 1948, 1967.

78. N.B.Karlstedt, M.V.Proskurnina, and I.F.Lutsenko, Zhur.Obshch.Khim., **46**, 2018 (1976).
79. D.A.Predvoditelev, E.E.Nifant'ev, and Z.A.Rogovin, Vysokomol.Soed., 7, 791 (1965).
80. D.A.Predvoditelev, E.E.Nifant'ev, and Z.A.Rogovin, in "Trudy III Konferentsii po Khimii i Primeneniyu Fosfororganicheskikh Soedinenii" (Proceedings of the Third Conference on the Chemistry and Application of Organophosphorus Compounds), Nauka, Moscow, 1972, p.409.
81. E.E.Nifant'ev, L.T.Elepina, and V.N.Balakhontseva, Zhur.Obshch.Khim., **41**, 707 (1971).
82. E.E.Nifant'ev, I.V.Fursenko, and V.L.L'vov, Vysokomol.Soed., **9B**, 18 (1967).
83. E.E.Nifant'ev, S.G.Fedorov, and I.V.Fursenko, see Ref.80, p.417.
84. E.E.Nifant'ev, V.P.Zubov, and L.M.Kolesova, Vysokomol.Soed., 17A, 1938 (1975).
85. Yu.V.Karyakin and I.I.Angelov, "Chistye Khimicheskie Reaktivy" (Pure Chemical Reagents), Goskhimizdat, Moscow, 1955, p.294.
86. K.A.Petrov, E.E.Nifant'ev, I.I.Sopikova, and M.A.Belavintsev, in "Tsellyuloza i ee Proizvodnye" (Cellulose and its Derivatives), Izd.Akad.Nauk SSSR, Moscow, 1963, p.90.
87. "Laboratornyi Praktikum po Khimii Fosfororganicheskikh Soedinenii" (Laboratory Manual on the Chemistry of Organophosphorus Compounds), Izd. Chuvashsk.Gos.Univ., Cheboksary, 1975.
88. E.Cherluliez, F.Hunkeler, G.Weber, and J.Rabinowitz, Helv.Chim.Acta, **47**, 1647 (1964).
89. L.M.Matveeva, R.G.Babkova, and E.E.Nifant'ev, Vestnik Moskov.Univ., 361 (1972).
90. V.D.D'yakov, L.Z.Marmur, M.G.Voronkov, and N.F.Orlov, Zhur.Obshch.Khim., **42**, 1291 (1972).
91. P.Hayward and D.M.Yost, J.Amer.Chem.Soc., **71**, 915 (1949).
92. V.Hovorka, Coll.Czech.Chem.Comm., 2, 559 (1930).
93. P.Neorgi and B.Sen, J.Indian Chem.Soc., **8**, 725 (1931).
94. B.NathSen, Coll.Czech.Chem.Comm., 10, 321 (1938).
95. B.NathSen, Gazzetta, **78**, 423 (1948).
96. W.A.Jenkins and D.M.Yost, J.Inorg.Nuclear Chem., 11, 297 (1959).
97. R.O.Griffith, A.McKeown, and R.P.Taylor, Trans. Faraday Soc., **36**, 752 (1940).
98. G.Schwarzenbach, Helv.Chim.Acta, **19**, 1043 (1936).
99. F.Gallias, Bull.Soc.chim.France, 425, 1947.
100. P.Hersch, J.Chem.Educ., **20**, 376 (1943).
101. P.Neogi and S.Mukezji, J.Indian Chem.Soc., **6**, 529 (1929).
102. G.S.Vozdvizhenskii and A.F.Gerasimov, Trudy Kazansk.Khim.-tekhnol.Inst.Butlerova, No.1, 108 (1934).
103. A.W.Mitchell, J.Chem.Soc., **121**, 1624 (1922).
104. A.D.Mitchell, J.Chem.Soc., **125**, 1013 (1924).
105. A.F.Bogoyavlenskii, Uch.Zap.Kazansk.Univ. Ul'yanova-Lenina, **100**, 69 (1940).
106. W.A.Jenkins and D.M.Jost, J.Chem.Phys., **20**, 538 (1952).
107. A.I.Brodskii and A.V.Sulima, Dokl.Akad.Nauk SSSR, **85**, 1277 (1952).
108. A.I.Brodskii, D.M.Stazhesko, and L.L.Chervyakova, Dokl.Akad.Nauk SSSR, **75**, 823 (1950).
109. J.Horak and V.Effel, Coll.Czech.Chem.Comm., **26**, 2410 (1961).
110. A.J.Kirby and S.G.Warren, "Organic Chemistry of Phosphorus" (Translated into Russian), Mir, Moscow, 1971, p.30.
111. G.O.Doak and L.D.Freedman, Chem.Rev., **61**, 31 (1961).
112. M.I.Kabachnik and Yu.M.Polikarpov, Dokl.Akad. Nauk SSSR, **115**, 512 (1957).
113. A.E.Arbuzov, M.I.Batuev, and V.S.Vinogradova, Dokl.Akad.Nauk SSSR, **54**, 603 (1946).
114. J.E.Griffiths and A.B.Burg., J.Amer.Chem.Soc., 82, 1507 (1960).
115. E.Wiberg and G.Müller-Schiedmayer, Z.anorg. Chem., **308**, 352 (1960).
116. J.F.Lutsenko, M.V.Proskurnina, and A.A.Borisenko, Organometallic Chem.Symp., **169** (1970/1971).
117. V.L.Foss, Yu.A.Veits, and I.F.Lutsenko, Zhur. Obshch.Khim., **42**, 954 (1972).
118. W.J.Stec, B.Uznanski, and J.Michalski, Phosphorus, 2, 237 (1973).
119. I.F.Lutsenko, in "Trudy V Konferentsii po Khimii i Primeneniyu Fosfororganicheskikh Soedinenii" (Proceedings of the Fifth Conference on the Chemistry and Application of Organophosphorus Compounds), Nauka, Moscow, 1974, p.172.
120. L.Z.Marmur, N.F.Orlov, and M.G.Voronkov, USSR P.No.306130 (1971); Byull.Izobr., No.19, 85 (1971).
121. M.G.Voronkov, L.Z.Marmur, O.N.Doglov, V.A.Pestunovich, E.M.Pokrovskii, and Yu.I.Popel, Zhur. Obshch.Khim., 41, 1987 (1971).
122. M.J.Ville, Compt.rend., **109**, 71 (1889).
123. M.C.Marie, Compt.rend., 133, 219 (1901).
124. D.Purdela and R.Vilceanu, "Chemistry of Organophosphorus Compounds and their Acid Derivatives" (Translated into Russian), Khimiya, Moscow, 1972.
125. T.A.Zyablikova, I.M.Magdeev, and I.M.Shermergorn, Izv.Akad.Nauk SSSR, Ser.Khim., 397 (1968).
126. A.N.Pudovik, I.V.Gur'eva, and E.A.Ishmaeva, in "Reaktsii i Metody Issledovaniya Organicheskikh Soedinenii" (Reactions and Methods of Investigation of Organic Compounds), edited by B.A.Kazanskii, Khimiya, Moscow, 1968, Vol.19, p.45.
127. K.V.Nikonorov, E.A.Gurylev, L.G.Urazaeva, M.N.Nazinov, R.A.Asadov, and S.A.Anisin, Izv. Akad.Nauk SSSR, Ser.Khim., 2241 (1969).
128. Z.physiol.Chem., **305**, 143 (1956).
129. G.Schrader, "Entwicklung neuer insektizider phosphorsaurer Ester" (Translated into Russian), Mir, Moscow, 1965.
130. Austral.P.219495 (1957).
131. G.V.Solov'eva, E.I.Saranov, and N.I.Kalinichenko, Izv.Vys.Ucheb.Zaved., Khim.i Khim.Tekhnol., **19**, 622 (1976).
132. "Reaktsii i Metody Issledovaniya Organicheskikh Soedinenii" (Reactions and Methods of Investigation of Organic Compounds), Khimiya, Moscow, 1966, Vol.19.
133. M.P.Viout, J.Recherches CNRS, **28**, 15 (1954).
134. US P.2370903 (1945); Chem.Abs., **39**, 4892 (1945).
135. BRD P.1005063 (1959); Chem.Abs., **53**, 15008 (1959).
136. S.A.Buckler and V.P.Wystrach, J.Amer.Chem. Soc., **83**, 168 (1961).
137. K.V.Nikonorov and E.A.Gurylev, USSR P.No.182155 (1965); Byull.Izobr., No.11, 21 (1966).
138. K.V.Nikonorov, E.A.Gurylev, and F.F.Fakhrislamova, Izv.Akad.Nauk SSSR, Ser.Khim., 1095 (1966).
139. V.Ettel and J.Horak, Coll.Czech.Chem.Comm., **26**, 2087 (1961).

140. M.Polono, M.Pesson, and G.Polmauss, Compt.rend, **239**, 1506 (1954).
141. S.A.Buckler, J.Amer.Chem.Soc., **82**, 4215 (1960).
142. G.Quesnel and M.Botton, Compt.rend., **251**, 1974 (1960).
143. US P.2904586 (1959); Chem.Abs., **54**, 2216 (1960).
144. A.-G.Siegfried, Swed.P.311982 (1956); Chem.Abs., **51**, 10559 (1957).
145. H.Ruschig and W.Aumüller, BRD P.1009623 (1957); Chem.Abs., **53**, 16063 (1959).
146. W.J.Pope and C.S.Gibson, J.Chem.Soc., **101**, 735 (1912).
147. A.S.Skobun, V.I.Vysotskii, and M.I.Tilichenko, USSR P.No.525695 (1976); Byull.Izobr., No.31, 63 (1976).
148. B.E.Ivanov and T.I.Karpova, Izv.Akad.Nauk SSSR, Ser.Khim., 1230 (1964).
149. V.I.Yudelevich, B.A.Vovsi, and D.O.Taube, "Osnovy Razvitiya Farmatsii i Izyskanie Novykh Sposobov Prigotovleniya Lekarstv i Metodov ikh Analiza (Materialy Konferentsii)" (Principles of the Development of Pharmacy and the Search for New Processes for the Preparation of Medicinals and Methods for their Analysis—Proceedings of a Conference), Kursk Medical Institute, 1972, p.12.
150. B.E.Ivanov and L.A.Kudryavtseva, Izv.Akad.Nauk SSSR, Ser.Khim., 1633 (1968).
151. F.U.Stacey and J.F.Harris, in Org.Reactions 1963 (Translated into Russian) Mir, Moscow, **13**, 170 (1966).
152. E.E.Nifant'ev and M.P.Koroteev, Zhur.Obshch.Khim., **37**, 1366 (1967).
153. B.C.Gilbert, J.P.Larkin, R.O.C.Norman, and P.M. Storey, J.Chem.Soc., Perkin Trans.II, 1508 (1972).
154. V.A.Al'fonsov, L K.Stefanskaya, and A.I.Grebnev, Zhur.Obshch.Khim., **45**, 314 (1975).
155. Neth.P.69357 (1952); Chem.Abs., **47**, 143 (1953).
156. M.G.Imlev, "Fosforsoderzhashchie Poverkhnostno-aktivnye Veshchestva i Moyushchie Sredstva (Obzor)" (Phosphorus-containing Surface-active and Wetting Agents—Survey), Nauch.-issled.Inst.Tekh.-ekon. Issled., Moscow, 1965, p.41.
157. B.P.660918 (1951); Chem.Abs., **46**, 8145 (1952).
158. A.R.Stiles, D.Harman, and F.F.Rust, US P. 2724718 (1955); Chem.Abs., **50**, 10124 (1956).
159. K.A.Petrov, T.N.Lysenko, B.Ya.Libman, and V.Z.Pozdnev, in "Khimiya Organicheskikh Soedinenii Fosfora" (Chemistry of Organic Compounds of Phosphorus), Nauka, Leningrad, 1967, p.181.
160. G.M.Vinogradova and I.A.Aleksandrova, Izv.Akad. Nauk SSSR, Ser.Khim., 884 (1969).
161. C.W.Smith, US P.2648695 (1953); Chem.Abs., **48**, 8252 (1954).
162. I.A.Aleksandrova and L.I.Ufimtseva, Izv.Akad. Nauk SSSR, Ser.Khim., 1315 (1971).
163. "Khimiya Organicheskikh Soedinenii Fosfora" (Chemistry of Organic Compounds of Phosphorus), in Sbornik Zhur.Obshch.Khim., Nauka, Moscow, 1968, p.181.
164. US P.2957931 (1960); Chem.Abs., **55**, 10317 (1961).
165. A.L.J.Beckwith, Austral.J.Chem., **25**, 1887 (1972).
166. R.H.Williams and L.H.Hamilton, J.Amer.Chem. Soc., 77, 3411 (1955).
167. G.Quesnel, M.Botton, A.Chambolle, and K.Dubou, Compt.rend., **251**, 1074 (1960).
168. A.N.Pudovik, T.M.Moshkina, and N.V.Konovalova, Zhur.Obshch.Khim., **29**, 3301 (1959).
169. E.E.Nifant'ev and L.M.Matveeva, Zhur.Obshch.Khim., **37**, 1692 (1967).
170. J.M.Gallagher and J.Sussman, Phosphorus, **5**, 91 (1975).
171. U.K.Kanitkar and B.V.Bhide, Current Sci., **16**, 223 (1947).
172. J.D.Thayer, H.J.Magnuson, and M.S.Gravatt, Antibiotics and Chemotherapy, **3**, 256 (1953).
173. R.Kuhn, E.F.Moller, and G.Wendt, Ber., **75**, 711 (1942).
174. A.T.Guttman, E.Jungermann, and W.M.Linfield, US P.3424788 (1969).
175. P.C.Hamm, US P.3556762.
176. W.H.Shelver, M.Schreibman, N.S.Tanner, and V.S.Rao, J.Medicin.Chem., 17, 120 (1974).
177. E.D.Korn, D.G.Dearborn, H.M.Fules, and E.A.Sokolski, J.Biol.Chem., **248**, 2257 (1973).
178. M.Horiguchi and M.Kandatsu, Agric.Biol.Chem. (Japan), 26, 721 (1962).
179. M.Horiguchi and M.Kandatsu, Agric.Biol.Chem. (Japan), **28**, 408 (1964).
180. M.Horiguchi and M.Kandatsu, Nature, **184**, 901 (1959).
181. H.Schmidt, DRP.870701 (1942); Chem.Abs., **52**, 10060 (1954).
182. H.Schmidt, DRP.875662 (1942); Chem.Abs., **52**, 10060 (1954).
183. A.T.Guttmann, E.Jungermann, and W.M.Linfield, US P.3432547 (1969).
184. A.T.Guttman, W.L.Linfield, and E.Jungermann, US P.3506579 (1970).
185. W.M.Linfield, E.Jungermann, and A.T.Guttman, J. Org.Chem., **26**, 4088 (1961).
186. N.Kreutzkamp, E.Schimpfky, and K.Stock, Arch. Pharm., **300**, 868 (1967).
187. F.D.Popp and W.Kirsch, J.Org.Chem., **26**, 3858 (1961).
188. T.Ya.Medved', M.V.Rudomino, N.M.Dyatlova, and M.I.Kabachnik, Izv.Akad.Nauk SSSR, Ser.Khim., 1211 (1968).
189. N.Kreutzkamp, C.Schimpfky, and K.Stock, Arch. Pharm., **301**, 247 (1968).
190. J.E.Willems, Belg.P.557556 (1957); Chem.Abs., **51**, 17545 (1957).
191. D.Kh.Yarmukhametova and B.V.Kudryavtsev, Izv. Akad.Nauk SSSR, Ser.Khim., 1571 (1971).
192. L.Maier, Helv.Chim.Acta, **50**, 1742 (1967).
193. L.Maier, Swiss P.475287 (1969).
194. V.I.Yudelevich and L.B.Sokolov, Zhur.Obshch. Khim., **45**, 1646 (1975).
195. V.I.Yudelevich, L.B.Sokolov, B.I.Ionin, and L.G.Myasnikova, Zhur.Obshch.Khim., **45**, 2554 (1975).
196. V.I.Yudelevich, L.B.Sokolov, and B.I.Ionin, Zhur.Obshch.Khim., **46**, 2669 (1976).
197. E.E.Nifant'ev, N.V.Zyk, and M.P.Korotaev, Dokl. Akad.Nauk SSSR, **218**, 1371 (1974).
198. E.E.Nifant'ev, N.V.Zyk, M.P.Korotaev, and V.N.Abramov, Zhur.Obshch.Khim., **45**, 2162 (1975).
199. A.H.Blatt, N.Gross, and E.W.Tristram, J.Org. Chem., **22**, 1988 (1957).
200. A.H.Blatt and N.Gross, J.Org.Chem., 22, 1046 (1957).
201. J.Mai, Ber., **35**, 162 (1902).
202. N.Kornblum, Org.Synth.Coll.Vol., **3**, 295 (1955).
203. M.M.Robinson and B.L.Robinson, Org.Synth. Coll.Vol., **4**, 947 (1963).

204. C.Wolling and M.S.Pearson, Topics in Phosphorus Chemistry, 3, 42 (1966).
205. A.F.Levit, L.A.Kiprianova, and I.P.Gragerov, Dokl. Akad.Nauk SSSR, **213**, 634 (1973).
206. G.C.Bakulina and B.V.Erofeev, Katalitich.Reaktsii v Zhidk.Faze, **1**, 99 (1974); Chem.Abs., **83**, 146837 (1975).
207. A.F.Levit, L.A.Kiprianova, and I.P.Gragerov, Zhur. Org.Khim., 11, 2351 (1975).
208. B.N.Kornblum, G.D.Cooper, and J.E.Taylor, J. Amer.Chem.Soc., 72, 3013 (1950).
209. V.I.Yudelevich, L.B.Sokolov, and B.I.Ionin, Zhur. Obshch.Khim., **46**, 2394 (1976).
210. R.Fosse, Bull.Soc.chim.France, **4**, 228 (1910).
211. O.Stelling, Z.phys.Chem., 117, 161 (1925).
212. H.H.Hatt, J.Chem.Soc., 776 (1933).
213. E.E.Nifant'ev, "Khimiya Fosfororganicheskikh Soedinenii" (Chemistry of Organic phosphorus Compounds), Izd.Moskov.Gos.Univ., 1971, p.105.
214. N.K.Kochetkov, E.E.Nifant'ev, and I.P.Gudkova, Zhur.Obshch.Khim., **31**, 277 (1967) [sic].
215. E.E.Nifant'ev, I.P.Gudkova, and N.K.Kochetkov, Zhur.Obshch.Khim., **40**, 460 (1970).
216. V.M.Plets, "Organicheskie Soedineniya Fosfora" (Organic Compounds of Phosphorus), Oborongiz, Moscow, 1940, p.42.
217. F.Kasparek, Sborník Prací Prírodovedecké Fakulty Univ́ersity Palackeho v Olomouci, **21**, 221 (1966); Monatsh., **94**, 809 (1963).
218. F.Kasparek, Z.anorg.Chem., **362**, 205 (1968).
219. E.E.Nifant'ev, V.S.Blagoveshchenskii, A.M.Sokurenko, and L.S.Sklyarskii, Zhur.Obshch.Khim., **49**, 1644 (1971) [sic].
220. I.F.Lutsenko, M.V.Proskurina, and N.B.Karlsted, USSR P.No.539035 (1976); Byull.Izobr., No.46, 88 (1976).
221. O.I.Lomovskii, Yu.I.Mikhailov, and A.B.Brosalin, Izv.Sibirsk.Otd.Akad.Nauk SSSR, **2**, 47 (1978).
222. S.A.Mikhalyuk and N.V.Romanova, Ukrain.Khim. Zhur., **44**, 715 (1978).
223. V.I.Yudelevich, A.P.Fetter, L.B.Sokolov, and B.I.Ionin, Zhur.Obshch.Khim., **48**, 2379 (1978).
224. A.I.Kapralov, R.K.Magdeeva, and E.E.Nifant'ev, USSR P.No.596593 (1978); Byull.Izobr., No.9, 109 (1978).
225. L.B.Vlasov, P.A.Gemitskii, N.M.Dyatlova, G.N.Esina, D.S.Zhuk, M.I.Kabachnik, S.B.Makarova, T.Ya.Medved', Yu.M.Polikarpov, and A.V.Smirnov, USSR P.No.575363 (1975); Byull.Izobr., No.37, (1977).
226. Yu.M.Polikarpov, G.N.Esina, A.V.Smirnov, S.B.Makarova, T.Ya.Medved', and M.I.Kabachnik, Izv.Akad.Nauk SSSR, Ser.Khim., 2117 (1978).
227. R.M.Khomutov and T.I.Osipova, Izv.Akad.Nauk SSSR, Ser.Khim., 1951 (1978).
228. V.I.Vysotskii, K.G.Chuprakova, A.S.Skobun, E.V.Pavlycheva, S.M.Kalinov, V.N.Chernii, and M.N.Tilichenko, in "Yubileinaya Konferentsiya po Khimii Fosfororganicheskikh Soedinenii, posvyashchennaya 100-letiyu so Dnya Rozhdeniya Akademika A.E.Arbuzova, Tezisy Dokladov" (Conference on the Chemistry of Organophosphorus Compounds celebrating the Centenary of the Birth of A.E.Arbuzov—Abstracts of Papers), Kiev, 1977, p.153.
229. V.I.Vysotskii, A.S.Skobun, and M.N.Tilichenko, Zhur.Obshch.Khim., **48**, 2442 (1978).
230. V.I.Vysotskii, A.S.Skobun, and M.N.Tilichenko, Zhur.Obshch.Khim., **49**, 329 (1979).
231. V.I.Vysotskii, A.S.Skobun, and M.N.Tilichenko, Zhur.Obshch.Khim., **44**, 2109 (1974).
232 A.M.Tait and D.H.Busch, Inorg.Chem., **16**, 966 (1977).
233. S.H.Korzeniowski, L.Blum, and G.W.Gokel, J.Org. Chem., **42**, 1469 (1977).
234. Ya.A.Levin and E.I.Vorkunova, "Gomoliticheskaya Khimiya Fosfora" (Homolytic Chemistry of Phosphorus), Nauka, Moscow, 1978, pp.204, 221, 224, and 230–232.

All-Union Scientific and Technical
Research Institute of Antibiotics and
Enzymes for Medical Prescription

Lensovet Leningrad Institute
of Technology

Translated from *Uspekhi Khimii*, **49**, 118-146 (1979) U.D.C. 66.015.23

Problems of the Theory of Transport Processes in Systems with Intensive Mass Exchange

V.S.Krylov

The principles of the macroscopic theory of processes of convective heat and mass transfer in systems with mass exchange, taking place under conditions of large concentration gradients, have been presented. For these systems, the structure of the hydrodynamic fluxes (in particular the velocity profile in the boundary layer next to the wall) shows a marked dependence on the concentration field of the substance being transferred. Studies in which the effect of the interaction between the processes of mass transfer and momentum transfer has been analysed quantitatively in relation to problems of chemical and electrochemical technology have been reviewed. The bibliography contains 68 references.

CONTENTS

I. Introduction 59
II. Characteristics of the hydrodynamic conditions of intense mass exchange 59
III. Anodic dissolution of metals in a stream of electrolyte 60
IV. Influence of diffusion on hydrodynamics under conditions of mass transfer to the surface of a rotating disc 67
V. Mutual influence of the components of a gaseous mixture on condensation from a turbulent stream 68
VI. Electrodeposition of metals from concentrated salt solutions 70

I. INTRODUCTION

Present-day chemical and electrochemical technology, and many other fields of science and technology (for example thermophysics, hydrometallurgy, nuclear and electrochemical energetics, purification of gases, etc.) are engaged in the search for methods of intensifying interphase heat and mass transfer. Extensive possibilities in this connection are being opened up by the development of effective methods of dispersing and mixing, and the use of hydrodynamically non-stabilised conditions of convective transport and input regions of heat and mass exchange. High rates of the processes of interphase exchange are realised when these processes are carried out under markedly non-equilibrium conditions, that is with high temperature and concentration gradients.

Traditional methods of mathematical description, based on the separate solution of the equations of hydrodynamics and convective heat and mass transfer, are not applicable to systems in which transfer processes are taking place under conditions of intense mass exchange. In the traditional approach, the distribution of hydrodynamic velocities is found first (for example by solving the Navier–Stokes equations in the case of laminar flow conditions), after which this distribution is substituted in the equation of convective heat or mass exchange and solved for specific boundary conditions to determine the rate of interphase exchange. When applied to systems having large concentration gradients, however, this method of solution is not correct, since convective motion induced by mass exchange takes place[1,2]. The velocity of the induced movement is at right angles to the interphase boundary and the movement takes place in the direction of mass transfer. The physical factor responsible for this movement is the mechanical momentum, which is transferred from one phase to the other by the particles responsible for mass exchange. Since the transmitted momentum is proportional to the diffusion flow of the particles involved is mass transfer, the velocity field close to the interphase boundary depends on the concentration field. The specific form of this dependence is determined by the system of equations for the simultaneous transfer of momentum and mass, and also by the boundary conditions relating the fluxes of momentum and mass at the interphase boundary.

II. CHARACTERISTIC FEATURES OF THE HYDRODYNAMIC CONDITIONS OF INTENSIVE MASS EXCHANGE

The mechanical momentum, proportional to the velocity of interphase mass exchange, influences primarily the boundary conditions for the equations of hydrodynamics and mass transfer: these equations, unlike the case of systems with low velocities of interphase mass exchange, cannot be solved separately. To establish the relationship between the local velocity of movement of a continuous medium (liquid or gas) at the phase interface and the rate of interphase mass exchange, it is possible to take as an example the isothermal transfer of a solute from phase 1 to phase 2. For simplicity it will be assumed that each of the phases is a two-component liquid mixture (a solution of substance m in the corresponding solvent), and that the solvents are immiscible. The diffusion flux $j_m^{(i)}$ of the substance m at any point in space within the phase i is defined as follows[3]:

$$j_m^{(i)} = M_m c_m^{(i)} (\mathbf{v}_m^{(i)} - \mathbf{v}^{(i)}). \quad (1)$$

Here, $c_m^{(i)}$ is the molar concentration of the substance being transferred in the phase i; M_m the molecular mass of this substance; $\mathbf{v}_m^{(i)}$ the mean statistical velocity of the movement of the particles of the substance m in an arbitrary but fixed system of coordinates; and $\mathbf{v}^{(i)}$ the velocity of movement of the centre of mass of the entire liquid mixture in the same system of coordinates.

The velocity $\mathbf{v}^{(i)}$ is described by the system of equations of hydrodynamics (in the case of laminar flow conditions by the Navier–Stokes system of equations). At the same time, this velocity, by definition, is related to the velocities of the movement of the components of the mixture by

the relationship

$$\rho^{(i)}\mathbf{v}^{(i)} = M_m c_m^{(i)}\mathbf{v}_m^{(i)} + M_0 c_0^{(i)}\mathbf{v}_0^{(i)}, \qquad (2)$$

where the quantities having the subscript "0" refer to the corresponding solvent, and $\rho^{(i)} = M_m c_m^{(i)} + M_0 c_0^{(i)}$ is the total density of the solution in the phase i (in the general case this density is a function of the spatial coordinates and time). Each velocity in Eqn.(2) is represented as the sum of the velocity of movement of the interphase surface $d\mathbf{r}_s/dt$ ($\mathbf{r}_s$ is the radius vector of an arbitrary point at the phase interface) and the velocity relative to this surface $\mathbf{v}_{rk}^{(i)}$ ($k = m, 0$). Since the solvents are immiscible, the normal components of the velocities $v_{r0}^{(1)}$ and $v_{r0}^{(2)}$ at the interphase boundary should be equal to zero. Thus Eqn.(2), projected on to the direction of the normal n to the interphase boundary, has at each point on this boundary the following form:

$$\rho^{(i)}(\mathbf{v}_r^{(i)}, \mathbf{n}) = M_m c_m^{(i)}(\mathbf{v}_{rm}^{(i)}, \mathbf{n}); \quad i = 1, 2. \qquad (3)$$

The analogous operation of projecting Eqn.(1) on to the direction of the normal n leads, with allowance for Eqn.(3), to the equation

$$(\mathbf{v}_s^{(i)}, \mathbf{n}) = \left(\frac{d\mathbf{r}_s}{dt}, \mathbf{n}\right) + \frac{(\mathbf{j}_{ms}^{(i)}, \mathbf{n})}{\rho_s^{(i)} - M_m c_{ms}^{(i)}}, \qquad (4)$$

applicable for any point on the interphase surface. The subscript "s" in this equation indicates that the corresponding quantity refers to the interface between the phases. If the form of the interface is given by one of the equations

$$y = f_1(x, t), \; z = f_2(r, t), \; r = f_3(\vartheta, t),$$

the following expressions give the first term on the right-hand side of Eqn.(4)

$$\left(\frac{d\mathbf{r}_s}{dt}, \mathbf{n}\right) = \begin{cases} \left[1 + \left(\frac{\partial f_1}{\partial x}\right)^2\right]^{-1/2} \frac{\partial f_1}{\partial t} & \text{(in a rectangular system of coordinates);} \\ \left[1 + \left(\frac{\partial f_2}{\partial r}\right)^2\right]^{-1/2} \frac{\partial f_2}{\partial t} & \text{(in a cylindrical system of coordinates);} \\ \left[1 + \left(\frac{\partial f_3}{f_3 \partial \vartheta}\right)^2\right]^{-1/2} \frac{\partial f_3}{\partial t} & \text{(in a spherical system of coordinates).} \end{cases}$$

The condition (4) can readily be generalised to the case where several substances are transferred simultaneously through the interface. According to this condition, the normal component of the velocity of the movement of a continuous medium close to the interphase boundary is determined by the rate of displacement of the boundary itself, the rate of interphase mass exchange, and the surface values of the concentrations of the substance, responsible for mass exchange. It follows from Eqn.(4) that in the case of sufficiently high rates of mass exchange, the hydrodynamic problem cannot be solved independently of the problem of convective diffusion.

A large number of examples of systems of practical interest have been described, in which intensive mass exchange leads to a significant change in the hydrodynamic conditions of heat and mass transfer[4-13]. The most typical examples in this connection are the condensation of a mixture of vapours on a cooled wall[4], the evaporation of a liquid on the surface of drops and bubbles[8,9], and the crystallisation and dissolution of salts[10-13]. One of the theoretical problems in which the velocity field being calculated is found to depend on the concentration field of the particles responsible for mass exchange is the problem of the anodic dissolution of a metal surface in a stream of electrolyte solution at a high electrical current density. This problem is directly related to the theory of the technique of three-dimensional electrochemical machining of metals and alloys which has wide practical uses[14-19]. Existing approaches to the analyses of the processes of intensive anodic dissolution are examined in the next section.

III. ANODIC DISSOLUTION OF METALS IN A STREAM OF ELECTROLYTE

The mathematical description of the macrokinetics of the processes of anodic dissolution, used in practice for the three-dimensional machining of metals, is usually based on the so-called model of the "ideal" electrochemical process[20-22]. This model assumes that: 1) Ohm's law applies throughout the entire space occupied by the solution, as far as the actual electrode surfaces; 2) the distribution of electrical potential in solution is everywhere described by the Laplace equation (in other words, the existence of regions of bulk charge close to the electrodes is not taken into account); and 3) the ionisation of the atoms of the dissolving metal takes place at a constant current efficiency (generally 100%). This means that calculations within the framework of the model of the "ideal" process can lead to satisfactory results only for systems in which the effects of chemical and concentration overvoltage do not play a significant role, and the basic electrical resistance is determined by the bulk properties of the solution, which are constant at all points in the gap between the electrodes.

Mathematically, the problem of the "ideal" process of anodic dissolution does not differ in principle from the problem of the filtration of liquids through porous media under conditions in which the hydrodynamic resistance of the medium is described by Darcy's law[23]. The main difficulty in this case lies in finding the solution of the Laplace equation for the region, the boundaries of which are related to this solution by a familiar differential equation. Even in this simplified formulation, the problem of determining the form of the gap between the electrodes is still extremely complex, and its solution usually requires the use of numerical methods. The problem can be solved in analytical form only in individual cases, mainly for regions having two-dimensional geometry, to which the methods involving the theory of the functions of a complex variable are applicable[24-28]. An elegant analytical method, based on the establishment of the relationship between the components of the complex potential being sought and the solution of the characteristic hypergeometric equation, was developed by Polubarinova-Kochina[23] for application to problems of the theory of filtration. This method can be used without any modification to solve the stationary problems of electrochemical machining within the framework of the model of the "ideal" process (the given values of the flux at the boundaries of the filtration region, the configuration of which is to be determined, are direct analogues of the given values of the potential at the electrodes of the electrochemical cell).

Since in practice it is necessary to deal with non-ideal processes, the calculations carried out on the basis of the "ideal" model generally do not give satisfactory results. It has been shown[18] that Ohm's law cannot be extrapolated from the bulk of the solution to the region of the diffusion boundary layer next to the anode. The results[18] indicate that the true value of the electric potential gradient next to the anode at current densities of the order of 10 A cm^{-2} and electrolyte concentrations of the order of 1 M may differ by several factors of tens from the value obtained without allowance for the effect of concentration overvoltage. For this reason, published methods[17,29,30] for solving the problems of electrochemical machining can hardly be regarded as corresponding to the actual conditions. This statement will be illustrated below by a specific example.

1. Electrochemical Dissolution of a Surface Uniformly Accessible for Ionic Mass Exchange

The problem of the anodic dissolution of a metal in a solution of its own salt (for example the dissolution of iron in iron chloride solution) can be considered. To obtain the analytical solution of this problem, the following simplifying assumptions are made[31-33].

1. The dissolving surface is uniformly accessible with respect to diffusion.

2. The dissolution process is stationary, that is the concentration of each component of the solution at any fixed distance from the surface of the anode (this surface will be regarded as planar) is independent of time.

3. Ionic mass transfer in the solution takes place at very large Schmidt numbers, so that the velocity profile within the diffusion boundary layer may be approximated by a uniform distribution with a constant velocity, equal to the velocity of the movement of the solution directly at the anode surface.

4. The ratio of the effective thicknesses of the diffuse and diffusion boundary layers next to the anode is negligibly small, so that the solution can be regarded as electrically neutral at all points up to the interphase boundary.

5. The physical and transport properties of the solution are independent of the local concentration of cations of the dissolving metal.

6. Dissolution takes place under isothermal conditions.

The condition of uniform accessibility with respect to mass exchange means that the local concentration of each component of the solution depends only on the distance to the surface of the anode:

$$c_k = c_k((\boldsymbol{r} - \boldsymbol{r}_s), \boldsymbol{n}).$$

The stationary form of the equation for the differential mass balance of the kth component of the solution is as follows:

$$\operatorname{div} \boldsymbol{j}_k + M_k(\boldsymbol{v}, \nabla c_k) = 0,$$

where the quantities $\mathbf{j}_k$, $\mathbf{v}$, and c_k are functions of the spatial coordinate $\boldsymbol{r}$. The replacement of $\boldsymbol{r}$ by the new independent variable $x = (\boldsymbol{r}, \boldsymbol{n}) - (\boldsymbol{r}_S, \boldsymbol{n})$ gives

$$\left\{(\boldsymbol{v}, \boldsymbol{n}) - \left(\frac{\mathrm{d}\boldsymbol{r}_s}{\mathrm{d}t}, \boldsymbol{n}\right)\right\}\frac{\mathrm{d}c_k}{\mathrm{d}x} + \frac{1}{M_k}\frac{\mathrm{d}}{\mathrm{d}x}(\boldsymbol{j}_k, \boldsymbol{n}) = 0.$$

The assumption that the velocity field next to the anode is uniform makes it possible to replace the expression in braces by the right-hand side of Eqn.(4):

$$\frac{M_k(\boldsymbol{j}_1^{(s)}, \boldsymbol{n})}{\rho^{(s)} - M_1 c_1^{(s)}}\frac{\mathrm{d}c_k}{\mathrm{d}x} + \frac{\mathrm{d}}{\mathrm{d}x}(\boldsymbol{j}_k, \boldsymbol{n}) = 0; \quad k = 1, 2, 3. \tag{5}$$

Here, the subscripts $k = 1,2,3$ refer to the cations of the dissolving metal, the anions of the salt, and the solvent molecules respectively.

From the definition of the diffusion flux (1) and the mass-average hydrodynamic velocity (2) it follows that the vector sum of the diffusion fluxes of all the components present in the solution is equal to zero:

$$\sum_k \boldsymbol{j}_k = 0.$$

This means that in the three-component system being considered here, only two fluxes are independent. Subsequently, therefore, the mass transfer problem will be solved only for two components of the solution (for example 1 and 2).

In the formulation of the boundary conditions for Eqns.(5) it will be assumed that at a certain fixed distance $x = \delta$ from the surface of the anode, the ion concentrations c_1 and c_2 take their constant bulk values $c_1^{(0)}$ and $c_2^{(0)}$. The quantity δ in this approach is equivalent to the effective thickness of the diffusion boundary layer.

If the only electrochemical reaction taking place at the anode is the ionisation of the metal atoms, the normal component of the total mass flux of the metal cations at the surface of the anode

$$(\boldsymbol{j}_1^{(s)}, \boldsymbol{n}) + M_1 c_1^{(s)}\left\{(\boldsymbol{v}^{(s)}, \boldsymbol{n}) - \left(\frac{\mathrm{d}\boldsymbol{r}_s}{\mathrm{d}t}, \boldsymbol{n}\right)\right\},$$

should be proportional to the anodic current density i with proportionality coefficient equal to M_1/z_1F (F is the Faraday number):

$$\frac{iM_1}{z_1F} = (\boldsymbol{j}_1^{(s)}, \boldsymbol{n}) + M_1 c_1^{(s)}\left\{(\boldsymbol{v}^{(s)}, \boldsymbol{n}) - \left(\frac{\mathrm{d}\boldsymbol{r}_s}{\mathrm{d}t}, \boldsymbol{n}\right)\right\}.$$

Allowance for Eqn.(4) gives

$$(\boldsymbol{j}_1^{(s)}, \boldsymbol{n}) = \frac{iM_1}{\rho^{(s)}z_1F}(\rho^{(s)} - M_1 c_1^{(s)}). \tag{6}$$

The normal n in the last expression, and subsequently throughout, is assumed to be directed from the anode towards the solution, and the current density is assumed to be positive.

When an analogous expression is written for the total mass flux of the electrochemically inert anion and this flux is put equal to zero at the anode surface, the following relationship is obtained:

$$(\boldsymbol{j}_2^{(s)}, \boldsymbol{n}) = -M_1M_2ic_2^{(s)}/\rho^{(s)}z_1F. \tag{7}$$

Eqns.(6) and (7) can be regarded as the boundary conditions for Eqns.(5). According to condition (7), the diffusion flux of an electrochemically inert anion at the interphase boundary is nonzero. The physical factor responsible for this fact is the existence of a nonzero normal component of the rate of movement of the centre of mass of the solution at the anode surface; this component leads to a diffusion of the anion from the solution to the surface.

Single integration of Eqn.(5) with boundary conditions (6) and (7) gives:

$$(\boldsymbol{j}_k, \boldsymbol{n}) = \frac{iM_1}{\rho^{(s)}z_1F}(\rho^{(s)}\delta_{1k} - M_k c_k); \quad k = 1, 2, \tag{8}$$

where δ_{1k} is the Kronecker symbol.

The fluxes $\mathbf{j}_k$ are related to the ionic concentration gradients by the following expressions[18]:

$$\boldsymbol{j}_1 = -\frac{D_{\mathrm{eff}}M_1M_3c}{\rho}\zeta(c_1, c_2)\nabla c_1 + \frac{M_1D_{13}\boldsymbol{i}}{F(z_2D_{23} - z_1D_{13})}\left[\frac{c_1}{\rho D_{13}}(M_1D_{13} - M_2D_{23}) - 1\right], \tag{9}$$

$$\boldsymbol{j}_2 = -\frac{D_{\mathrm{eff}}M_2M_3c}{\rho}\zeta(c_1, c_2)\nabla c_2 - \frac{M_2D_{23}\boldsymbol{i}}{F(z_2D_{23} - z_1D_{13})}\left[\frac{c_2}{\rho D_{23}}(M_1D_{13} - M_2D_{23}) + 1\right]. \tag{10}$$

Here, $\mathbf{i} = F[(z_1\mathbf{j}_1/M_1) + (z_2\mathbf{j}_2/M_2)]$ is the vector of the electric current density, related to the scalar current density i by the relationship $(\mathbf{i},\mathbf{n}) = i$, $\rho = M_1c_1 + M_2c_2 + M_3c_3$ is the local density of the solution, $c = c_1 + c_2 + c_3$ the total concentration of the liquid phase, D_{ik} the coefficients of mutual diffusion in the corresponding binary mixtures, and D_{eff} the effective coefficient of ionic mass transfer, defined by the expression

$$D_{\mathrm{eff}} = \frac{\rho(z_2 - z_1)D_{13}D_{23}}{(z_1c_1 + z_2c_2)(M_1D_{13} - M_2D_{23}) + \rho(z_2D_{23} - z_1D_{13})}. \tag{11}$$

The function $\zeta(c_1, c_2)$ is expressed in terms of the mean activity coefficient of the electrolyte γ_{12} by the relationship

$$\zeta(c_1, c_2) = 1 + \frac{\mathrm{d}\ln\gamma_{12}}{\mathrm{d}\ln(c_1/c_1^{(0)})}. \tag{12}$$

Using the fourth simplifying assumption above, which postulates that the condition of local electrical neutrality is fulfilled, the mass transfer problem will subsequently be examined only for the cations "1" (the concentration of the anions c_2 in this case is determined directly from the electrical neutrality condition). Substitution of Eqn.(9) in Eqn.(8) and simple transformation give:

$$\left(1+\frac{d\ln\gamma_{12}}{d\ln(c_1/c_1^{(0)})}\right)\frac{dc_1}{dx}+\frac{i}{F(z_1-z_2)M_3D_{23}c}\times$$
$$\times\left\{\frac{M_1D_{13}-M_2D_{23}}{D_{13}}c_1-\rho\left[1-\frac{(z_1-z_2)D_{23}}{z_1D_{\text{eff}}}\left(1-\frac{M_1c_1^{(s)}}{\rho^{(s)}}\right)\right]\right\}=0. \quad (13)$$

If the functional form of the relationship $\gamma_{12}=\gamma_{12}(c_1, c_2)$ is known, it follows that Eqn.(13), together with the condition of local electrical neutrality and the boundary condition (6), determines completely the solution of the problem posed. Since however the published[34] empirical correlations for the relationships $\gamma_{12}(c_1, c_2)$ have an extremely complex form, the rigorous integration of Eqn.(13) is impossible without using numerical methods.

To analyse the most characteristic features of ionic mass exchange under conditions of intensive anodic dissolution, a number of further simplifications can be carried out. Thus it is possible to examine the particular case of a solution composition at which, on the one hand, the local concentrations of the ions are low compared with the concentration of the solvent ($c\cong c_3$) and on the other hand, as a consequence of the high molecular mass of the dissolving metal, the local density of the cations M_1c_1 is comparable with the local density of the solution ρ. Putting $c=c_3=$ const. in Eqn.(13) gives

$$\left(1+\frac{d\ln\gamma_{12}}{d\ln(c_1/c_1^{(0)})}\right)\frac{dc_1}{dx}-\frac{iM_1c_1}{Fz_1\rho^{(s)}D_{\text{eff}}}=$$
$$=\frac{i}{F(z_1-z_2)D_{23}}\left[1-\frac{(z_1-z_2)D_{23}}{z_1D_{\text{eff}}}\left(1-\frac{M_1c_1^{(s)}}{\rho^{(s)}}\right)\right]. \quad (14)$$

If the influence of the mass flux of the cations on the hydrodynamics [this influence is described by the boundary conditions (6) and (7)] were not taken into account, the transfer equation would have the form

$$\left(1+\frac{d\ln\gamma_{12}}{d\ln(c_1/c_1^{(0)})}\right)\frac{dc_1}{dx}=\frac{z_2i}{Fz_1(z_1-z_2)D_{12}}. \quad (15)$$

Comparison of Eqns.(14) and (15) shows that the effect of the mutual influence of the processes of momentum and mass transfer begin to be observed under conditions of intensive anodic dissolution, when the partial density of the cations $M_1c_1^{(s)}$ in the layer next to the anode becomes comparable with the density of the solution next to the anode $\rho^{(s)}$.

The quantitative assessment of the contribution of this effect can be carried out, without loss of generality, by examining a restricted range of concentrations close to the minimum of the function giving the dependence of $\ln\gamma_{12}$ on c_1 (for most aqueous electrolyte solutions this minimum lies at concentrations of ~1 M,[34] that is in the range where the ratio $M_1c_1^{(s)}/\rho^{(s)}$ may amount to several tens %). In this case, putting $d\ln\gamma_{12}/d\ln(c_1/c_1^{(0)})=0$ in Eqn.(14) and integrating gives

$$c_1=(c_1^{(0)}+\chi)\exp\left[-\frac{iM_1(\delta-x)}{z_1F\rho^{(s)}D_{\text{eff}}}\right]-\chi, \quad (16)$$

where

$$\chi=c_1^{(s)}+\frac{z_2\rho^{(s)}D_{23}}{M_1(z_1D_{13}-z_2D_{23})}. \quad (17)$$

Eqns.(16) and (17) can be used to obtain an equation for determining the concentration of cations $c_1^{(s)}$ next to the anode:

$$[2z_1M_1D_{13}-(z_1M_2+z_2M_1)D_{23}]c_1^{(s)}+z_2M_3D_{23}c=$$
$$=[(z_1D_{13}-z_2D_{23})M_1c_1^{(0)}+z_1(M_1D_{13}-M_2D_{23})c_1^{(s)}+z_2M_3D_{23}c]\times$$
$$\times\exp\left(-\frac{z_2iM_1\delta(z_1D_{13}-z_2D_{23})}{z_1(z_1-z_2)FD_{13}D_{23}[(z_2M_1-z_1M_2)c_1^{(s)}+z_2M_3c]}\right). \quad (18)$$

If the diffusion flux had no influence on convective ion mass transfer from the anode surface, it follows from Eqn.(15) that the equation for $c_1^{(s)}$ would have the form

$$c_1^{(s)}=c_1^{(0)}-\frac{z_2i\delta}{z_1(z_1-z_2)FD_{13}}. \quad (19)$$

Analysis of Eqn.(18) shows that the value of $c_1^{(s)}$ which it gives, for any fixed current density i, is less than the corresponding value determined by Eqn.(19). The $c_1^{(s)}(i)$ relationship described by Eqn.(18) is monotonic, and for a formally unrestricted increase in current, in contrast to Eqn.(19), it gives not an infinitely large value of $c_1^{(s)}$ but a finite asymptotic value, defined by the equation

$$c_{1\max}^{(s)}=-\frac{z_2D_{23}\rho^{(s)}}{2M_1(z_1D_{13}-z_2D_{23})}. \quad (20)$$

Fig.1 gives the $c_1^{(s)}(i)$ relationship for the dissolution of bivalent iron in aqueous 1 *N* $FeCl_2$ at $\delta=10^{-3}$ cm, and for comparison the linear graph corresponding to the absence of mass flux at the anode surface. Fig.1 shows that for a given anodic current density, the true value of the concentration of cations in the layer next to the anode is always lower than the value calculated without allowance for the mutual influence of the processes of mass and momentum transfer. An important conclusion from this result is the prediction of the possibility of achieving higher current densities (compared with those obtained within the framework of the traditional theory of convective diffusion, applicable for systems having low rates of interphase mass exchange) for a given "critical" value of the concentration of metal cations next to the anode. The existence of this "critical" value under real conditions may be related either to supersaturation of the solution or to other restrictions, for example complex formation or bulk chemical reactions, the formation of passivating films, etc.

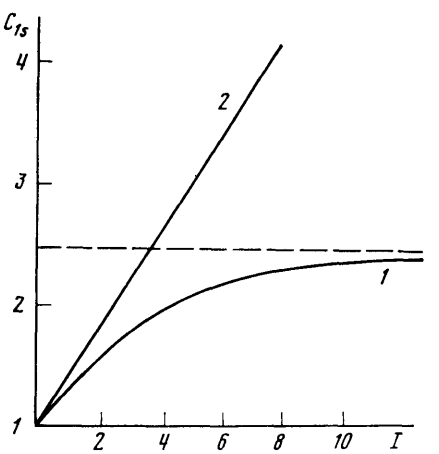


Figure 1. Dependence of the concentration of iron cations next to the anode (curve *1*) on the dimensionless current density $I=i\delta/Z_1FD_{13}c_2^{(0)}$ under the conditions of the dissolution of iron in 1 *N* aqueous $FeCl_2$ solution for $\delta=10^{-3}$ cm; the straight line corresponds to the conditions in which there is no mass flux at $x=0$ and no translational movement of the anode; $C_{1S}=c_1^{(s)}/c_2^{(0)}$.

Thus the above analysis indicates that it is necessary to take account of the interaction of the processes of mass and momentum transfer in the mathematical description of intensive electrochemical mass exchange. Estimates show that this interaction has a significant influence on the accuracy of the calculations at current densities of the order of 10 A cm^{-2} or more in molar (or more concentrated) solutions.

2. Macrokinetics of Intensive Electrochemical Mass Exchange in Solutions Containing Three Kinds of Ion

In many cases of practical interest, the process of anodic dissolution takes place in solutions containing ions of three kinds: the cations of the dissolving metal and the ions of the indifferent electrolyte. The latter is used to ensure that the electrical conductivity of the solution is sufficiently high. Since the intensive mass exchange accompanying the dissolution process can make the concentration of the cations of the dissolving metal close to the anode surface comparable with the local concentration of the ions of the indifferent electrolyte, it follows that in the equations for ionic mass transfer, even within the electricially neutral diffuse layer, it is necessary to consider the mechanism of electromigration.

It is appropriate to use the Nernst diffusion model[35] as a completely satisfactory approximation for application to the processes involved in the steady-state dissolution of surfaces uniformly accessible for mass exchange, when the local concentrations c_k and mass diffusion–migration fluxes j_k of all the ionic components of the solution depend only on the distance x to the anode surface. This model postulates the existence of a layer of a certain thickness δ next to the anode, in which the main change in the concentration of the components of the solution, limiting the rate of mass exchange, occurs.

The results obtained within the framework of the Nernst model show good agreement with the results of a theoretical analysis, based on the correct non-model allowance for the hydrodynamic conditions of mass transfer, if it is assumed that the effective thickness of the diffusion layer δ depends, in a definite manner, on the coefficient of molecular diffusion of the component being transferred. This relationship is a power dependence with exponent varying from 0.33 to 0.25 with change from laminar to turbulent mixing conditions[36]. Estimates based on the published equations[36] show that in the case of turbulent mixing conditions, the values of the thickness δ corresponding to different ionic components of the solution differ from one another by not more than 20%, if the coefficients of molecular diffusion of these components differ by a factor of not more than three. For this reason, in the examination of mass transfer in solutions containing ions of three kinds, it has been assumed[37–40] that the thickness δ is the same for all three kinds.

In the case of steady-state conditions of dissolution of a surface uniformly accessible for mass exchange, the system of equations of ionic mass transfer can be represented as follows[18]:

$$j_k = \frac{M_1 i}{z_1 F}\left(\delta_{1k} - \frac{M_k c_k}{\rho^{(s)}}\right); \quad k = 1, 2, 3. \tag{21}$$

Here, the subscript "1" for all quantities refers to the cations of the dissolving metal, and the subscripts "2" and "3" to the anions and cations respectively of the indifferent electrolyte. As before, the fluxes j_k are assumed to be positive if they are directed from the anode to the solution.

The fluxes j_k are related to the gradients of the ionic concentrations c_k and the electric potential ϕ by Onsager's equations[41]. In the case of solutions containing ions of three kinds, however, these equations contain the coefficients of mutual diffusion D_{12}, D_{13}, and D_{23}, which cannot be calculated theoretically or determined experimentally. It is therefore appropriate to examine as a first approximation the case of a sufficiently dilute solution, when it is possible to neglect the mutual influence of the ion fluxes and to approximate these fluxes by the expression

$$j_k = -M_k D_k \frac{dc_k}{dx} - \frac{z_k M_k D_k c_k F}{RT}\frac{d\varphi}{dx}; \quad k = 1, 2, 3, \tag{22}$$

where D_k is the diffusion coefficient of the ions of type k in the pure solvent, and z_k the valency of the ions. Substituting Eqn.(22) in Eqn.(21) gives the set of equations

$$\frac{dc_k}{dx} + \left(\frac{z_k F}{RT}\frac{d\varphi}{dx} - \frac{M_1 i}{z_1 F \rho^{(s)} D_k}\right) c_k + \frac{i\delta_{1k}}{z_1 D_1 F} = 0. \tag{23}$$

This set must be supplemented by the equation for the electric potential ϕ and by boundary conditions defining the values of the ion concentrations and the potential in the bulk of the solution (more accurately, beyond the limits of the diffusion layers). In the case of sufficiently high concentrations of the indifferent electrolyte, when the ratio of the effective thicknesses of the diffuse and diffusion boundary layers next to the anode is small, the Poisson equation describing the electrical field distribution can be replaced by the condition for local electrical neutrality of the solution:

$$\sum_{k=1}^{3} z_k c_k = 0. \tag{24}$$

It will be assumed that beyond the limits of the diffusion layer, the concentrations of the ions of the indifferent electrolyte are uniform, and that the concentration of the ions of the dissolving metal is equal to zero. Since outside the diffusion layer the electric field is purely ohmic, the potential can be measured from the plane $x = \delta$ (the value of the potential in the region next to the cathode can be determined if the magnitude of the ohmic electric field and the thickness of the gap between the electrodes are known). Thus the boundary conditions for the system of equations (23) and (24) can be formulated as follows:

$$c_1 = 0, \; c_2 = c_2^{(0)}, \; c_3 = -\frac{z_2}{z_3} c_2^{(0)}, \; \varphi = 0 \text{ for } x = \delta.$$

It is convenient to look for solutions using the following dimensionless variables:

$$y = x/\delta, \; C_k = c_k/c_2^{(0)}, \; \psi = F\varphi/RT, \; I = i\delta/z_1 F D_1 c_2^{(0)}, \; \xi_k = M_1 D_1 c_2^{(0)}/D_k \rho^{(s)}.$$

In these variables, the system of equations (23) and (24) has the form

$$\frac{dC_k}{dy} + \left(z_k \frac{d\psi}{dy} - \xi_k I\right) C_k + \delta_{1k} I = 0, \tag{25}$$

$$\sum_{k=1}^{3} z_k C_k = 0, \tag{26}$$

with boundary conditions

$$C_1 = 0, \; C_2 = 1, \; C_3 = -z_2/z_3, \; \psi = 0 \text{ for } y = 1. \tag{27}$$

The system of equations (25) and (26) has an analytical solution when the diffusion coefficients of all types of ion present in the solution are equal ($D_1 = D_2 = D_3 = D$). In this case, the following expressions are obtained for the distributions of the ionic concentrations and the electric potential:

$$C_1 = \frac{1}{2\xi Y}\left\{\frac{4 z_2 z_3 Y^2}{(z_1 - z_2)(z_2 - z_3)} + \frac{\xi^2 (z_1 - z_2)(z_2 - z_3)}{z_1^2}\exp\left[-2\xi I (1 - y)\right]\right\}, \tag{28}$$

$$C_2 = -\frac{2 z_1 z_3 Y}{\xi (z_1 - z_2)(z_2 - z_3)}, \tag{29}$$

$$C_3 = -\frac{\xi (z_1 - z_2)(z_2 - z_3)}{2 z_1 z_3 Y}\exp\left[-2\xi I (1 - y)\right], \tag{30}$$

$$\psi = \frac{z_2 - z_3}{2z_2z_3}\left\{\xi I(1-y) + \frac{1}{2}\ln\frac{a_1\exp[-2\xi I(1-y)] + a_2\exp[-\xi I(1-y)] + a_3}{a_1 + a_2 + a_3}\right\}. \quad (31)$$

Here, the following symbols are introduced:

$$Y = 1 - \left[1 - \xi\left(1 - \frac{z_2}{z_3}\right)\right]\exp[-\xi I(1-y)];$$

$$\xi = \frac{M_1 c_2^{(0)}}{\rho^{(s)}};$$

$$a_1 = 2 + \frac{z_3}{\xi(z_2 - z_3)} + \frac{\xi(z_2 - z_3)}{z_3}\left[1 + \frac{z_3(z_1 - z_2)(z_1 - z_3)}{4z_1^2 z_2}\right];$$

$$a_2 = -\frac{2}{\xi(z_2 - z_3)}[\xi z_2 + z_3(1 - \xi)];$$

$$a_3 = \frac{z_3}{\xi(z_2 - z_3)}.$$

When the charges of all the ions are the same ($z_1 = z_3 = -z_2 = z$). Eqns.(28)–(31) are transformed into the corresponding equations obtained in Ref.38.

As noted above, the chief difference between the equations describing the transfer phenomena in electrolyte solutions under conditions of intensive interphase mass exchange and the traditional equation of ionic mass transfer, which assumes that the hydrodynamics are independent of mass exchange, lies in the allowance for additional convective transfer, associated with the existence of the normal component of the hydrodynamic velocity at the interphase surface. The additional convective flux arises as a consequence of the influence of mass exchange on the hydrodynamics, and this process is more intense, the higher the value of the parameter ξ. To illustrate quantitatively the effect brought about by the influence of ionic mass exchange on hydrodynamics, it is possible to compare the values of the concentrations, next to the anode, of the ions of the dissolving metal $C_1(0)$ and $C_1^*(0)$ determined by Eqn.(28) for a certain finite value of ξ and for $\xi = 0$ (that is under conditions where the solution "adheres" to the anode) respectively. Table 1 gives the values of these concentrations as functions of the current density for the cases of the dissolution of bivalent iron in 1 M and 5 M aqueous solutions of a 2–2-valent indifferent electrolyte.

Table 1. Dependence of the quantities $C_1(0)$ and $C_1^*(0)$ on the anodic current density and the concentration of the indifferent electrolyte.

I	$C_1^*(0)$	$C_1(0)$		I	$C_1^*(0)$	$C_1(0)$	
		$c_2^{(0)}$=1 M	$c_2^{(0)}$=5 M			$c_2^{(0)}$=1 M	$c_2^{(0)}$=5 M
0	0	0	0	10	5.83	4.29	1.74
1	0.833	0.802	0.716	15	8.38	5.46	1.77
5	3.21	3.06	1.56	20	10.9	6.30	1.79

Table 1 shows that the existence of a mass flux of solution to the anode surface decreases the concentration gradient of the ions of the dissolving metal next to the anode. Eqns.(28) to (31) lead to the predicted[38] effect of increase in the electric field intensity close to the anode compared with conditions in which dissolution is not accompanied by the transfer of the mechanical momentum of the solution. In fact, the extent of the increase in the intensity can be characterised by the parameter τ, given by

$$\tau = (d\psi/dy)_{x=0}/(d\psi^*/dy)_{x=0},$$

where $\psi^*(y)$ is the distribution of the potential, calculated without allowance for the influence of mass exchange on hydrodynamics. In the particular case where the charges of all the ions are equal ($z_1 = z_3 = -z_2 = z$), this distribution has the form[38]:

$$\psi^* = \frac{1}{z}\ln\left[1 + \frac{1}{2}I(1-y)\right].$$

It can readily be shown that the parameter τ is always greater than unity, and with an unrestricted increase in the current density it increases according to the law $\tau = \xi I$. Table 2 gives the numerical values of the parameter τ, calculated for the dissolution of nickel in a 2 *N* aqueous solution of a 2–2-valent indifferent electrolyte.

Table 2. Influence of the mass flux of the solution at a nickel surface dissolving in 2 *N* aqueous $CuSO_4$ solution on the electric field intensity next to the anode.

I	0	1	5	10	15	20	40
τ	1.00	1.12	1.41	1.80	2.21	2.68	4.70

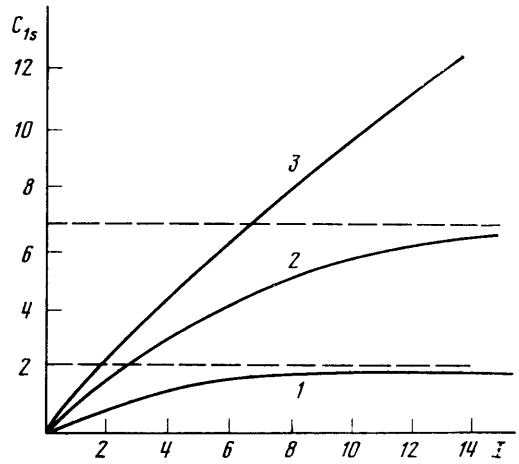


Figure 2. Concentration of nickel cations next to the anode during the dissolution of nickel in 5 *N* (curve *1*) and 1 *N* (curve *2*) aqueous $CuSO_4$ solutions; curve *3* was calculated without allowance for the influence of mass exchange on hydrodynamics; $C_{1S} = c_1^{(s)}/c_2^{(0)}$; $I = i\delta/z_1FD_1c_2^{(0)}$.

Eqn.(28) leads to the effect, described in the previous section, of "saturation" of the layer next to the anode by cations of the dissolving metal. Fig.2 gives graphs showing the change in the value of C_{1S} with change in the current density for the system $Ni^{2+}/CuSO_4$. These graphs were calculated with the assumption that the density of the solution is constant ($\rho = \rho^{(s)} = 1$ g cm^{-3}) for $\delta = 10^{-3}$ cm. According to the results obtained[32,38], the maximum deviation of the value of the concentration of nickel cations next to the anode is independent of the concentration of the indifferent electrolyte and amounts to ~9 M. Calculations show that for $\delta = 10^{-3}$ cm, the limiting value of the cation concentration can be achieved only at current densities greater than 100 A cm^{-2}. At current densities less than 10 A cm^{-2}, however, the concentration of nickel cations close to the anode, according to estimates carried out, does not exceed 0.8 M for $c_2^{(0)} = 1$ M, and 3.6 M for $c_2^{(0)} = 5$ M.

The physical factor responsible for the effect of "saturation" of the layer next to the anode is that at high anodic current densities, the rate of removal of cations from the anode by a convective transport mechanism, associated with the influence of mass exchange on hydrodynamics, becomes equal to the rate of accumulation of cations close to the anode as a result of dissolution.

3. Dissolution of the Wall of a Plane-Parallel Channel

The problem of intensive mass exchange between the wall of a circular or plane-parallel channel and a liquid flux moving along this channel is of interest from the viewpoint of the quantitative description of the elementary act of processes of dissolution and precipitation, which find extensive application in chemical and electrochemical technology. Problems of analogous type have been examined in the thermophysical literature[42–45] in connection with the analysis of systems in which gas is blown in or sucked out via a porous wall in order to intensify heat transfer. An analysis of this kind is applicable to osmotic membranes[46]: in all these cases, at the interphase boundary, there is a normal component of the hydrodynamic velocity, related either to the pressure drop on different sides of the permeable wall or to the diffusion flux of substance responsible for mass exchange. The difference between the problem of intensive electrochemical dissolution in a stream of electrolyte and the problem in which an inert medium is blown into the main stream lies in the fact that the mechanical momentum transferred to the liquid phase on dissolution is not independent of the conditions of mass exchange, as in the case where an inert medium is blown in, but is determined by the solution of the convective–diffusion problem.

A typical example of systems in which there is intense electrochemical dissolution of a metal in a stream of electrolyte is a plane-parallel channel, along which a concentrated electrolyte solution is flowing, where one of the walls of the channel (the anode) is dissolving under the influence of an electric current of high density. The dissolving surface in this case is not uniformly accessible for mass exchange, and the Nernst diffusion model is not applicable to it. Correct allowance for the contribution of convective mass transfer to the resulting rate of interphase mass exchange in this system is possible only by simultaneous solution of the system of equations of hydrodynamics and convective diffusion[47].

A plane-parallel channel $-a \leqslant x \leqslant a$ can be considered, along which a laminar flow of a solution of an indifferent electrolyte is moving in the positive direction of the z axis (the ions of this electrolyte do not take part in heterogeneous processes at the walls of the channel). It is assumed that the following quantities are given at the inlet to the channel (at $z = 0$): the average rate of flow of the electrolyte u_0, the pressure $p = p_0(x)$, the longitudinal pressure gradient $(\partial p/\partial z)_0 = \gamma_0$, and the average bulk concentration of the indifferent electrolyte c_0. It is also assumed that the wall $x = a$ consists of a metallic anode, which is dissolving under the influence of an electric current of density $i(z)$. Under real conditions, the average density $\bar{i}$ of the current flowing through the gap between the electrodes is usually fixed:

$$\bar{i} = \frac{1}{l}\int_0^l i(z)\,dz,$$

where l is the length of the channel.

It will be assumed that the concentration of the cations M^{z_1+} of the dissolving metal (z_1 is the charge of the cations) is equal to zero at the inlet to the channel, and that at the cathode surface ($x = -a$) the liquid adheres to the surface ($v_x = v_z = 0$) and there is no mass flux of the cations M^{z_1+}. It will also be assumed that in the dissolution process, the anode is kept in a fixed position (at $x = a$) by means of a special regulating device. In accordance with condition (4), the x component of the velocity of the liquid v_x at $x = a$, in the case of a stationary anode, is related to the current density i by the expression

$$v_x = -\frac{M_1 i}{z_1 \rho^{(s)} F}, \qquad (32)$$

where M_1 is the atomic mass of the dissolving metal, and $\rho^{(s)}$ the local density of the solution at $x = a$.

The steady-state conditions for the transfer of the momentum and mass of the metal cations within the channel is described by the system of Navier–Stokes, continuity, and convective diffusion equations. It is convenient to write this system of equations using the following dimensionless variables:

$$X = \frac{x}{a}, \quad Z = \frac{D_1 z}{a^2 u_0}, \quad V_x = \frac{a}{D_1} v_x, \quad V_z = \frac{v_z}{u_0},$$
$$P = \frac{D_1 p}{\mu u_0^2}, \quad C = \frac{c}{c_0}, \quad \mathrm{Re} = \frac{a u_0 \rho}{\mu}, \quad \beta = \frac{D_1}{a u_0}.$$

Here, c is the local concentration of ions of the dissolving metal, and μ the dynamic viscosity of the solution. In dimensionless variables, the system of transfer equations has the form

$$\beta^3 \mathrm{Re}\left\{V_x \frac{\partial V_x}{\partial X} + V_z \frac{\partial V_x}{\partial Z}\right\} = -\frac{\partial P}{\partial X} + \beta^3\left\{\frac{\partial^2 V_x}{\partial X^2} + \beta^2 \frac{\partial^2 V_x}{\partial Z^2}\right\},$$
$$\beta \mathrm{Re}\left\{V_x \frac{\partial V_z}{\partial X} + V_z \frac{\partial V_z}{\partial Z}\right\} = -\frac{\partial P}{\partial Z} + \frac{\partial^2 V_z}{\partial X^2} + \beta^2 \frac{\partial^2 V_z}{\partial Z^2},$$
$$\frac{\partial V_x}{\partial X} + \frac{\partial V_z}{\partial Z} = 0,$$
$$V_x \frac{\partial C}{\partial X} + V_z \frac{\partial C}{\partial Z} = \frac{\partial^2 C}{\partial X^2} + \beta^2 \frac{\partial^2 C}{\partial Z^2}.$$

This system does not take account of the influence of the gravitational field.

The mathematical analysis of the problem is simplified considerably by examining a region of the channel separated by a sufficient distance from the inlet section $z = 0$; it can be shown that for the region $z \geqslant a^2 u_0/D_1$, where D_1 is the diffusion coefficient of the ions of the dissolving metal, it is possible to omit terms containing second derivatives with respect to the coordinate Z in the original system of transfer equations. Moreover, according to condition (32), the x component of the velocity can be represented in the form

$$v_x = \frac{\bar{i} M_1}{z_1 \rho^{(s)} F} V_x = \beta \varepsilon u_0 V_x,$$

where $\varepsilon = a\bar{i}M_1/z_1 F \rho^{(s)} D_1$.

The boundary conditions for this system are:

$$V_x = -(i/\bar{i}) = -W(Z) \quad \text{for } X = 1; \qquad (33)$$

$$V_z = 0 \text{ for } X = \pm 1; \; V_x = 0 \text{ for } X = -1; \qquad (34)$$

$$P = P_0' = \frac{D_1 p_0}{\mu u_0^2}, \quad \frac{\partial P}{\partial Z} = \Gamma_0 = \frac{a\gamma_0}{\mu} \quad \text{for } Z = 0; \qquad (35)$$

$$C = 0 \text{ for } Z = 0; \qquad (36)$$

$$\frac{\partial C}{\partial X} = 0 \text{ for } X = -1; \qquad (37)$$

$$\frac{\partial C}{\partial X} = \frac{a\bar{i}}{z_1 F D_1 c_0}\left(1 - \frac{M_1 c_0}{\rho^{(s)}} C_s\right) \quad \text{for } X = 1. \qquad (38)$$

Since by definition[18] the current density i is related to the diffusion flux of the cations M^{z_1+} by the expression

$$j_1^{(s)} = -D_1\left(\frac{\partial c}{\partial x}\right)_s = -\frac{i}{z_1F}\left(1-\frac{M_1c_s}{\rho^{(s)}}\right) = \frac{\rho^{(s)}D_1}{aM_1}V_x^{(s)}\left(1-\frac{M_1c_s}{\rho^{(s)}}\right),$$

it follows that conditions (33) and (38) are essentially identical and give the relationship between the velocity and concentration profiles.

The parameter β is inversely proportional to the Peclet number, and for many systems of practical interest it is negligible compared with unity. For example, for the flow of pure water at an average velocity of 1 m s^{-1} along a channel of width 1 mm, this parameter is of the order of 10^{-6}. It is therefore possible to neglect terms containing the parameter β in the original system of equations, and to write this system in the following simplified form:

$$\frac{\partial P}{\partial X} = 0,\ \frac{\partial P}{\partial Z} = \frac{\partial^2 V_z}{\partial X^2},\ \frac{\partial V_x}{\partial X} + \frac{\partial V_z}{\partial Z} = 0,$$
$$V_x\frac{\partial C}{\partial X} + V_z\frac{\partial C}{\partial Z} = \frac{\partial^2 C}{\partial X^2}. \qquad (39)$$

To simplify the problem further and obtain a solution in analytical form, it will also be assumed that the parameter ε is small.

The numerical value of this parameter depends to a significant extent on the average anodic current density $\bar{i}$. Thus in the case of the dissolution of bivalent iron for a width of the gap between the electrodes equal to 1 mm, the parameter ε satisfies the relationship $\varepsilon \cong 0.3\,\bar{i}$, where the current density is expressed in units of A cm^{-2}; this means that for $\bar{i} < 1$ A cm^{-2}, the parameter ε can in fact be regarded as small. By representing the functions being sought in the form of the expansions

$$V_x = V_x^{(0)} + \varepsilon V_x^{(1)} + \ldots$$
$$V_z = V_z^{(0)} + \varepsilon V_z^{(1)} + \ldots$$
$$P = P^{(0)} + \varepsilon P^{(1)} + \ldots$$
$$C = C^{(0)} + \varepsilon C^{(1)} + \ldots$$

and using the boundary conditions (33)–(38), it is possible to obtain in the zeroth approximation the following solution of the hydrodynamic problem:

$$P^{(0)} = P_0^{(0)} + \Gamma_0^{(0)}Z,\ V_x^{(0)} = 0,\ V_z^{(0)} = -\frac{1}{2}\Gamma_0^{(0)}(1-X^2), \qquad (40)$$

where the quantities $P_0^{(0)}$ and $\Gamma_0^{(0)}$ are the first nonzero terms of the expansions

$$P_0 = P_0^{(0)} + \varepsilon P_0^{(1)} + \ldots,\quad \Gamma_0 = \Gamma_0^{(0)} + \varepsilon\Gamma_0^{(1)} + \ldots$$

Equating the terms linear with respect to the parameter ε in Eqns.(39) and in the boundary conditions (33)–(35) gives

$$P^{(1)} = P_0^{(1)} + \Gamma_0^{(1)}Z - \frac{3}{2}\int_0^Z d\xi \int_0^\xi W(\xi')\,d\xi',$$
$$V_x^{(1)} = -\frac{1}{2}W(Z)\left(1+\frac{3}{2}X-\frac{1}{2}X^3\right), \qquad (41)$$
$$V_z^{(1)} = (1-X^2)\left[\frac{3}{4}\int_0^Z W(\xi)\,d\xi - \frac{1}{2}\Gamma_0^{(1)}\right].$$

Analysis of Eqns.(41) shows that, for sufficiently large values of Z at least, the existence of the normal component of the hydrodynamic velocity at the surface of the anode leads to an increase in the velocity of the flux in the direction Z.

With the assumptions made, the concentration field is described by the equations

$$V_z^{(0)}\frac{\partial C^{(0)}}{\partial Z} - \frac{\partial^2 C^{(0)}}{\partial X^2} = 0, \qquad (42)$$

$$V_z^{(0)}\frac{\partial C^{(1)}}{\partial Z} - \frac{\partial^2 C^{(1)}}{\partial X^2} = -V_x^{(1)}\frac{\partial C^{(0)}}{\partial X} - V_z^{(1)}\frac{\partial C^{(0)}}{\partial Z} \qquad (43)$$

with boundary conditions

$$C^{(0)} = 0,\ C^{(1)} = 0 \quad \text{for } Z = 0; \qquad (44)$$

$$\frac{\partial C^{(0)}}{\partial X} = 0,\ \frac{\partial C^{(1)}}{\partial X} = 0 \quad \text{for } X = -1; \qquad (45)$$

$$\frac{\partial C^{(0)}}{\partial X} = J_0(Z),\ \frac{\partial C^{(1)}}{\partial X} = -C_s^{(0)}(Z) \quad \text{for } X = 1, \qquad (46)$$

where $J_0(Z) = a\bar{i}W(Z)/z_1FD_1c_0$.

The function $J_0(Z)$ in the general case cannot be regarded as small, since for any fixed value of Z it is proportional to the product of two parameters, ε and $\rho^{(s)}/M_1c_0$. The latter, even for extremly concentrated solutions (1 M and above), may be significantly greater than unity.

The extreme problems defined by Eqns.(42)–(46) are solved by the standard methods of mathematical physics. The solution obtained is very cumbersome, however, and it is not appropriate to give it here. Nevertheless, it is appropriate to analyse the asymptotic behaviour of the concentration profile for large values of the longitudinal coordinate Z under conditions of uniform distribution of the current density at the anode (J_0 = const). Using the published method[43], the solution of Eqn.(42) can be sought in the form

$$C^{(0)} = A^{(0)}Z + B^{(0)}(X), \qquad (47)$$

where $A^{(0)}$ and $B^{(0)}(X)$ are the unknown constant and function. It can readily be seen that the first boundary condition (44) cannot be satisfied by Eqn.(47). Thus the boundary condition (44) is replaced by the condition

$$J_0Z = \int_{-1}^{1} C^{(0)}V_z^{(0)}\,dX. \qquad (48)$$

This condition means that in the zeroth approximation with respect to the parameter ε, the quantity of metal cations entering the channel in unit time as a result of the dissolution of its wall is equal to the quantity of cations transferred by the flux through a given transverse cross section in the same time interval.

Substituting Eqn.(47) in Eqn.(42), integrating the latter twice with respect to X, and using the boundary conditions (45), (46), and (48) give:

$$C^{(0)} = \frac{1}{2}J_0\left\{-\frac{3}{\Gamma_0^{(0)}}Z + X + \frac{3}{4}X^2\left(1-\frac{1}{6}X^2\right) - \frac{117}{280}\right\}. \qquad (49)$$

Sine $\Gamma_0^{(0)} < 0$, the concentration $C^{(0)}$ increases linearly with distance from the channel inlet.

The correction to the concentration, associated with the existence of the normal component of the hydrodynamic velocity at the anode surface, can be found analogously. For large values of the argument Z, this correction can be sought in the form

$$C^{(1)} = A^{(1)}Z^2 + B^{(1)}(X)\,Z + G^{(1)}(X). \qquad (50)$$

Here, instead of the second boundary condition (44), it is necessary to use the condition

$$-C_s^{(0)}Z = \int_{-1}^{1}(C^{(0)}V_z^{(1)} + C^{(1)}V_z^{(0)})\,dX, \qquad (51)$$

which has the same physical significance as condition (48), but is written in a higher linear approximation with respect to the parameter ε.

Simple but cumbersome operations give the expression

$$C^{(1)} = -\frac{9}{4}\frac{J_0}{(\Gamma_0^{(0)})^2}Z^2 + \frac{3}{4}\frac{J_0}{\Gamma_0^{(0)}}Z\left\{\frac{3}{4}X^2\left(1-\frac{1}{6}X^2\right)+X-\frac{39}{280}\right\}+ \\ +\frac{1}{64}J_0\left\{-\frac{1}{8}X^8+\frac{3}{2}X^6-\frac{4}{5}X^5-\frac{669}{140}X^4-12X^3- \right. \\ \left. -\frac{443}{70}X^2+\frac{568}{35}X+\frac{519919}{333400}\right\}. \quad (52)$$

From this expression it follows that at a sufficient distance from the channel inlet, the additional convective transfer induced by interphase mass exchange leads to a decrease in the concentration of the ions of the dissolving metal next to the anode. This is illustrated by Fig.3, where the broken line corresponds to the solution of the problem of ionic mass transfer with allowance for the convective flux described above.

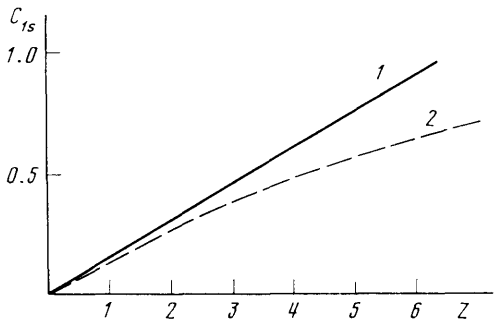


Figure 3. Theoretical profiles of the concentration of the cations of a dissolving metal next to the anode as a function of distance from the inlet to the gap between the electrodes at a given anodic current density: *1*) assuming that the liquid adheres to the anode surface; *2*) with allowance for the normal component of the hydrodynamic velocity, induced by the mass exchange.

The above analysis confirms the results obtained in the two previous sections for the dissolution of surfaces uniformly accessible with respect to mass exchange. They lead to the conclusion, important in practice, that it is possible to achieve higher current densities under conditions in which the concentration of the cations of the dissolving metal cannot, for various reasons, exceed a particular value.

IV. INFLUENCE OF DIFFUSION OF HYDRODYNAMICS UNDER CONDITIONS OF MASS TRANSFER TO THE SURFACE OF A ROTATING DISC

A disc rotating in a laminar liquid represents a typical example of a surface uniformly accessible with respect to mass exchange. Surfaces of this kind are often examined using the Nernst diffusion model[35], which makes it possible to obtain clear and simple expressions for describing the kinetics of mass transfer. In many cases, however, this model cannot reflect the quantitative aspect of the relationship between the processes of mass and momentum transfer. The reason for this is that convective mass transfer, which is essentially not included in the equations postulated by this model, not only leads to a change in the dependence of the thickness of the diffusion layer on the transport properties of the solution but also leads to a change in the actual type of mass transfer equations. For this reason, attempts have been made to develop a method which on the one hand would make it possible to take correct account of the contribution of convective mass transfer to the resulting rate of interphase mass exchange, and on the other hand could be used to estimate the accuracy of the results given by the Nernst model.

The equations of hydrodynamics for a rotating disc with allowance for the mass flux, induced by mass exchange, and the variable transport properties, have been formulated and solved for various specific cases[10–13,16,43,44,45]. The most general method of solution, based on a procedure involving "splicing" of the asymptotic expansions for the velocity field, was developed in Refs.13 and 16. The application of this method to the case of mass exchange limited by the resistance of convective diffusion in a liquid phase for large Schmidt numbers is examined below.

The Navier–Stokes equations are written in a cylindrical system of coordinates with a polar axis x passing through the centre of the disc. The property of uniform accessibility of the surface of the disc with respect to diffusion makes it possible to assume that the density ρ and kinematic viscosity ν of the solution, which depend on the concentration of the substance responsible for mass exchange, are functions only of the coordinate x. The coordinate x is replaced by the new independent variable ζ, defined by the expression

$$\zeta = \sqrt{\omega}\int_0^x \frac{dx'}{\sqrt{\nu(x')}},$$

where ω is the angular velocity of rotation of the disc. The distributions of the velocities v_r, v_ϑ, and v_x are represented in the form

$$v_r = r\omega F(\zeta),\quad v_\vartheta = r\omega G(\zeta),\quad v_x = \sqrt{\nu\omega}\,H(\zeta).$$

Substitution of these expressions in the system of Navier–Stokes equations, and simple transformations, give[49]:

$$F^2 - G^2 + HF' - F'' = F'\left(\ln\sqrt{\frac{\rho^2\nu}{\rho_0^2\nu_0}}\right)', \\ 2FG + HG' - G'' = G'\left(\ln\sqrt{\frac{\rho^2\nu}{\rho_0^2\nu_0}}\right)', \quad (53) \\ 2F + H' = -H\left(\ln\sqrt{\frac{\rho^2\nu}{\rho_0^2\nu_0}}\right)',$$

where ρ_0 and ν_0 are the values of the density and viscosity at a distance from the disc (as $x \to \infty$); the primes denote the corresponding derivatives with respect to ζ. Since the transfer equations do not contain derivatives of the function $H(\zeta)$ higher than the first derivative, it follows that one boundary condition is sufficient for the determination of this function. With allowance for the mass flux of the solution at $x = 0$, due to the movement of the centre of mass of the liquid phase as a consequence of mass exchange (see Eqn.(4)), the boundary conditions for the functions F, G, and H take the form

$$F(0) = 0,\ G(0) = 1,\ H(0) = -\sigma^3 M\left(\frac{\partial c}{\partial\zeta}\right)_s \frac{1}{\rho^{(s)} - Mc^{(s)}}, \quad (54)$$

$$F(\infty) = 0,\ G(\infty) = 0. \quad (55)$$

Here, $\sigma = (D/\nu_0)^{1/3}$, M and D are the molecular mass and diffusion coefficient of the substance being transferred, c is its local concentration, and the symbol "s" refers to the conditions at the surface of the disc.

The boundary conditions (54) show that to solve the hydrodynamic problem it is necessary to know the distribution of concentration close to the surface of the disc. At the same time, the equation of convective diffusion, which in the case of stationary conditions of mass transfer has the form

$$(\mathbf{u}, \nabla c) = D \operatorname{div} \nabla c, \qquad (56)$$

contains the hydrodynamic velocity **v**, and therefore cannot be solved independently of Eqns.(53). To find the simultaneous solution of the problem of the transfer of mass and momentum close to the rotating disc it is necessary to substitute the boundary conditions for the concentration field. It is assumed that the values of the concentration at the surface of the disc ($c^{(s)}$) and in the bulk of the solution (c_0) are given. In the case of large Schmidt numbers ($Sc = \nu_0/D \gg 1$), Eqn.(56) can be simplified by making use of the condition that the parameter σ be small. If this parameter is small compared with unity, it can be shown[49] that the concentration c depends only on the single coordinate ξ. Eqn.(56) then takes the form

$$H(\zeta)\frac{dc}{d\zeta} = \sigma^3 \frac{d^2 c}{d\zeta^2},$$

which, with allowance for the above boundary conditions, gives:

$$c(\zeta) = c^{(s)} - (c^{(s)} - c_0)\int_0^{\zeta} \exp\left\{\sigma^{-3}\int_0^{\zeta'} H(\zeta'')\,d\zeta''\right\} d\zeta' \Big/ \int_0^{\infty} \exp\left\{\sigma^{-3}\int_0^{\zeta'} H(\zeta'')\,d\zeta''\right\} d\zeta'. \qquad (57)$$

The determination of the derivative $(dc/d\zeta)_S$ from Eqn.(57) gives for the third boundary condition (54):

$$H(0) = \frac{\sigma^3 (c^{(s)} - c_0) M}{\rho^{(s)} - Mc^{(s)}} \left\{\int_0^{\infty} \exp\left[\sigma^{-3}\int_0^{\zeta} H(\zeta')\,d\zeta'\right] d\zeta\right\}^{-1}. \qquad (58)$$

The analytical solution of the system of equations (53) can be obtained by the method of "spliced" asymptotic expansions, which represent a generalisation of the boundary layer method and has been described in detail[50]. According to this method, the functions F, G, and H are sought in the form of the following expansions:

$$F = F_0(\zeta) + \sigma F_1(y) + \ldots,$$
$$G = G_0(\zeta) + \sigma G_1(y) + \ldots,$$
$$H = H_0(\zeta) + \sigma^2 H_1(y) + \ldots,$$

where $y = \zeta/\sigma$, and the functions F_0, G_0, and H_0 represent the solution of the hydrodynamic problem in the absence of mass exchange, that is for $H(0) = 0$. For $\zeta \ll 1$, these functions are given by the expressions[51]:

$$F_0 = a\zeta,\ G_0 = 1 - b\zeta,\ H_0 = -a\zeta^2,\ a = 0.51,\ b = 0.62.$$

By substituting the expansions introduced above in Eqn. (53) and equating terms with identical powers of σ, it is possible to obtain equations for the functions F_1, G_1, and H_1. These functions should satisfy the following boundary conditions for $y = 0$:

$$F_1(0) = 0,\ G_1(0) = 0,\ H_1(0) = \frac{(a/3)^{1/3} M (c^{(s)} - c_0)}{\Gamma\left(\frac{4}{3}\right)(\rho^{(s)} - Mc^{(s)})},$$

where $\Gamma(4/3)$ is the gamma function. As $y \to \infty$, the "splicing" conditions should be satisfied:

$$\lim_{y\to\infty}[F_0(\sigma y) + \sigma F_1(y)] = a\zeta,$$
$$\lim_{y\to\infty}[G_0(\sigma y) + \sigma G_1(y)] = 1 - b\zeta,$$
$$\lim_{y\to\infty}[H_0(\sigma y) + \sigma^2 H_1(y)] = -a\zeta^2.$$

Simple mathematical operations give the following result[16]: with an accuracy corresponding to terms of order σ^2, the function $H(y)$ is given by

$$H(y) = \sigma^2\left\{H_1(0) - 2a\rho_0\int_0^y\int_0^{y'} \frac{\rho(y')\sqrt{\nu(y')}}{\rho(y'')\sqrt{\nu(y'')}}\,dy''\,dy'\right\}. \qquad (59)$$

Substitution of Eqn.(59) in Eqn.(57) gives the solution to the problem of convective mass transfer. Since the quantity $H_1(0)$ is proportional to the difference $\Delta c = c^{(s)} - c_0$, that is the driving force of mass transfer, it follows from Eqns.(57) and (59) that under the conditions of intensive mass exchange, the rate of mass transfer is not a linear function of the driving force. When the values of the difference Δc are not too large, the diffusion flux $j^{(s)} = -D(dc/dx)_S$ can be represented, using Eqns.(57) and (59), as a power series in Δc. In the particular case where the physical properties are constant ($\rho = \rho_0 = \text{const}$, $\nu = \nu_0 = \text{const}$), this series has the form[13]:

$$j^{(s)} = \frac{(a/3)^{1/3}}{\Gamma\left(\frac{4}{3}\right)} MD^{2/3}\nu_0^{-1/6}\sqrt{\omega}\,\Delta c\left(1 - \frac{0.57M\Delta c}{\rho_0 - Mc^{(s)}} + \ldots\right).$$

The resulting rate of mass transfer w is determined by the sum of the contributions of the diffusion and convective mechanisms of mass transfer:

$$w = j^{(s)} + Mc^{(s)}v_x^{(s)}.$$

Use of the expressions given above for $j^{(s)}$ and $v_x^{(s)}$ gives, with an accuracy corresponding to terms quadratic in the difference Δc:

$$w = 0.62MD^{2/3}\nu_0^{-1/6}\sqrt{\omega}\,\Delta c\,\frac{\rho_0 - 0.57M\Delta c}{\rho_0 - Mc^{(s)}}. \qquad (60)$$

In the particular case where $c_0 = 0$, Eqn.(60) becomes

$$w = 0.62MD^{2/3}\nu_0^{-1/6}\sqrt{\omega}\,\Delta c\left(1 + 0.43\frac{M\Delta c}{\rho_0}\right).$$

It follows from Eqn.(60) that the existence of additional convective movement, induced by mass exchange, leads, for a given value of the driving force of mass transfer Δc, to an increase in the rate of interphase mass exchange. A measure of this increase is provided by the ratio $(\rho_0 - 0.57M\Delta c)/(\rho_0 - Mc^{(s)})$.

V. MUTUAL INFLUENCE OF THE COMPONENTS OF A GASEOUS MIXTURE ON CONDENSATION FROM A TURBULENT STREAM

Convective fluxes induced by mass exchange may also arise in systems with mass transfer in multicomponent gaseous mixtures (for example in condensation, evaporation, or rectification). These are usually called "Stefan" fluxes[2]. When Stefan fluxes are present, there is a significant change in the nature of the interaction between the components being transferred in gaseous mixtures, since this interaction may take place through the velocity field, modified by mass exchange. To illustrate this effect, it is possible to examine a multicomponent gaseous phase containing components which differ sharply in their molecular transport properties. Since the transfer of all components of this system takes place under identical hydrodynamic conditions, it is possible in principle, by obtaining quantitative information on the magnitude of the individual mass fluxes, to establish an unambiguous correlation between the effective coefficients of mass transfer for each component of the mixture and the molecular properties of all the other components. This correlation represents a

measure of the mutual influence of the substances being transported[52].

The process involved in the condensation of one component from a fully developed turbulent stream of a three-component ideal gaseous mixture on to the surface of a planar hard wall can be examined. The molecular properties of the component condensing will be denoted by the symbol "1". It will be assumed that the rate of condensation is determined entirely by the resistance of the gaseous phase. It will also be assumed that the surface of the film of condensate is uniformly accessible with respect to mass transfer and that the process of interphase mass exchange takes place under stationary conditions, that is that the concentration of each component of the gaseous phase at any fixed distance from the surface of the film is independent of time. With these conditions, the equation of convective mass transfer for any ith component of the mixture will have the following form:

$$\frac{d}{dx}\left(j_i - M_i D_t \frac{dc_i}{dx}\right) + M_i(v - V)\frac{dc_i}{dx} = 0; \quad i = 1, 2, 3. \tag{61}$$

Here, j_i is the molecular-diffusion flux of the ith component, M_i its molecular mass, c_i the molar concentration, $D_t = D_t(x)$ the coefficient of turbulent diffusion, $v = v(x)$ the velocity of the turbulent stream, averaged over the period of turbulent pulsations, and V the velocity of translational movement of the surface of the film of condensate relative to the solid wall, that is the linear velocity of growth of the condensate film. The coordinate x is measured from the surface of the film in the direction of the gaseous phase.

The relationship between the fluxes j_i and the gradients of the concentrations c_i in the case of ideal mixtures is described by the familiar Stefan–Maxwell equations. In the particular case when one of the inert, that is non-condensing, components of the mixture (for example component 3) is present in excess and it can be assumed that the conditions $c_1 \ll c_3$ and $c_2 \ll c_3$ are fulfilled, there is no direct diffusion interaction between components 1 and 2, determined by the laws of the thermodynamics of irreversible processes. In this case, the simple expressions corresponding to Fick's first law are applicable for the fluxes j_1 and j_2:

$$j_1 = -D_{13}M_1\frac{dc_1}{dx}, \quad j_2 = -D_{23}M_2\frac{dc_2}{dx}.$$

Here, D_{13} and D_{23} are the coefficients of mutual molecular diffusion in the corresponding binary mixtures.

The above-mentioned particular case of an excess of one of the inert components of the mixture will subsequently be examined, and it will be assumed that the mass transfer of components 1 and 2 takes place in a turbulent diffusion boundary layer $0 \leq x \leq d$, beyond which the concentrations of the components being transferred are distributed uniformly:

$$c_1 = c_1^{(0)}, \; c_2 = c_2^{(0)} \text{ for } x \geqslant d. \tag{62}$$

On the surface of the film of condensate, the total mass flux of the component condensing should be equal to the rate of interphase mass exchange. If the latter is denoted by I and it is assumed that the fluxes directed from the surface of the film in the direction of the gaseous phase are positive, the boundary condition for component 1 at $x = 0$ will have the form:

$$\frac{1}{M_1}j_1^{(s)} + c_1^{(s)}(v^{(s)} - V) = -I, \tag{63}$$

where the symbol "s", as before, refers to the values of the liquid–gas interface. The boundary condition for the inert component 2 is formulated analogously:

$$\frac{1}{M_2}j_2^{(s)} + c_2^{(s)}(v^{(s)} - V) = 0. \tag{64}$$

The rate of convective mass transfer, brought about by the Stefan flux, is determined by Eqn.(4) given above:

$$v^{(s)} = V + \frac{j_1^{(s)}}{\rho^{(s)} - M_1 c_1^{(s)}}.$$

Allowance for Eqns.(63) and (64) gives the following boundary conditions for the diffusion fluxes:

$$j_1^{(s)} = -M_1 I\left(1 - \frac{M_1 c_1^{(s)}}{\rho^{(s)}}\right), \tag{65}$$

$$j_2^{(s)} = \frac{M_1 M_2 c_2^{(s)}}{\rho^{(s)}} I. \tag{66}$$

It may be noted that, according to Eqn.(66), the diffusion flux of the inert component at the interphase boundary is non-zero. The physical reason for this is the existence of a non-zero normal component of the rate of movement of the centre of mass of the gaseous mixture at the interphase boundary: this component, in the case where the surface of the film is not permeable to the inert component, brings about diffusion of this component in the direction away from the surface.

To analyse Eqns.(61) it is necessary to obtain the form of the relationship $D_t(x)$ more accurately. According to general theoretical considerations[53] and published[54–58] experimental data on transport phenomena in turbulent streams, the intensity of convective mass transfer brought about by turbulent pulsations of the velocity field decreases with decrease in the distance from the solid interphase boundary approximately according to a power law with exponent lying in the range between 3 and 4. In the case of a mobile interface (liquid–gas and liquid–liquid), the effect of damping of the turbulent pulsations is much less marked: the role of stabilising factor bringing about damping in this case is played by the interphase surface tension. Experimental data[59–62] indicate that the decrease in the effective coefficient of turbulent diffusion as the mobile interphase boundary is approached, as in the case of a solid wall, takes place according to a power law, but with a smaller exponent (equal to approximately two). If allowance is made for the fact[36] that beyond a viscous hydrodynamic sub-layer of thickness δ_0 (in the range $x > \delta_0 \cong \nu/u^*$, where u^* is the characteristic velocity of turbulent pulsations in the direction perpendicular to the interphase boundary), the relationship $D_t(x) \sim x$ should be fulfilled, it is possible to write for $D_t(x)$ the following interpolation equation:

$$D_t(x) = \frac{\varkappa_1 u^* x^n}{x^{n-1} + \varkappa_2 \delta_0^{n-1}}, \tag{67}$$

where $\varkappa_1$, $\varkappa_2$, and n are empirical constants.

Estimation of the relative contribution of the terms of Eqn. (61) responsible for different transfer mechanism shows that in the layer directly adjoining the surface of the film and having a thickness δ_i defined by the expression

$$D_{i3} = D_t(\delta_i) = \frac{\varkappa_1 u^* \delta_i^n}{\delta_i^{n-1} + \varkappa_2 \delta_0^{n-1}}, \tag{68}$$

turbulent mass transfer does not play a significant role, and the rate of convective transfer brought about by the averaged velocity field in a direction perpendicular to the film surface can be approximated with a high degree of accuracy by the velocity of the Stefan flux (4). Thus within the range $0 \leq x \leq \delta_i$, the mass transfer equations (61) can be simplified considerably and written in the form

$$\frac{d}{dx}\left(j_i + \frac{M_i c_i j_1^{(s)}}{\rho^{(s)} - M_1 c_1^{(s)}}\right) = 0; \quad i = 1, 2.$$

With allowance for the boundary conditions (65) and (66), the first integral of these equations has the form

$$\frac{dc_i}{dx} = \frac{M_1 I}{M_i D_{i3}}\left(\delta_{i1} - \frac{M_i c_i}{\rho^{(s)}}\right),$$

where δ_{i1} is the Kronecker symbol. Subsequent integration gives the expression

$$c_i = \frac{1}{M_i}\rho^{(s)}\delta_{i1} + A_1^{(i)} \exp\left(-\frac{M_1 I x}{\rho^{(s)} D_{13}}\right); \quad i = 1, 2, \tag{69}$$

where $A_1^{(i)}$ represents the constants of integration.

In the ranges $\delta_i \leq x \leq d$, molecular diffusion plays no part, and convective mass transfer is brought about chiefly by turbulent pulsations, so that the transfer equations (61) can be approximated as follows:

$$\frac{d}{dx}\left\{D_t(x)\frac{dc_i}{dx}\right\} = 0; \quad i = 1, 2.$$

With allowance for Eqn.(68) and the boundary conditions (62), the following concentration profiles are obtained for the regions $\delta_i \leq x \leq d$:

$$c_i = c_i^{(0)} + \frac{A_2^{(i)}}{\varkappa_1 u^*}\left\{\ln\left(\frac{x}{d}\right) + \frac{\varkappa_2 \delta_0^{n-1}}{n-1}\left(\frac{1}{d^{n-1}} - \frac{1}{x^{n-1}}\right)\right\}, \tag{70}$$

where $A_2^{(i)}$ represents arbitrary constants, which can be found from the conditions for smooth linking of the profiles (69) and (70) at $x = \delta_i$:

$$\left(\frac{dc_i}{dx}\right)_{\delta_i - 0} = \left(\frac{dc_i}{dx}\right)_{\delta_i + 0}, \quad (c_i)_{\delta_i - 0} = (c_i)_{\delta_i + 0}.$$

Simple calculations give the following result:

$$A_1^{(i)} = \left(c_1^{(0)} - \rho^{(s)}\frac{\delta_{i1}}{M_i}\right)\exp\left(\frac{M_1 I \delta_1}{\rho^{(s)} D_{i3}}\right) \times$$
$$\times\left\{1 + \frac{M_1 I}{\rho^{(s)}\varkappa_1 u^*}\left[\ln\left(\frac{\delta_i}{d}\right) - \frac{\varkappa_2 \delta_0^{n-1}}{n-1}\left(\frac{1}{\delta_i^{n-1}} - \frac{1}{d^{n-1}}\right)\right]\right\}^{-1}. \tag{71}$$

Eqns.(69) and (71) can be used to obtain the relationship between the rate of condensation I and the concentration of the component condensing on the surface of the film $c_1^{(s)}$ (if condensation is to take place, this concentration must be equal to the saturation concentration):

$$\frac{c_1^{(s)} - \rho^{(s)}/M_1}{c_1^{(0)} - \rho^{(s)}/M_1} = \exp\left(\frac{M_1 I \delta_1}{\rho^{(s)} D_{13}}\right) \times$$
$$\times\left\{1 + \frac{M_1 I}{\rho^{(s)}\varkappa_1 u^*}\left[\ln\left(\frac{\delta_1}{d}\right) - \frac{\varkappa_2 \delta_0^{n-1}}{n-1}\left(\frac{1}{\delta_1^{n-1}} - \frac{d}{d^{n-1}}\right)\right]\right\}^{-1}. \tag{72}$$

If the molecular masses of all the components of the mixture are identical and $\delta_1 = d$ (that is within the framework of the film model), Eqn.(72) becomes the familiar Stefan equation[2] for the rate of condensation in the presence of non-condensing gases.

The nature of the "hydrodynamic" interaction between components 1 and 2 can be analysed by comparing the surface ($x = 0$) values of the concentration of the inert component 2 in the presence and absence of condensation. According to Eqns.(69) and (71), the surface concentration of component 2 is given by

$$c_2^{(s)} = c_2^{(0)} \exp\left(\frac{M_1 I \delta_2}{\rho^s D_{23}}\right) \cdot \left\{1 + \frac{M_1 I}{\rho^{(s)}\varkappa_1 u^*}\left[\ln\left(\frac{\delta_2}{d}\right) - \frac{\varkappa_2 \delta_0^{n-1}}{n-1}\left(\frac{1}{\delta_2^{n-1}} - \frac{1}{d^{n-1}}\right)\right]\right\}^{-1} \tag{73}$$

and increases sharply with increase in the rate of condensation (in the absence of condensation, that is for $I = 0$, the concentration profile $c_2(x)$ would be completely uniform). It follows from Eqns.(72) and (73) that the driving force for the transfer of component 2 from the surface of the film into the depth of the gaseous phase (proportional to the difference $c_2^{(s)} - c_2^{(0)}$) depends to a significant extent on the molecular transport properties of the condensing component 1. The nature of this relationship can be analysed for the case of the condensation of ethanol from a vapour–air mixture, formed during the convective drying of the polymer carboxymethylcellulose. The main components of the mixture are ethanol ($C_1^{(0)} = 0.1$), oxygen ($C_2^{(0)} = 0.1$), and nitrogen ($C_3^{(0)} = 0.8$). The concentrations $C_i^{(0)}$ are given in mole fractions. The temperature of the surface on which condensation takes place is 20 °C. This temperature corresponds to a saturation concentration $C_1^{(s)} = 0.058$ at atmospheric pressure[63].

The Reynolds number Re for the stream of vapour–gas mixture is 10^4 for an average linear velocity $u_0 = 10$ m s^{-1}. The coefficients of mutual diffusion of the components of the mixture are (m^2 s^{-1}): $D_{13} = 0.10 \times 10^{-4}$, $D_{23} = 0.15 \times 10^{-4}$, $D_{12} = 0.10 \times 10^{-4}$. The rate of condensation I and the difference $c_2^{(s)} - c_2^{(0)}$ were calculated using Eqns.(72) and (73) for the chosen real mixture and four hypothetical mixtures. The only difference between the latter and the real mixture was that the coefficient D_{13} was given the arbitrary values 0.06, 0.08, 0.12, and 0.14 cm^2 s^{-1}. The Schmidt numbers in all cases had an order of magnitude of unity (from 1 to 2.5). In the calculations, the parameter n was put equal to 2.

Table 3 gives the calculated values of the rate of condensation I, the concentration $c_2^{(s)}$, and the driving force of mass transfer $c_2^{(s)} - c_2^{(0)}$.

Table 3. Dependence of the kinetic characteristics of the transfer of an inert component on the coefficient of molecular diffusion of a condensing component.

D_{13}, cm^2 s^{-1}	0.06	0.08	0.10	0.12	0.14
$10^4 I$, kg mole m^{-2} s^{-1}	4.8	5.5	6.0	6.3	6.3
$10^3 c_2^{(s)}$, kg mole m^{-3}	4.73	4.77	4.80	4.82	4.84
$10^3(c_2^{(s)} - c_2^{(0)})$, kg mole m^{-3}	0.27	0.31	0.34	0.36	0.38

Table 3 shows that the difference $c_2^{(s)} - c_2^{(0)}$ increases approximately linearly with increase in the diffusion coefficient D_{13}.

VI. ELECTRODEPOSITION OF METALS FROM CONCENTRATED SALT SOLUTIONS

In the cathodic deposition of metals (in electroplating, the development of electrochemical information transformers, etc.) it is often necessary to predict the magnitude of the limiting diffusion current with respect to the discharging metal cations. This calculation is also of interest for the determination of the mechanism of the electrochemical deposition of a metal; in this case the values of the limiting current calculated for the assumed mechanism, and the experimentally measured values,

should be compared. An analogous calculation is also necessary to determine the concentration dependence of the diffusion coefficient for a known mechanism of the electrochemical reaction.

At diffusion current densities close to the limiting value, the local values of the viscosity and density of the solution, and also of the ionic diffusion coefficients close to the cathode surface, in the diffusion boundary layer, correspond to the conditions of ionic mass transfer in infinitely dilute solutions. With increase in the distance from the cathode surface, however, the local transfer coefficients and the physical properties of the solution, particularly in concentrated solutions, may differ significantly from the values next to the electrode, and this should be reflected in the profiles of the ion concentrations and the electric potential close to the electrode, and also in the magnitude of the limiting diffusion current.

The numerical calculation of the limiting current has been carried out[49] for the electrochemical deposition of copper from copper sulphate solution with allowance for the empirical concentration dependence of the diffusion coefficient of the salt. In a theoretical examination of the same process[64], but under non-stationary conditions, a linear concentration dependence of the diffusion coefficient was postulated. The calculations showed that the theoretical concentration profiles next to the electrode are in much better agreement with the experimental profiles, determined by an optical method, than the relationship given by Sand's familiar equation[65].

To derive an analytical relationship which would make it possible to carry out a more detailed comparison of theory and experimental data and to use this equation to obtain information on the effective transfer coefficients in concentrated electrolyte solutions, it is appropriate to examine the problem of ionic mass transfer to a rotating disc electrode (in this case the problem has one-dimensional geometry) with possibly a more general form of concentration dependence of the transfer properties of the solution. From an analysis of available experimental data on the viscosity ν, density ρ, and activity coefficient g of the salt, the following relationships can be postulated[66–68]:

$$\nu = \nu^s \exp\left[\frac{n}{c_2^{(0)}}(c_1 - c_1^{(s)})\right], \quad \rho = \rho^s \exp\left[\frac{m}{c_2^{(0)}}(c_1 - c_1^{(s)})\right], \quad g = g^s \exp\left[-\frac{k}{c_2^0}(c_1 - c_1^{(s)})\right]. \tag{74}$$

Here, $c_2^{(0)}$ is the bulk concentration of the anions of the salt, c_1 the local concentration of cations, the superscript "s" refers to the conditions at the interphase boundary, and n, m, and k are positive empirical constants.

Equations and boundary conditions have been derived[18], describing the transfer of cations close to the surface of a rotating disc under the conditions of the dissolution of the metal in a concentrated solution of its own salt (for example iron in $FeCl_2$ solution). The problem of the mass transfer of cations, accompanying the cathodic deposition of a metal from a binary electrolyte solution, is formulated analogously, the only difference being that there is a change in the direction of the mass flux of the particles being transferred[67]. If the cathodic current density is denoted by i, and it is assumed that $i < 0$, the equation for the transfer of the cations will have the form

$$(v - V)\frac{dc_1}{dy} - \frac{D_{eff}t(M_1D_1 - M_2D_2)}{(z_1 - z_2)FD_1D_2}\frac{d}{dy}\left(\frac{c_1}{\rho}\right) = \frac{D_{eff}M_3\nu_0^{1/6}\sqrt{\omega}}{D_1^{1/3}}\frac{d}{dy}\left(\frac{cg}{\rho\sqrt{\nu}}\frac{dc_1}{dy}\right). \tag{75}$$

Here, v is the component of the velocity of the liquid at right angles to the surface of the disc; y the dimensionless distance from the surface of the disc, related to the effective thickness of the diffusion boundary layer; V the linear rate of increase in the thickness of the deposited layer of metal; c the total molar concentration of the solution (as before, the subscript "3" refers to the solvent molecules); and D_1 and D_2 the ionic diffusion coefficients in an infinitely dilute solution.

The boundary conditions for this equation are:

$$\frac{dc_1}{dy} = \frac{z_2 i\rho^s\sqrt{\nu^s}}{z_1(z_1 - z_2)F\sqrt{\omega}D_1^{2/3}M_3c^{(s)}g^{(s)}} \quad \text{for } y = 0; \tag{76}$$

$$c_1 = -\frac{z_2}{z_1}c_2^{(0)} \quad \text{for } y = \infty. \tag{77}$$

The integration of Eqn.(75) with boundary conditions (76) and (77) can be carried out in analytical form by expanding the concentration profile as a power series in the distance y. The additional condition that $c_1 = 0$ for $y = 0$ makes it possible to obtain an expression for the limiting diffusion current i_{lim}. This expression has the form[66]:

$$i_{lim} = i_{lim}^{(0)}L, \tag{78}$$

where $i_{lim}^{(0)}$ is the value of the limiting current for the electrochemical deposition of the metal, calculated without allowance for the concentration dependence of the physical properties of the solution:

$$i_{lim}^{(0)} = z_1FD_1\left(1 - \frac{z_1}{z_2}\right)\frac{c_1^{(0)}\sqrt{\omega}}{1{,}61D_{eff}^{1/3}\nu_0^{1/6}}.$$

The coefficient L is given by the expression

$$L = \left\{1 + [0.418m + 0.089n + 0.258k + 0.281B]\frac{z_2}{z_1}\right\}\cdot\left(\frac{\nu_0\rho_0}{\nu^s\rho^s}\right)^{1/3}, \tag{79}$$

where

$$B = \sqrt{\frac{\nu^s}{\nu_0}}\frac{(z_1M_2 - z_2M_1)c_2^{(0)}}{(z_1 - z_2)\rho^s}. \tag{80}$$

Eqn.(79) shows that for $m = n = k = 0$, the coefficient L is not equal to zero, but makes a correction to $i_{lim}^{(0)}$ which is independent of the changes in the physical properties of the solution as the concentration varies and which arises as a result of the more accurate solution of the equation of convective diffusion, which includes terms quadratic in the driving force of ionic mass transfer.

Since one of the most important directions in present-day chemical and electrochemical technology is the development of the theoretical principles of transport phenomena in highly non-equilibrium systems with mass and heat fluxes which are not linear functions of the corresponding driving forces, a rigorous and systematic mathematical theory of processes of intensive mass exchange is undoubtedly urgently required. From the examples examined in the present review it is possible to obtain a picture of the fields of science and technology in which the effects of the interaction between the processes of mass and momentum transfer play the most important role, and the magnitude of these effects. Moreover, the examples given demonstrate the weakness and unsystematic character of the traditional theory of convective diffusion, developed for systems with low rates of interphase mass exchange, for the description of systems in which the hydrodynamic conditions are not an external factor, but are established under the influence of the technological conditions of the process of mass transfer.

REFERENCES

1. J.Stefan, Annalen Phys., **17**, 550 (1882); **41**, 725 (1890).
2. D.A.Frank-Kamenetskii, "Diffuziya i Teploperedacha v Khimicheskoi Kinetike" (Diffusion and Heat Transfer in Chemical Kinetics), Izd.Nauka, Moscow, 1967.
3. J.O.Hirschfelder, C.F.Curtiss, and R.S.Bird, "Molecular Theory of Gases and Liquids" (Translated into Russian), Izd.Inostr.Lit., Moscow, 1961.
4. J.C.Slattery, "Momentum, Energy, and Mass transfer in Continua" (Translated into Russian), Izd.Energiya, Moscow, 1978.
5. W.E.Ranz and P.F.Dickson, Industr.Engng.Chem. Fundamentals, **4**, 345 (1965).
6. J.L.Duda and J.S.Vrentas, Int.J.Heat Mass Transfer, **14**, 395 (1971).
7. J.Y.Parlange, Acta Mech., **18**, 157 (1973).
8. W.S.Chang, Int.J.Heat Mass.Transfer, **16**, 2275, 2283, 2290 (1973).
9. B.I.Brounshtein and G.A.Fishbein, "Gidrodinamika, Masso- i Teploobmen v Dispersnykh Sistemakh" (Hydrodynamics and Mass and Heat Exchange in Disperse Systems), Izd. Khimiya, Leningrad, 1977.
10. D.R.Olander, Int.J.Heat Mass Transfer, **5**, 765 (1962).
11. A.S.Emanuel and D.R.Olander, Int.J.Heat Mass Transfer, **7**, 539 (1964).
12. R.Unahabhokha, A.W.Nienow, and J.W.Mullin, Chem. Eng.Sci., **26**, 357 (1971).
13. A.M.Golovin, N.M.Rubinina, and V.M.Khokhrin, Teor.Osnovy Khim.Tekhnol., **5**, 651 (1971).
14. B.N.Kabanov, V.D.Kashcheev, and A.D.Davydov, Zhur.Vses.Khim.Obshch.im.D.I.Mendeleeva, **16**, 669 (1971).
15. A.E.De Barr and D.A.Oliver (Editors), "Electrochemical Machining" (Translated into Russian), Izd. Mashinostroenie, Moscow, 1973.
16. V.S.Krylov and V.N.Malienko, Elektrokhimiya, **9**, 3 (1973).
17. J.A.McGeough, Principles of Electrochemical Machining, Chapman and Hall, London, 1974.
18. V.S.Krylov, A.D.Davydov, and E.Kozak, Elektrokhimiya, **11**, 1155 (1975).
19. J.Bannard, J.Appl.Electrochem., **7**, 1 (1977).
20. Yu.S.Volkov and I.I.Moroz, Elektronnaya Obrabotka Materialov, Nos.5–6, 59 (1965).
21. A.L.Krylov, Dokl.Akad.Nauk SSSR, **178**, 321 (1968).
22. R.H.Nilson and Y.G.Tsuei, J.Appl.Mech.Trans. ASME, Ser.E, N 1, 54 (1976).
23. P.Ya.Polubarinova-Kochina, "Teoriya Dvizheniya Gruntovykh Vod" (The Theory of the Movement of Ground Water), Gostekhizdat, Moscow, 1952.
24. J.Kozak, Arch.budowy maszyn, **14**, 239 (1967).
25. A.L.Krylov, V.G.Shuster, and R.D.Eidel'man, Elektronnaya Obrabotka Materialov, No.3, 21 (1969).
26. D.E.Collett, R.C.Hewson-Browne, and D.W.Windle, J.Engng.Maths., **4**, 29 (1970).
27. R.C.Hewson-Browne, J.Engng.Maths., **5**, 233 (1971).
28. A.L.Krylov and N.I.Gavrilenko, Elektronnaya Obrabotka Materialov, No.6, 13 (1972).
29. J.M.Fitz-Gerald and J.A.McGeough, J.Inst.Math. Applic., **5**, 387 (1969).
30. J.M.Fitz-Gerald, J.A.McGeough, and L.McL.Marsh, J.Inst.Math.Applic., 5, 409 (1969).
31. V.S.Krylov and A.D.Davydov, "Trudy V Vsesoyuznogo Soveshchaniya po Elektrokhimii" (Proceedings of the Fifth All Union Conference on Electrochemistry), Izd.VINITI, Moscow, 1974, p.216.
32. V.S.Krylov, in collected papers "Razmernaya Elektrokhimicheskaya Obrabotka Detalei Mashin" (Collected Papers on the Three-dimensional Electrochemical Machining of Machine Parts), Izd.Tul'skogo Politekhn.Inst., Tula, 1975, p.15.
33. V.S.Krylov, Elektrokhimiya, **12**, 843 (1976).
34. R.A.Robinson and R.H.Stokes, "Electrolyte Solutions" (Translated into Russian), Izd.Inostr.Lit., Moscow, 1963.
35. W.Nernst, Z.phys.Chem., 2, 613 (1888).
36. H.Schlichting, "Boundary Layer Theory" (Translated into Russian), Izd.Nauka, Moscow, 1969.
37. V.S.Krylov, A.D.Davydov, and V.N.Malienko, Elektrokhimiya, **8**, 1461 (1972).
38. V.S.Krylov, Elektronnaya Obrabotka Materialov, No.4, 10 (1976).
39. V.S.Krylov and A.D.Davydov, Zashchita Metallov, **13**, 90 (1977).
40. V.S.Krylov, Elektrokhimiya, **13**, 103 (1977).
41. L.Onsager, Annalen, N.Y.Acad.Sci., **46**, 241 (1945).
42. S.W.Yuan and A.B.Finkelstein, J.Heat Transfer, Trans.ASME, Ser.C, **78**, 719 (1956).
43. E.M.Sparrow and J.L.Gregg, J.Heat Transfer, Trans.ASME, Ser.C, **82**, 294 (1960).
44. D.R.Olander, J.Heat Transfer, Trans.ASME, Ser.C, **84**, 185 (1962).
45. S.W.Yuan, in C.C.Lin (Editor), "Turbulent Flow and Heat Transfer" (Translated into Russian), Izd. Inostr.Lit., Moscow, 1963, p.468.
46. S.M.Ross, J.Fluid Mech., **63**, 157 (1974).
47. V.S.Krylov, G.R.Engel'gardt, and Yu.N.Petrov, Elektronnaya Obrabotka Materialov, No.1, 20 (1978).
48. R.B.Bird, W.E.Stewart, and N.E.Lightfoot, "Transport Phenomena" (Translated into Russian), Izd. Khimiya, Moscow, 1974.
49. J.Newman and L.Hsueh, Electrochim.Acta, **12**, 417 (1967).
50. M.Van Dyke, "Perturbation Methods in Fluid Mechanics" (Translated into Russian), Izd.Mir, Moscow, 1967.
51. T.Karman, Z.angew.Math.und Mech., **1**, 233 (1921).
52. V.S.Krylov, V.E.Bogoslovskii and N.N.Mikhnevich, Zhur.Prikl.Khim., **49**, 1769 (1976).
53. B.A.Kader and A.M.Yaglom, Int.J.Heat Mass Transfer, **15**, 2329 (1972).
54. P.Harriott and R.M.Hamilton, Chem.Eng.Sci., 20, 1073 (1965).
55. D.W.Hubbard and E.N.Lightfoot, Industr.Engng.Chem. Fundamentals, **5**, 370 (1966).
56. J.S.Son and T.J.Hanratty, A.I.Ch.E.Journal, **13**, 689 (1967).
57. A.A.Gukhman and B.A.Kader, Teor.Osnovy Khim. Tekhnol., **3**, 216 (1969).
58. K.K.Sirkar and T.J.Hanratty, Industr.Engng. Chem.Fundamentals, **8**, 189 (1969).
59. I.A.Gil'denblat, A.L.Lashakov, S.A.Krasheninnikov, and A.I.Rodionov, Teor.Osnovy Khim.Tekhnol., **3**, 305 (1969).
60. I.A.Gil'denblat, A.I.Rodionov, and A.L.Lashakov, Teor.Osnovy Khim.Tekhnol., **3**, 344 (1969).
61. G.N.Chernykh, V.A.Malyusov, and N.A.Malafeev, Teor.Osnovy Khim.Tekhnol., **3**, 776 (1969).
62. I.A.Gil'denblat, A.I.Rodionov, and B.I.Demchenko, Teor.Osnovy Khim.Tekhnol., **6**, 10 (1972).
63. V.N.Stabnikov, "Peregonka i Rektifikatsiya Spirta" (Distillation and Rectification of Alcohol), Pishchepromizdat, Moscow, 1962.

64. F.R.McLarnon, R.H.Muller, and C.W.Tobias, Electrochim.Acta, **21**, 101 (1976).
65. H.J.S.Sand, Z.phys.Chem., **35**. 641 (1900).
66. A.D.Davydov, G.R.Engel'gardt, and V.S.Krylov, Elektrokhimiya, **13**, 458 (1977).
67. G.R.Engel'gardt, V.S.Krylov, and A.D.Davydov, Zashchita Metallov, **13**, 606 (1977).
68. G.R.Engel'gardt, A.D.Davydov, and V.S.Krylov, Elektrokhimiya, **14**, 812 (1978).

Institute of Electrochemistry,
Academy of Sciences of the
USSR, Moscow

Translated from *Uspekhi Khimii*, 49, 147-170 (1980) U.D.C. 543.253

Extraction Polarography and Its Analytical Applications

G.K.Budnikov and N.A.Ulakhovich

The review is devoted to extraction polarography as a method for the determination of microelements. The possibilities of polarography in combination with a preliminary chemical separation of the elements by extraction are discussed. The types of extraction-polarographic systems known at present are described. It is shown that the selectivity of extraction separations increases if the reagents form complexes with the ions to be determined, which are manifested by effects on the polarisation curves at different potentials. The influence of extracting and ionising solvents on the analytical signal is examined from the standpoint of modern ideas of the chemistry of coordination compounds in non-aqueous media. Examples of the use of extraction polarography for the determination of microelements are presented.
The bibliography includes 116 references.

CONTENTS

I. Introduction 74
II. The role of the organic solvent in extraction polarography 75
III. Types of extraction-polarographic systems 77
IV. The use of extraction polarography in the determination of metals 79

I. INTRODUCTION

The usefulness of the preliminary concentration, by extraction in the form of complexes of the metal ions to be determined, has begun to attract attention recently. The metals are determined directly in the organic extracts[1-4]. The combination of separation and concentration with subsequent determination by physicochemical methods has proved to be one of the most promising fields in chemical analysis. In many instances such combination has become so intimate that it is possible to distinguish a new category of analytical methods which have been called hybrid[3].

Extraction-photometric, extraction-spectroscopic, extraction-polarographic and extraction-radioactive methods as well as extraction chromatography and extraction emission and atomic-absorption flame photometry can be included among the hybrid methods. The simultaneous application of concentration by extraction and of a sensitive apparatus greatly extends the scope of analytical methods. The selectivity of the analysis can be varied both as a function of the type of extraction system (reagent, acidity of the phase, etc.) and as a function of the method of measurement of the analytical signal. The use of a hybrid method in which preliminary extraction determines the absolute and relative concentrations of microelements in combination with an appropriate detection method permits in certain cases the analysis of multicomponent systems. Extraction polarography is one such method.

The present review surveys the results of studies in the field of extraction polarography during the last five years. The first investigations up to 1971 have been summarised in a familiar monograph[1] and also in a review[5]†. Since then the number of publications on extraction polarography has increased continuously. The interest in this method is explained by its universality, simplicity, the rapidity of analysis, the possibility of the simultaneous determination of a group of elements, and the lack of the need for re-extraction with associated inevitable losses.

The polarography is carried out by different methods. The use of versions such as oscillographic and a.c. polarography and catalytic hydrogen currents greatly enhances the scope of the extraction-polarographic methods. In examining the possibilities and advantages of the direct polarography of the extracts, one should note the first studies carried out by amalgam polarography with accumulation[11-15]. In this case concentration of the metal on the stationary electrode was achieved by electrolysing the solution of the test metal (in the form of a complex in an organic solvent). The essential feature of the method of extraction polarography with accumulation consists in the determination of traces of elements directly in the extracts. In this case one carries out a double concentration—by extraction and electrochemically[16-20].

However, the possibilities of the extraction-polarographic methods have been by no means exhausted—one should note in the first place an empirical approach to the selection of both the reagents for the binding of the metal in a complex and of the polarographic conditions as well as the method of recording the polarisation curves itself. The medium in which the polarography is carried out consists of at least two solvents. One of these is used to extract the metal in the form of a complex and the other to ensure the solubility of the supporting electrolyte and the conductivity of the medium. Consequently the second component must have a fairly high dielectric constant. The ratio of these components influences the analytical signal.

The combination of extraction and polarography gives rise to new possibilities and advantages. For example, the employment of non-aqueous solvents for polarography extends the range of potentials in which experiments can be performed as well as the range of values of $E_{1/2}$ for the reduction of ions bound in complexes. Hence it follows that the study of the influence of the nature of the solvent is an essential stage in the development of extraction-polarographic methods.

A conscious choice of rational conditions for extraction-polarographic determinations is impossible without knowing the electrochemical properties of the corresponding complexes. The knowledge of the mechanism of the electrode process permits rational extraction-polarographic determinations with recording of the maximum possible analytical signal. It is then possible to employ specifically polarographic characteristics such as the reversibility of the reduction, the maximum number of electrons involved in a particular stage, the adsorbability and associative accumulation of the substance on the surface of the electrode, and other ways of increasing the sensitivity and selectivity.

†The work of the Kiev School of Analytical Chemistry[6-10] has made a definite contribution to the development of the extraction-polarographic methods.

Only after such studies is a foundation laid for the selection of the optimum polarographic conditions ensuring a fairly low concentration limit in the determination and a high selectivity of extraction-polarographic analyses.

II. THE ROLE OF THE ORGANIC SOLVENT IN EXTRACTION POLAROGRAPHY

The solution for polarography must have a fairly high conductivity. However, extracts are not as a rule electrolytes. It is therefore necessary to add to the extract solvents with a high dielectric constant containing a specific amount of supporting salts, ensuring a high conductivity. Thus homogeneous mixtures of extracting and ionising solvents are used in extraction polarography. The ratio of the mixture components is determined by the solubility of the extracted complex and of the supoorting salt. In terms of their electrical conductivity, such systems are not inferior to the traditional polarographic electrolytes[1].

The nature of both the extracting and ionising organic solvents can influence the stability of the complexes formed in the "metal ion–organic reagent" system. However, in most cases the depolariser is the metal chelate with a fairly high stability. The complex formation equilibrium and hence the question of the predominance of a particular complex species in the polarographed extract are not of decisive importance. This is particularly valid in relation to a large group of the so-called inert complexes. In order to solve problems associated with the increase of the selectivity and sensitivity of the analysis, it is necessary to make a rational choice of the extracting solvent, since it influences the parameters of the polarographic waves and hence the analytical signal. The most important factor for the analytical chemist is information about the properties of the limiting current recorded on the voltamperograms as a function of the nature of the organic solvent.

Table 1. The properties of extracting and ionising solvents at 20 °C.

Solvent	ε	η, cP	DN($SbCl_5$)[28]	Solvent	ε	η, cP	DN($SbCl_5$)[28]
Extracting solvents				Extracting solvents			
Benzene	2.28	0.70	4.9	Ethyl acetate	6.40	0.47	17.1
Toluene	2.38	0.63	—	Butyl acetate	5.01	0.73	—
m-Xylene	2.36	0.62	—	Pentyl acetate	4.75	0.92	—
Chloroform	4.80	0.59	—	Isopentyl alcohol	15.64	4.8	—
Carbon tetrachloride	2.24	—	—	Ethyl methyl ketone	18.51	0.42	—
				Butyl alcohol	17.0	3.37	29.0
Ionising solvents				Ionising solvents			
Acetonitrile	38.80	0.34	14.1	Methyl alcohol	33.60	0.54	19.0
Acetone	21.24	0.30	17.0	Ethyl alcohol	25.80	1.09	—
Dimethylformamide	37.65	0.79	26.6	Formamide	111.50	3.76	39.1
Dimethyl sulphoxide	48.90	1.96	29.8				

The physical constants of the most important solvents of both types are listed in Table 1. The influence of the nature of the extracting solvent on the height of the polarographic waves (i_{lim}) has been studied in relation to hydroxyquinolinates[7], benzoylphenylhydroxylaminates (BPHA),[9] *N*-cinnamoylphenylhydroxylaminates (CAPHA),[21] 4-benzoyl-3-methyl-1-phenyl-5-pyrazolonates[22], dithiocarbamates (DTC),[23–27] ethylxanthates (EXT),[25,26] dithiophosphates (DTP),[26,27,29] 8-mercaptoquinolinates[30,31], and tri-n-octylaminates (TOA).[32]

Useful information about the influence of the solvent on the reduction process can be obtained by comparing the polarographic characteristics of the complexes in aqueous (whenever possible) and non-aqueous media. The height of the reduction wave of copper(II) ions in the presence of 8-hydroxyquinoline in a non-aqueous solution (a mixture of toluene and methanol) is almost twice as high as in an aqueous solution[6]. The change in the limiting current in non-aqueous solvents compared with water is attributed to the change in the viscosity of the solution, which influences the diffusion coefficient of the depolariser[6]. However, such a difference between the values of i_{lim} is not always a consequence of the influence of the viscosity of the medium alone. Whereas in an aqueous solution copper(II) is reduced in the form of the aquo-ion, in the toluene–methanol system being compared it is reduced as the 8-hydroxyquinoline complex. One cannot agree with the postulate[6] that the complex dissociates prior to the electrode process: like other chelate complexes, the 8-hydroxyquinolinates usually do not dissociate in organic solvents[34]. It is therefore also impossible to account for the difference between the diffusion current constants by the non-identical electrochemical behaviour of the depolariser in aqueous and non-aqueous media, which should be reflected, like the viscosity of the solution, in the diffusion coefficient. For this reason, the use of non-aqueous media can apparently entail in many instances a decrease of i_{lim} compared with an aqueous medium[12,13].

In order to elucidate the influence of the nature of the organic solvent, it is more useful to investigate the same complex in different extracting solvents. The viscosities of the pure extracting solvents can be used to establish the relation between the viscosity of the solution and the limiting current for the reduction of the complex. The ionising solvent must be the same under these conditions and the ratio of the extracting and ionising solvents must be constant. Such a study has been made by Pyatnitskii and Ruzhanskaya in relation to copper, lead, and iron hydroxyquinolinates[7] and copper, iron, and indium benzoylphenylhydroxylaminates[9]. The results showed that the nature and properties of the solvent (Table 1) have a considerable influence on the height of the polarographic waves and hence also on the lower limit of the determination. In the general case the wave height diminishes with increasing viscosity of the solvent, which is due to the familiar inverse proportionality between the diffusion coefficient and the viscosity of the medium (η). On the other hand, the viscosity factor is not always decisive, because the product $i_{lim}\eta^{1/2}$ is not constant in many instances. A similar phenomenon has been observed, for example, in the reduction of metal complexes of CAPHA in mixed organic solvents[21]. Data concerning the influence of the nature of the extracting solvent on i_{lim} for the waves due to the metal complexes of dithiocarbamic, dithiophosphoric, and xanthic acid derivatives[23–27] show that the change in i_{lim} is related not only to the viscosity of the solvent but also to its capacity to solvate the depolariser species. The change in the degree of solvation of the complexes leads to the formation of solvates whose diffusion coefficients differ greatly and this is also reflected in the values of i_{lim}. The decrease of the limiting current for the reduction of iron(III) and zinc(II) dimethyldithiocarbamates in the sequence ethyl acetate > butyl acetate > pentyl acetate is probably associated with the fact that the complex solvated by ethyl acetate molecules is smaller than in pentyl acetate[23]. The increase of the size of the solvate in the above sequence entails a decrease of the diffusion coefficient of the complex. The highest limiting

current in the determination of metals as their complexes with organic ligands can be attained in the polarography of benzene extracts.

On passing to chelates of metals whose ions are more highly solvated (copper and cadmium), the change in i_{lim} with the change in the nature of the solvent is more distinct. For example, cadmium complexes of DTC in solutions in aromatic hydrocarbons in the presence of 0.2 M lithium perchlorate in methanol as the supporting electrolyte are reduced reversibly, whereas in acetate esters and in dimethylformamide (DMF) the reduction is irreversible[24] (Fig. 1). The tendency towards an increase of i_{lim} on passing from DMF to aromatic hydrocarbons is observed also for other dithiocarbamate complexes, but in the case of cadmium chelates the difference between the currents i_{lim} is particularly notable. This behaviour is associated with the strong solvating capacity of DMF.

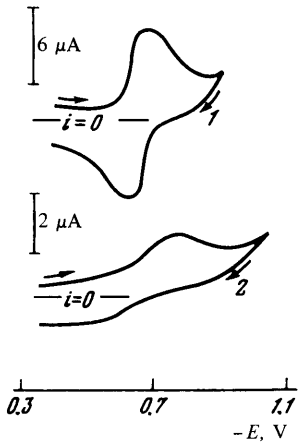


Figure 1. Oscillopolarograms of a 5×10^{-4} M solution of cadmium dibutyldithiocarbamate in an ethanol–benzene mixture (curve *1*) and dimethylforamide (curve *2*); supporting electrolyte—0.2 M lithium perchlorate[24].

Another parameter of the voltamperogram to which attention should be paid in selecting the solvent, the type of reagent for chelating the metal, and other analytical conditions is the velocity constant for charge transfer k_S, which determines the reversibility of the electrochemical system[35]. When $k_S > 10^{-2}$ cm s^{-1}, the electrochemical equilibrium at the electrode is fairly mobile during the recording of the voltamperogram. If there are no intermediate chemical stages, deactivating the electron addition product, then under these conditions the discharge is reversible. By selecting the appropriate organic solvent, it is possible to increase the stability of the electron transfer products and to ensure suitable conditions for the recording of curves with the aid of a.c. polarography. It is impossible to extend greatly the number of reversible electrochemical reactions at the electrode compared with an aqueous medium.

The different degrees of reversibility of the waves due to the complexes are caused by the nature not only of the central atom but also the ligand. Thus in the reduction of iron(III) dithiocarbamates[23] and xanthates[28] in aromatic hydrocarbons the wave corresponding to the transfer of the first electron to the complex species is reversible only in the former instance. The polarographic waves of metal xanthates obtained under the same conditions are as a rule less reversible than those for the dithiocarbamates. The differences in the reversibility of the reduction waves of metal dithiocarbamates and xanthates can be explained by the more marked ability of the xanthates to form comparatively stable solvates for which a slow charge transfer in the electrochemical stage proper is observed. The reduction of the copper(II) complex of CAPHA in oxygen-free extracting solvents is also reversible; in isopentyl and hexyl alcohols the process is irreversible[21]. The irreversible reduction of the complex in carbon tetrachloride is an exception. It has been noted that, on passing to ethyl acetate, the reduction takes place with consumption of one electron. The slow electron transfer has been explained[21] by the adsorption of organic solvent molecules on the surface of the electrode.

The choice of a suitable ionising solvent to increase the sensitivity of the metal also merits attention. Various ionising solvents have been compared[7] (for the same extracting solvent) in relation to 8-hydroxyquinolinates: methanol, DMF, dimethyl sulphoxide (DMSO), and formamide; they differ from one another by their dielectric constants (ε) and viscosities. Analogous studies were made later for metal xanthates[28]. The replacement of methanol by another ionising solvent with a greater solvating capacity leads to a decrease in the height of the wave. On passing to solvents with a greater solvating capacity (DMF, DMSO), the change in i_{lim} becomes more appreciable. The fact that in solvents with similar viscosities the limiting current for the reduction of metal chelates is greater for the solvent with a lower donor number is striking[24]. Furthermore, when ethanol, the viscosity of which is greater than that of DMF (Table 1), is used as the ionising solvent, the i_{lim} observed for the xanthates is approximately twice as great as the current obtained in DMF.

Attempts have been made to explain from different standpoints the influence of the solvent on the parameters of the electrode process[36]. The replacement of one solvent by another can entail an appreciable change in the energy of the activated state, while the energy of the initial state of the chelate remains almost the same. This situation leads to an increase in activation energy for the reaction, i.e. to a decrease of the rate of charge transfer (a decrease of k_S).

On solvation, solvent molecules can enter the inner coordination sphere (particularly for a coordination-unsaturated complex) or remain bound to the complex, occupying a second coordination sphere[36]. In the former case the reduction of the complex is apparently less reversible than in the latter.

In studies of the influence of the organic solvent, both extracting and ionising, on the ease of reduction of complexes attempts have frequently been made to establish a correlation between $E_{1/2}$ and the dielectric constants[7,9,23]. The results of the study of hydroxyquinolinates[6], benzoylphenylhydroxylaminates[9], and dithiocarbamates[23] have shown that, when the solvent is changed, the values of ε are altered somewhat, but a consistent relation between them and the dielectric constants ε (Table 1) is not observed. Nor is there an appreciable change in the differences between the reduction potentials of the metal ions and their sequence. One should note that the displacement of the half-wave potential $E_{1/2}$ along the potential axis when the solvent is altered can be associated with the change in the interphase potential. In estimating the half-wave potential shift under the influence of the solvent, one must also take into account the adsorption of the depolariser[37].

It is of interest to examine the influence of the ratio of the volumes of the extracting and ionising solvents on the characteristics of the polarographic waves. The change in the

volume of the extracting solvent with a low viscosity and a slight solvating capacity (toluene, *m*-xylene, benzene) has almost no influence on the height of the polarographic waves of metal 8-hydroxyquinolinates[7,9], while the increase of the fraction of the extracting solvent with a greater viscosity and a satisfactory solvating capacity (butyl and isopentyl alcohols and cyclohexanone) leads to a decrease of i_{lim}. In order to ensure a better conductivity of the solution, it is sometimes necessary to increase the fraction of the ionising solvent, as happened in the reduction of the indium(III) complex of TOA,[32] the copper(II) complex of dithizon[38], and the molybdenum(VI) complex of BPHA.[39] The influence of η and ε of the extracting solvent is hardly manifested in this instance. The application of the method of differential oscillographic polarography makes it possible to do without ionising solvents altogether. In this method there is no need for a high conductivity of the solution. The low solubility of the supporting electrolyte in the extracts used in the study[40] (butyl and isobutyl alcohols, ethyl methyl ketone, and butyl methyl ketone) nevertheless proved sufficient to permit measurements.

From a practical point of view, solvents with high viscosities and high donor numbers are less convenient, since a rigorous control of the ratio of their volumes is then essential.

III. TYPES OF EXTRACTION-POLAROGRAPHIC SYSTEMS

An effective combination of extraction and voltamperometric methods necessitates a comprehensive knowledge of the characteristics of the electrochemical reactions of metal chelates in the extracting solvents or their mixtures. The general principles by which one must be guided in choosing the polarographic conditions for the solution of chemical-analytical problems can be easily examined in relation to the reduction of a large number of metal complexes with reagents containing different donor atoms in functional-analytical groups.

It is preferable to extract elements in the form of inner complexes and chelates, for which electrochemical processes are less complicated by the preceding and subsequent chemical reactions which influence both on the shape of the waves and their position along the potential axis. Furthermore, chelates are uncharged, which reduces the degree of their solvation and creates suitable conditions for increasing the analytical signal. This is why there is no slackening of interest at the present time in the traditional chelating extractants.

Among the metal chelates extracted by organic solvents, derivatives of dithio-acids and 8-hydroxyquinoline are used most frequently, in practice, as already mentioned. This is associated not only with the ready availability of the reagents but also with the fact that a very wide range of metals generate a current proportional to the metal concentrations in their presence during both electrochemical reduction and oxidation. The conditions for the electrode reactions can then be modified by varying the ratio of the extracting and ionising solvents and by slecting the supporting electrolyte, which makes it possible to apply different versions of polarography for the recording of the analytical signal.

The possibility of the polarography of certain metal dialkyldithiocarbamates in the chloroform–methylcellosolve–water ternary mixture was noted above. Methylcellosolve functions in this instance as a homogeniser for the system, chloroform is the extractant, and water creates conditions suitable for conductimetric measurements[41-43]. However, the use of this system is limited by the comparatively narrow region corresponding to the polarisation of the mercury dropping electrode (m.d.e.)—below −0.8 V relative to the saturated calomel electrode (sat.c.e.). The use of dioxan, dichloroethane, and formamide, in which there is a wide range of cathodic polarisations, in polarographic analysis of chelates involves certain difficulties. In electrochemical reduction in these solvents and their mixtures one frequently records rather indefinite voltage–current curves, which are unsuitable for analysis[7,9]. For many 8-hydroxyquinoline[7] and benzoylphenylhydroxylamine[9] complexes, it has been impossible to observe reduction waves under these conditions.

This is the reason why a search has been made for a solvent system which should not be inferior to chloroform in its capacity to dissolve chelates but would ensure the recording of readily reproducible voltage–current curves, suitable for the measurement of the potential and the current. Such a system is apparently provided by a mixture of aromatic hydrocarbons or acetate esters with methanol, which is added to dissolve the electrolyte salt (ionising solvent). Solvents of the benzene and acetate ester series dissolve readily the majority of complexes with organic ligands, are infinitely miscible with ionising solvents[1,7,13], and are polarographically inactive over a wide range of potentials[7-9]. Furthermore benzene and its analogues have a low solvating capacity (see above), which increases the reversibility of the process and makes it possible to increase the sensitivity of the determination by employing a more effective apparatus. The shape of the voltage–current curves depends significantly also on the concentration of the depolariser, in consequence of its adsorption activity. It has been established for metal complexes of dithiocarbamic acid derivatives that the adsorption phenomena observed in the polarography of such systems are determined by the solubility of the chelates in the given solvent and the position of the polarisation curve relative to the potential axis. The electrochemical reduction of complexes of a large group of metals (Tl, Pb, Cu, Hg, Cd, and Bi) takes place at the m.d.e. near the electrocapillary zero, where complex species with organic ligands are adsorbed to the greatest extent.

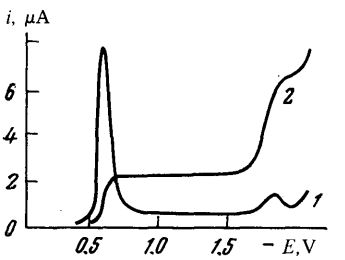


Figure 2. A.c. (curve *1*) and classical (curve *2*) polarograms of a 5×10^{-4} M solution of iron dimethyldithiocarbamate in a benzene–ethanol mixture; supporting electrolyte—0.2 M lithium perchlorate[23].

Thus, in selecting the extraction-polarographic system preference should be given to chelating agents and solvents which would make the electrochemical process reversible to the maximum extent. The presence of at least one reversible stage in the electrode reaction makes it possible to use a.c. polarography for the recording of the analytical signal[23].

The set of the data available at present permits a well-founded approach to the selection of not only the solvent but also of the extraction reagents. The choice of the ligand depends on the problem formulated and the objects of the analysis. If there is a need for an increased sensitivity of the analysis one can recommend dithiocarbamates as extraction reagents, because their complexes are reduced irreversibly in most instances, which makes it possible to employ a.c. polarography for the recording of voltage–current curves[23]. The analytical signals recorded with the aid of classical and a.c. polarography are compared in Fig.2. For extraction from hydrochloric acid solutions, dithiophosphates, which are stable under the given conditions in contrast to dithiocarbamates, are of greatest interest. This is especially important for the determination of elements such as bismuth, antimony, and arsenic, which are almost completely bound in complexes with dithiophosphates only when the acidity of the solution is high[29]. The extraction and hence the polarographic process can be made selective under these conditions by choosing an appropriate pH. Fig.3 presents the dependence of the extractability of metal dithiophosphates on pH in extraction with toluene.

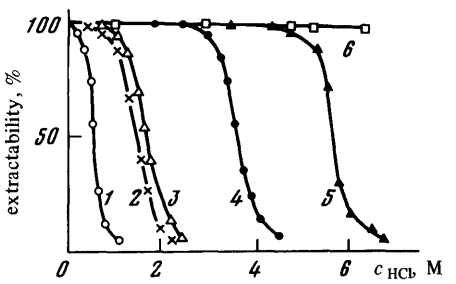


Figure 3. Dependence of the extractability of metal diethyl dithiophosphates on the acidity of the medium: 1) cadmium; 2) cobalt; 3) nickel; 4) lead; 5) bismuth; 6) arsenic[29].

When the complexes are extracted jointly, the polarographic method permits a separate determination of the elements in the same solution. For example, in the extraction of cobalt(II), nickel(II), and zinc(II) dithiophosphate complexes it is impossible to select a pH range where they would be separated, but the polarograms of the solutions in benzene (toluene)–ethanol mixtures shows distinct waves of the metal complexes at different potentials[29] (Fig.4).

Another way of increasing the selectivity in the determination of metals involves the use of metal complexes as extractants. There are very few examples of this type of application of complexes and these refer mainly to dithiocarbamates. The stability of metal complexes of DTA decreases in the sequence Hg(II) > Pd(II) > Ag(I) > Cu(II) > Tl(III) > Ni(II) > Bi(III) > Pb(II) > Co(III) > Cd(II) > Zn(II) > Tl(I) > Sb(III) > Fe(III) > Te(IV) > Mn(II).[44,45] With the aid of this stability series, it is possible to select a complex capable of participating in the extraction exchange with the metal to be determined[46]. Such an extractant complex can consist of a metal complex less stable than the complex of the element to be determined. A necessary condition governing the choice of the extractant is also its ability to be reduced or oxidised in a potential range different from the corresponding range for the dithiocarbamate of the element to be determined. In the determination of palladium(II) this requirement is met by copper(II) dithiocarbamate[47], which is reduced in a 2 : 3 toluene–ethanol mixture at a potential of −0.3 V relative to liquid mercury at the bottom of the cell. When a toluene solution of copper(II) diethyldithiocarbamate is added to an aqueous solution containing palladium(II) ions as well as ions of other elements, palladium(II) is almost completely extracted; other elements are not extracted, which is established on the basis of the absence of the waves of their dithiocarbamates from the polarograms. The copper(II) diethyldithiocarbamate complex has been used as the extractant in the determination of palladium(II) in a combined metallation electrolyte[47].

Zinc(II) diethyldithiocarbamate has been used as an extractant to determine microamounts of copper[48]. Down to 8.5 μg kg^{-1} of mobile copper in the soil can be determined from anodic voltamperograms obtained at a rotating graphite disc electrode in a 2 : 3 toluene–acetone mixture[48]. In procedures based on extraction-exchange reactions the determination is not always carried out directly in the organic extracts. Thus the extraction exchange between the bismuth(III) diethyldithiocarbamate complex in carbon tetrachloride and mercury(II) in an aqueous bromide solution is completed by the equivalent transfer of bismuth(III) to the aqueous phase. Its subsequent determination by inversion voltamperometry ensures a lower limit of detection down to 0.003 μg ml^{-1}.[49]

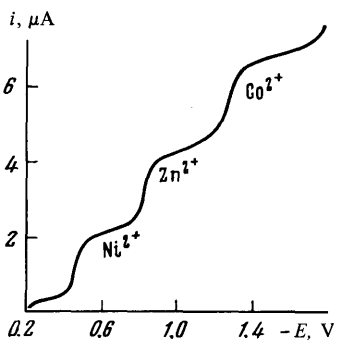


Figure 4. Polarograms of a benzene extract containing 10^{-3} M nickel(II), zinc(II), and cobalt(II) in 0.2 M lithium perchlorate in ethanol as the supporting electrolyte; extractant—diethyl dithiophosphate[44].

An essential requirement which must be made by the extraction-polarographic system is the purity of all its components. Apparently one must not accept without question the stated grade of commercial reagents. Studies have shown[23,24,31] that they require careful purification by repeated recrystallisation from alcohols, acetone, etc. Studies where the choice of rational conditions for the extraction-polarographic determinations based on specially synthesised, purified, and identified complexes, in the form of which the elements are extracted merit attention[50–52]. As regards the purification of solvents, the latter are subjected to fractional distillation in almost all cases. However, since the solvents are added to aqueous solutions in the extraction process, it is not always essential to dry them carefully. This is necessary only in those cases where the solvent hydrolyses when stored in the presence of an admixture of water with formation of polarographically active compounds. Table 2 presents the most typical extraction-polarographic systems used for the analysis of various elements.

Table 2. Types of extraction-polarographic systems.

Reagent	Solvent mixture	Method of recording	Polarisation potential of electrode	Elements determined	References
1. Sodium diethyl dithiocarbamate	chloroform – methylcellosolve – 0.1 M $HClO_4$ ($KClO_4$)	I, II	0.0 – –0.8 V	Bi(III), Cu(I), Cu(II), Tl(I), Pb(II), Hg(II)	41–43,50,51
2. Dithiocarbamates ($R_2NCS_2^-$, R = CH_3, C_2H_5, or n-C_4H_9) (n = 4, 5)	benzene, toluene, *m*-xylene, ethyl acetate, butyl acetate, pentyl acetate—0.2 M $LiClO_4$ ($NaClO_4$) in methanol or ethanol	I–III	+0.2 – –1.8 V**	Pb(II), Cd(II), Sn(II), Cu(II), Bi(III), Tl(I), Fe(III), Zn(II), Mn(II)	23,24,52,55
	benzene, toluene, chloroform, carbon tetrachloride—0.2 M $LiClO_4$ in acetone	IV	0.0 – +1.9 V**	Cu(II), Ni(II), Zn(II), Tl(I), Pb(II)	48,58,59
3. Alkyl xanthates ($ROCS_2^-$, R = CH_3, C_2H_5, n-C_3H_7, or iso-C_3H_7)	benzene, toluene, *m*-xylene, ethyl acetate, butyl acetate, pentyl acetate, pentyl and isopentyl alcohols, heptane—0.2 M $NaClO_4$ in ethanol	I, III	+0.3 – –2.0 V***	Fe(II), Fe(III), Ni(II), Zn(II), Cd(II), Pb(II), Sn(II), Tl(I), Bi(III), Sb(III), As(III)	25–28
($ROCS_2^-$, R = n-C_4H_9, iso-C_4H_9, n-C_5H_{11}, or iso-C_5H_{11})	toluene (chloroform)—0.2 M $LiClO_4$ in acetone	V	0.0 – +1.9 V**	Ni(II)	59
4. Diethyl hydrogen dithiophosphate	toluene (benzene)—0.2 M $LiClO_4$ in ethanol	I, III	+0.1 – –2.0 V***	V(IV), Cr(III), Mn(II), Co(II), Fe(II), Fe(III), Ni(II), Zn(II), Cd(II), Pb(II), Bi(III), As(III), Sb(III), Tl(I)	26,27,29
5. 8-Mercaptoquinoline	benzene, toluene, *m*-xylene, pentyl acetate, isopentyl alcohol—0.1 M LiCl in ethanol	I	–0.2 – –2.0 V***	Hg(II), Cu(II), Cr(III), Mo(VI), Zn(II)	30
6. 8-Hydroxyquinoline	benzene, toluene, *m*-xylene, pentyl acetate, butyl acetate, chloroform, dichloroethane, pentyl and butyl alcohols, cyclohexanone—0.1 M LiCl in methanol	I	–0.2 – –1.2 V	Cu(II), Pb(II), Fe(III), Cd(II), Bi(III)	7
	fused naphthalene-DMF—0.1 M $HClO_4$ + 0.1 M NaClO	I	0.0 – –1.0 V	Mo(VI), Cd(II), Pb(II), In(III)	61,62
	isobutyl methyl ketone, supporting electrolyte—0.1 M $(C_4H_9)_4NClO_4$	I	0.0 – –1.3 V	Cu(II)	63
7. *N*-Benzoylphenyl-hydroxylamine	benzene, *m*-xylene, butyl, pentyl, and isopentyl alcohols—0.1 M $(C_4H_9)_4NClO_4$ in methanol, DMF, formamide, and DMSO	I	-0.2 – -1.6 V (pH of aqueous phase 5 – 10); -0.2 – -0.9 V (pH of aqueous phase 3)	Pb(II), Cu(II), Cd(II), Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Zn(II), Pd(II), Bi(III), Ti(IV)	70,71
8. *N*-Cinnamoylphenyl-hydroxylamine	pentyl alcohol, ethyl acetate, benzene—0.1 M LiCl in methanol	I	0.0 – –1.2 V	Cu(II), Cd(II), Pb(II), Ga(III), In(III), Tl(III), Fe(III), Bi(III), Ti(IV), V(V), W(VI), Mo(VI)	72–75
9. Salicylaldoxime	toluene—0.1 M LiCl in methanol	I	–0.2 – –1.5 V	Cu(II), Pd(II), Pb(II), Cd(II), Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Zn(II), Bi(III), Ti(IV)	8
10. Phenoyltrifluoro-acetone	benzene—0.1 M LiCl in methanol and butanol—acetophenone mixt.	I	-0.2 – -0.75 V (pH 4.1); -0.2 – -0.6 V (5 *N* HCl)	Cu(II), Tl(I), Pb(II)	8
	isobutyl methyl ketone—0.1 M acetylacetone – acetate buffer at pH 5.8	I	0.0 – –1.5 V	Fe(III)	100
11. 4-Benzoyl-3-methyl-1-phenyl-5-pyrazolone	cyclohexanone, dichloroethane, ethyl acetate, chloroform, toluene, benzene—0.75 M NH_4Br in ethanol	I	0.0 – –1.2 V	In(III)	22
12. Dimethyl-α-furyl-, and α-benzyl-glyoximes	toluene, 1 M ammonia buffer in ethanol	I–III	–0.2 – –1.8 V*	Ni(II)	85
13. Acetylacetone, phenoyl-trifluoroacetone	isobutyl methyl ketone, supporting electrolyte—0.1 M $(C_4H_9)_4NClO_4$	I	—	Fe(III)	95,96
14. Diantipyrinylmethane	chloroform—1 M LiCl in ethanol	III	0.0 – –1.0 V	Sb(III), V(V), As(III)	92,93,96
15. Catechol	dichloroethane – diphenylguanidinium acetate	I	0.0 – –1.2 V		116

*Recording methods: I) classical polarography; II) a.c.polarography; III) oscillographic polarography; IV) anodic voltamperometry with a rotating graphite disc electrode; V) ditto with a stationary graphite electrode.

**Potential relative to mercury at bottom of cell.

***Potential relative to removable mercury electrode; in remaining cases relative to a saturated calomel electrode.

IV. THE USE OF EXTRACTION POLAROGRAPHY IN THE DETERMINATION OF METALS

The method of extraction polarography has come to be used comparatively widely in recent years. There has been an increase of the range of reagents investigated and studies have been made on extraction polarography using solid reagents. Among the metal chelates extracted by organic solvents at the present time, dithiocarbamates[18,23–27,47–60], hydroxyquinolinates[6–8,10,15,17,61–69], and substituted hydroxylaminates[9,70–82] have been most fully investigated. There have been reports also of the other reagents; oximes[8,83–85],

xanthates[25-28,56-60,86-91], dithiophosphates[25-27,29,56,60], pyrazolone derivatives[22,92-94], etc.[95-103].

8-Hydroxyquinoline is widely used for concentration by extraction in combination with different versions of polarography. Pyatnitskii and Ruzhanskaya investigated the influence of the nature and properties of organic solvents (benzene, toluene, *m*-xylene, pentyl acetate, chloroform, dichloroethane, pentyl, isopentyl, and butyl alcohols, and cyclohexanone) on the polarographic characteristics of the reduction waves for certain metal hydroxyquinolinates[6,7,10]. On the basis of the results, methods have been devised for the determination of copper in ferrotitanium, titanium-based alloys, alloyed steels, and babbitts[6,10]. Apart from 8-hydroxyquinoline, its various derivatives have been used. Cadmium, cobalt, and iron have been extracted quantitatively with butyl alcohol in the form of their complexes with 8-hydroxyquinoline-5-sulphonic acid with subsequent determination of the metals in the extract down to a lower limit of 7.5×10^{-8} g-ion litre^{-1}.[68]

Studies have been made on the extraction of metal hydroxyquinolinates by extraction amalgam polarography with accumulation using solvents of the benzene series[15,17]. The sensitivity of the determination of the elements by this method is in most cases not less than the sensitivity of the amalgam-polarographic analysis of impurities in aqueous media. The method of extraction polarography with accumulation is promising for the study of the extraction of substances present at low concentrations. The scope of this method has been investigated in the extraction of chelates in relation to the distribution of copper and cadmium *O*-hydroxyquinolinates in systems comprising water and solvents of the benzene series[15,17] and also copper diethyldithiocarbamate in the water–chloroform system[18]. The kinetics of the extraction of complexes with organic solvents and the influence of the pH of the aqueous phase on the extraction have been investigated, the extraction constants for the complexes have been calculated, and the composition of the complexes has been determined. It has been shown that the metal can be concentrated at the electrode either as a result of its transfer to the amalgam in the electrolysis of the solution of the chelate in the extracting mixture (chelate complexes of bismuth, cadmium, lead, thallium, copper, indium, and certain other metals[19]) or as a result of the formation of a colloid metal–mercury system (iron, nickel, manganese, cobalt, etc. compounds).

Extraction polarography with accumulation has been used to determine antimony in solutions of sodium chloride and specially pure hydrochloric acid[54] with the aid of chloroform and sodium diethyldithiocarbamate in the presence of EDTA and potassium iodide. The lower limit of the detection is 5×10^{-6}%. The use of 8-hydroxyquinoline in polarographic analysis has been described by Fujinaga and Puri[65]. Zinc, cadmium, manganese, and magnesium have been determined by an indirect method based on the decrease on the height of the reduction wave for 8-hydroxyquinoline itself in the presence of these metals.

The possibility of employing solid but readily fusible organic substances for extraction had been reported previously[104-106]. Such extraction is carried out in slightly heated solutions where the extractant is fused. After extraction and cooling, the extract solidifies rapidly and the aqueous layer is separated by simple decantation. Extraction by readily fusible substances does not require a separating funnel. A set of readily fusible extractants, permitting the extraction of elements from solutions with different acidities, has been published[106]; these are mainly paraffins in mixtures with various oxygen-containing solvents or with *N*,*N*-dimethyl- and *o*-chloro-aniline. Lobanov et al.[107] studied the possibility of the group concentration of metal ions by an 8-hydroxyquinoline melt. However, extractants of this class are still hardly used.

Several communications have been published recently[61,62,64,65] on the isolation of metal hydroxyquinolinates by extraction into fused naphthalene with subsequent polarography of the dimethylformamide solution of the extract. The use of such extraction-polarographic systems has definite advantages: simplicity of operation, faster attainment of equilibrium as a result of heating, the absence of risk of emulsification, and the disappearance of the need to dilute the solution with an ionising solvent when, for example, dimethylformamide is used, etc. The conditions for the extraction-polarographic determinations of Be, Bi, Mo, Cd, Hg, Ni, Pb, Pd, Sn, Ti, U, V, W, Ce, Cu, Tl, In, Mn, Sr,[65] Mo,[61] Pb and Cd,[63] and In [64] have been investigated. Waves suitable for analytical purposes have been obtained only for Mo, Pb, In, Bi, U, Cu, Pd, and Fe.[65] Other metals investigated do not give rise to reduction waves in the accessible range of potentials, since at potentials more negative than −1.1 V the organic reagent is reduced under these experimental conditions. Evidently it would be useful to find a supporting electrolyte other than pyridine + $HClO_4$ and $NaClO_4$ + $HClO_4$ mixtures, as a result of which the range of potentials for polarography would be narrowed down still further. The number of ions determined in the presence of the above supporting electrolytes is very small. Polarographic activity is not shown by 8-hydroxyquinoline alone. Substituted hydroxylamines and the oximes of certain aldehydes and ketones, which are reduced at an m.d.e., have been used in extraction-polarographic analysis. For example, *N*-benzoylphenylhydroxylamine (BPHA) permits studies in the range from −0.2 to −1.6 V. An increase of the acidity of the aqueous phase narrows down the range in the cathodic region to −0.9 V (pH 3), which can apparently be accounted for by the facilitation of the reduction of the protonated form of the reagent. The polarographic study of the reduction of the complexes was begun by Hudbard and Gernon[70], and thenumber of polarographically active complexes under the conditions employed by them is small: those of Sb, Bi, Cu, In, Fe, Pb, and V. Copper ($E_{1/2} = -0.28$ V relative to the sat.c.e.), iron ($E_{1/2} = -0.56$ V), and lead ($E_{1/2} = -0.62$ V) waves and to a lesser extent antimony ($E_{1/2} = -0.27$ V) and vanadium ($E_{1/2} = -0.62$ V) waves (because their heights are small), are suitable for analytical purposes[70]. Pyatnitskii and Ruzhanskaya[9] investigated the polarographic behaviour of lead(II), copper(II), cadmium(II), nickel(II), zinc(II), iron(III), gallium(III), indium(III), thallium(I), bismuth(III), cobalt(II), titanium(IV), vanadium(V), molybdenum(VI), tungsten(VI), manganese(II), chromium(III), and palladium(II) benzoylphenylhydrozylaminates in isopentyl alcohol and *m*-xylene. The influence of the solvent has been studied for copper(II), iron(III), and indium(III) complexes. It follows from the results that, with decrease of the dielectric constant, the reduction potentials are in most cases displaced to the negative region, but there is no clear-cut regular variation in this instance. The greatest sensitivity of the determinations has been obtained in extraction by weak polar solvents of the benzene series. They also have the advantage that waves with a more definite shape are obtained.

The results of a study of the same metal benzoylphenylhydroxylaminates have been published by Pilipenko et al.[71]; in this case the influence of the solvents was investigated (in contrast to Pyatnitskii and Ruzhanskaya[9]) also for all the remaining benzoylhydroxylaminates. The BPHA complexes of many metals are reduced in benzene, toluene,

dichloroethane, carbon tetrachloride, butyl, pentyl, isopentyl, and hexyl alcohol, ethyl acetate, and ethyl methyl ketone extracts in the presence of 0.1 M LiCl supporting electrolyte and methanol. It was established that the values of $E_{1/2}$ for metal *N*-benzoylphenylhydroxylaminates in organic solvents are displaced towards more negative potentials compared with the $E_{1/2}$ of the metal ions in aqueous solutions as a result of complex formation or solvation. The cathodic shift of the waves in ethyl acetate and pentyl alcohol relative to benzene and chloroform has been explained[72] by the solvating capacity of oxygen-containing organic solvents. In terms of their reduction potentials at the m.d.e., metal *N*-benzoylphenylhydroxylaminates can be arranged in the following sequence (polarographic spectrum)[71]: Cu(II) < V(V) < Tl(I) < Bi(III) < Fe(III) < Pb(II) < Cd(II) < Mo(VI) < W(VI) < Ga(III). In some cases the values of $E_{1/2}$ for metal ions in the aqueous medium are very close, while in organic solvents they differ significantly. Thus in an aqueous medium the values of $E_{1/2}$ for the copper(II)–bismuth(III), indium(III)–cadmium(II), copper(II)–lead(II), copper(II)–cadmium(II), and indium(III)–lead(II) systems are less than 0.1 V which makes it difficult to determine the above components in mixtures.

The application of extraction polarography makes it possible to determine certain elements when these are present jointly. For example, in a benzene extract the values of $\Delta E_{1/2}$ are as follows: 0.19 V for copper(II) and bismuth(III), 0.29 V for copper(II) and lead(II), 0.30 V for copper(II) and cadmium(II), 0.13 V for lead(II) and thallium(I), 0.30 V for indium(III) and cadmium(II), 0.35 V for indium(III) and lead(II), and 0.48 V for indium(III) and thallium(I). A similar observation has been made for extracts in isopentyl alcohol and ethyl acetate. The values of $E_{1/2}$ in these solvents are sufficient for the joint polarographic determination of the above pairs of ions even when one is present in a considerable excess. The possibility of the polarographic determination of molybdenum in the presence of other metals after extraction of its BPHA complex with chloroform has been noted[39].

The results of the polarographic study of *N*-cinnamoylphenylhydroxylamine (CAPHA) and its metal complexes have been published[72–81]. In organic solvents CAPHA is reduced at −1.2 V relative to the saturated calomel electrode, so that the limit of the polarographic determination is 0.0 to −1.2 V. The CAPHA complexes of thallium(I), lead(II), copper(II), cadmium(II), zinc(II), nickel(II), iron(III), gallium(III), bismuth(III), indium(III), titanium(IV), vanadium(V), zirconium(IV), tungsten(VI), and molybdenum(VI) have been investigated in pentyl alcohol, ethylacetate, benzene, and chloroform with added methanol.

The dependence of the height of the wave for the copper, indium, and iron complexes of CAPHA in the benzene extract on the initial metal concentration in aqueous solution is linear and indicates the possibility of the determination of these elements by the extraction-polarographic method. Since this entails an increase of the selectivity of the elements as a result of the different polarographic behaviour of the CAPHA complexes of metals in organic solvents, indium(III) can be determined in the presence of copper(II) and lead(II) and in mixtures with cadmium(II) and gallium(III), copper(II) can be determined in the presence of bismuth(III), thallium(I) can be determined in the presence of indium(III) and gallium(III), etc. Furthermore, the selectivity of the determination increases owing to the unequal capacities of the metal complexes of CAPHA for extraction under the conditions of different acidities of the aqueous solution. Thus the lead, zinc, nickel, and cadmium complexes are not extracted μat pH 3 and in the extraction polarographic method do not therefore interfere in the determination of molybdenum, tungsten, gallium(II), iron(III), titanium(IV), vanadium(V), and indium. It is possible to determine indium and copper in the presence of various elements.

It has been observed that metal *N*-cinnamoylphenylhydroxylaminates give rise to the following polarographic spectrum in benzene extracts in terms of their ability to be reduced at the m.d.e.: Cu(II) < Tl(I) < Bi(III) < Mo(VI) < V(V) < Fe(III) < Cd(II) < Pb(II) < W(VI) < Ti(IV) < In(III).[74] By introducing tartaric acid and sodium fluoride into the aqueous phase before extraction, the interfering influence of tin, vanadium, titanium, molybdenum, and iron is eliminated. An extraction-polarographic method has been developed on the basis of experimental studies for the determination of copper and lead in various materials; it is distinguished by a high sensitivity and a fairly high selectivity[74].

Various oxime derivatives have found applications in extraction polarography[83–85]. The possibility of the extraction-polarographic determination of microgram amounts of nickel after its concentration in the form of the dimethylglyoximate has been investigated[85]. The method is based on the use of the catalytic hydrogen wave and is therefore one of the most sensitive polarographic procedures for the determination of nickel. When dimethylglyoxime is added to a solution containing nickel, the height of the nickel reduction wave increases by a factor of approximately 6. The lower limit of the determination of nickel under the recommended conditions is 1×10^{-6} M at a m.d.e. and 1×10^{-7} at a stationary mercury electrode. The sensitivity increases appreciably when oscillographic polarography is used (as far as 1.5×10^{-8} M).

A study of the possibility of using α-furylglyoxime and α-benzylglyoxime showed[85] that it is better to employ dimethylglyoxime, since it dissolves more readily than α-benzylglyoxime, and the wave heights do not differ quite so much (in the case of α-furylglyoxime the wave height is much smaller). Copper and cobalt are extracted together with nickel from ammonia solutions in the form of hydroxyquinolinates. Although the extraction is not quantitative, copper and cobalt nevertheless interfere with the photometric determination of nickel. On the other hand, the proposed extraction polarographic method makes it possible to determine nickel quantitatively in the presence of amounts of copper and cobalt in the extract greater by a factor of 100.

Polarographic data for metal *salicylaldoximates* and *thenoyltrifluoroacetonates* in toluene and benzene extracts and in butanol–acetophenone mixtures have been published[8]. In toluene polarographic waves were observed for copper, iron, cobalt, nickel, palladium, and titanium salicylaldoximates, i.e. a much greater number of metal compounds of this reagent are reduced in toluene than in the case of hydroxyquinolinates[6].

Among the thenoyltrifluoroacetonates (TTA), only copper, lead, thallium, and uranyl complexes are reduced polarographically[8]. This makes it possible to determine copper and lead in the presence of much greater amounts of bismuth, which does not give rise to a wave. The use of isobutyl methyl ketone (IBMK) as the extracting solvent makes it possible to include iron ions among those of the elements investigated[100]. When iron(III) is extracted in the form of a complex with TTA, the extraction is carried out from an acetate buffer solution at pH 5.8; a complex anodic-cathodic wave is observed in the organic phase at a potential characteristic of the reduction of $Fe(TTA)_3$, which indicates the presence of iron(III) and iron(II) complexes in the organic phase. A polarographic determination of thallium(III), which is difficult to determine in aqueous media, is also possible.

TTA is unsuitable for extraction polarography as a result of the narrow range of polarisations. With increase of the acidity of the medium, the comparatively narrow range of m.d.e. cathodic polarisations (−0.20 – −0.75 V) becomes narrower still (is reduced to −0.60 V).

Phosphorus dithio-acids are widely used as analytical reagents in separations by the extraction method, mainly with spectrophotometric detection. However, not all complexes formed by phosphorus dithio-acids with metal ions absorb in the accessible region of the spectrum. This imposes certain limitations on extraction-photometric determinations. Extraction polarography is more promising in such cases. There are few literature data concerning the use of this method for the determination of metals in the form of dithiophosphate complexes. The polarographic properties of a number of transition and non-transition metal diethyl dithiophosphates and their extractability by certain aromatic hydrocarbons have been investigated[26,27,29]. Under the conditions used, the electrochemical reduction of thallium, lead, and copper diethyl dithiophosphates is inhibited by the reduction product adsorbed on the electrode[29].

Diethyl dithiophosphate complexes in another group, including vanadium(IV), chromium(III), nickel(II), cobalt(II), zinc(II), manganese(II), and cadmium(II) compounds, are reduced with fnrmation of waves uncomplicated by adsorption phenomena[29], which is due primarily to the fact that the reduction occurs in the range of potentials more negative than the electrocapillary zero potential[29].

Dithiocarbamates are used in extraction-polarographic analysis mainly for the determination of elements which do not form coloured complexes and which cannot be determined spectrophotometrically.

The extraction of lead(II) by benzene in the form of $Pb(R_2NCS_2)_2$ and $Pb[(CH_2)_nNCS_2]_2$ ($R = C_2H_5$ or C_4H_9; $n = 4, 5$) has been investigated polarographically. The distribution of the chelates between water and the organic phase was followed by oscillographic polarography[55]. The presence of nickel(II), chromium(III), zinc(II), aluminium(III), molybdenum(VI), tungsten(VI), vanadium(V), and titanium(IV) in the test solution does not interfere with the determination of lead(II), because the chelates of the first four metals are reduced at more negative potentials than $Pb(R_2NCS_2)_2$; the chelates of the remaining elements are hardly extracted at pH >7. The high resolving power of oscillographic polarography makes it possible to determine lead(II) in the presence of comparable amounts of bismuth(III) and thallium(I).

Taking into account data for the extraction of zinc(II) as $Zn(R_2NCS_2)_2$ by pentyl acetate at pH 3, a method has been developed for the extraction-polarographic determination of zinc(II) in the blood of animals[55]. The concentration of zinc(II) was found from the limiting current for the wave with $E_{1/2} = -1.45$ V (relative to s.c.e.). In order to eliminate the interference by cobalt(II) and manganese(II), sodium thiosulphate was added. The optimum conditions for the distribution of $Zn(R_2NCS_2)_2$ in the benzene–water system obtain at pH 10–11.

The possibility of the selective extraction of copper(II), lead(II), zinc(II), manganese(II), cadmium(II), nickel(II), and bismuth(III) in the form of their dithiocarbamate complexes has been investigated[52]. Best results are achieved in in a 1:1 benzene–methanol medium (an emulsion is formed in toluene). The values of $E_{1/2}$ for these complexes are similar. In order to determine the metal ions present jointly in the same solution, use was made of extraction at different pH in conjunction with masking reagents.

Other aspects of the electrochemical behaviour of metal chelates in relation to derivatives of dithiocarbamic, xanthic, and dithiophosphoric acids were discussed in detail in previous sections of the review.

Dithizone is used to a lesser extent as an extractant in extraction polarography. A method has been developed for the determination of copper in natural waters based on the concentration of copper by extraction in the form of a dithizonate and the polarography of the toluene extract in the presence of a hydrochloric acid buffer solution as the supporting electrolyte[38].

Extraction polarography can prove to be irreplaceable in those cases where the technological processes are carried out in non-aqueous media, for example in polymerisation in the presence of catalysts. The concentration of a copper catalyst has been determined[99] directly in the reaction mixture. In such cases re-extraction is impracticable in view of the long duration and laborious nature of the operations, and extraction polarography therefore significantly simplifies and facilitates analysis.

Among different electrochemical analytical methods, particular interest attaches to anodic extraction voltamperometry at solid electrodes, which involves a preliminary extraction of the complexes into a diluent and the measurement of their oxidation current. In a 2:3 toluene–acetone mixture in the presence of 0.1 M $LiClO_4$ supporting electrolyte chromium(III), manganese(II), iron(III), cobalt(II), cobalt(III), nickel(II), copper(II), zinc(II), cadmium(II), lead(II), bismuth(III) and thallium(I) dithiocarbamate, xanthate, and dithiophosphate complexes are oxidised at graphite and platinum disc electrodes with formation of diffusion waves whose positions along the potential axis are determined by the nature of the central ion and the ligand[57–59]. The results make it possible to select the extractant as a function of the object of the analysis. For example, in the determination of nickel(II) and zinc(II) extraction should be carried out with dithiocarbamates, since the dithiophosphate complexes of the above metals are oxidised virtually at the same potential (1.13 and 1.08 V respectively). In extraction from strongly acid media preference should be given to dithiophosphates. Account must be taken also of the electrode. In the oxidation of dithiophosphate complexes at a platinum electrode no waves were observed on voltage–current curves.

Anodic voltamperometry makes it possible to extend the range of extracting solvents compared with polarography. Apart from toluene, chloroform and carbon tetrachloride have been used in the determination of copper(II).[48,59] The extraction of metal dithiocarbamates by these solvents has been thoroughly investigated[108]. However, their use in polarography encounters difficulties owing to the narrow range of cathodic polarisation potentials. The oxidation of copper(II) dithiocarbamate at graphite in mixtures of acetone with $CHCl_3$ and CCl_4 gives rise to a single distinct diffusion wave at a potential of 0.6 V. The oxidation current at a rotating electrode in a 2:3 carbon tetrachloride–acetone mixture is several times higher than in a 2:3 toluene–acetone mixture at the same concentration. The lower limit of the detection of copper(II) is 0.5 – 0.7 μg ml^{-1}.[59]

Anodic extraction voltamperometry has a somewhat higher detection limit than polarography; the error of the determination is also increased (from 3–6% to 8–12%). Nevertheless this method also has undoubted advantages. Firstly, mercury as the electrode material is eliminated. Secondly, the duration of analysis is greatly reduced, because there is no need to remove the dissolved oxygen from the electrolyser (this is particularly important in routine analyses). Finally, it is possible to eliminate highly toxic solvents such as benzene and its analogues.

Together with the extraction of inner complexes, procedures based on the extraction of elements into an organic solvent in the form of thiocyanate complexes[109] or metal halide acids[22,32,110,111] have become common in voltamperometry.

In the determination of antimony and arsenic in industrial objects, they were extracted with benzene in the form of bromide complexes[112] and the extracts were polarographed in

a LiCl solution in ethanol or glacial acetic acid as the supporting electrolyte. The oscillopolarogram of the arsenic(III) extract shows two peaks at potentials of −0.3 and −0.8 V (relative to the mercury at the bottom of the cell). The second peak is suitable for the determination of arsenic(III) in the presence of antimony and tin in proportions of 1 : 100. In these supporting electrolytes antimony(III) is reduced at a potential of −0.2 V with formation of a distinct peak. Antimony(III) has been determined in objects free from arsenic(III).

Among the new extractants used for concentration and determination mention should be made of α-dibutylphosphinyl-α-hydroxypropionic acid (DPHP) with added isopentyl alcohol. This system has been recommended for the determination of cadmium(II) on the basis of the limiting current for the reduction of its complex with DPHP in the presence of copper(II).[101] The reaction of copper(II) with DPHP is masked by the addition of ethylenediamine.

The conditions for the extraction of indium(III) and tin(IV) ionic association complexes with tri-n-octylamine (TOA) in dichloroethane and the polarography of the extract in methanol in the presence of NH_4Br as the supporting electrolyte have been used to determine indium and tin in the $CdSiAs_2$ semiconducting compound alloyed with indium[102]. The change in the TOA concentration from 0.25 to 1.25 M increases the percentage extraction of indium from 54 to 99%. The composition of the extracted ionic association complex $(TOAH)_2SnCl_2$ was determined from the bilogarithmic plot of the partition coefficient against the amine concentration. A lower limit of $(2–5) \times 10^{-8}$ M in the detection of the indium impurity in $CdSiAs_2$ has been achieved as a result of a combination of extraction by concentration with polarographic accumulation of indium[103].

The principal results of the extraction-polarographic determinations of metals in various objects are summarised in Table 3. The Table does not include the results of studies involving re-extraction before polarography[113–116].

Table 3. Extraction-polarographic determination of elements in various objects.

Element	Reagent	Object of study	Conditions of extraction-polarographic determination	Remarks	References
Copper	8-hydroxy-quinoline	alloyed steels, babbitts	pH 3–14, toluene : methanol = 2 : 3; supporting electrolyte—0.1 M LiCl; Fe^{3+} ions masked by sodium fluoride	measurable concentration limits 4×10^{-6}–5×10^{-5} M	6,10
Copper	8-hydroxy-quinoline	petroleum	pH 2.4–12.0; benzene : methanol = 1 : 1; supporting electrolyte–NH_4NO_3 + NH_4SCN; accumulation potential = –0.4 V	relative error of extraction-polarographic determination 5.6%	17
Copper	dithizone	natural waters	extracted with 0.001% solution of dithizone in toluene at pH 2.15; polarographed mixture: toluene–acetone–hydrochloric acid buffer (1 : 19 : 5)	wave height proportional to concentration in the range 1×10^{-6}–8×10^{-5} M; 0.12 mg litre^{-1} determined in the water of Belaya River with a relative error of 3.7%	38
Copper and lead	CAPHA	silts and natural waters	pH 5.6–6.0; benzene (chloroform) : methanol = 2 : 3; supporting electrolyte—0.1 M LiCl	limits of proportionality of i_{lim} for a lead complex 1×10^{-5}–6×10^{-4}M and for a copper complex 1×10^{-5}–8×10^{-4} M; Ni, Co, Zn, Mn, In, Ga, Fe, and Cd do not interfere with determinations; sensitivity 5×10^{-4}% in silts and 10 mg litre^{-1} in water; relative error not exceeding 5%	74
Copper and lead	CAPHA	sedimentary rocks and minerals	pH 5.6–7.7; benzene : methanol = 2 : 3; supporting electrolyte—0.1 M LiCl	simultaneous determination based on difference in $E_{1/2}$ ($\Delta E_{1/2}$ = 0.25 V); sensitivity of method 5×10^{-4}%; relative error not exceeding 5%	73
Lead	sodium dialkyl-dithiocarbamates	heat resistant EI-437B nickel alloy	pH 8.5; benzene : ethanol = 2 : 3; supporting electrolyte—0.1 M $NaClO_4$	upper limit of proportionality 7×10^{-4}M (R = C_2H_5) and 1×10^{-3} M (R = C_4H_9); Ni, Cr, Zn, Al, Mo, V, Ti, Bi, and Tl do not interfere with determination; lower limit of determination 1×10^{-6} M (oscillopolarography)	55
Lead	8-hydroxy-quinoline	–	pH 9–12; extractant—fused naphthalene; supporting electrolyte—0.1 M pyridine + 0.1 M $HClO_4$; extract dissolves in dimethyl-formamide	limits of calibration graph 0–112 μg/10 ml; Pd, Cd, and Hg interfere with determination	61
Lead and zinc	xanthates	standard specimens and industrial objects	pH 3–5; extractant—benzene (CCl_4 or $CHCl_3$); supporting electrolyte—LiCl in ethanol	tenfold amounts of Fe, Ni, and Cu interfere with determination (oscillopolarography)	86
Zinc	sodium diethyl-dithiocarbamate	animal blood	pH 3; pentyl acetate : ethanol = 2 : 3; supporting electrolyte— 0.2 M $NaClO_4$; optimum conditions for zinc: benzene–ethanol at pH 10–11	interference by Co and Mn is eliminated with sodium thiosulphate; lower limit of determination 8×10^{-6}M	55
Iron, manganese, and zinc	sodium dimethyl-dithiocarbamate, ethylenebis-dithiocarbamate	residual amounts of ferbam, ziram, and maneb	benzene : methanol = 2 : 3; supporting electrolyte—0.2 M $LiClO_4$	lower limit of determination for Fe and Mn 1×10^{-7} M (a.c. polarography)	23
Iron	acetylacetone, thenoyltrifluoro-acetone	–	extractant—isobutyl methyl ketone; supporting electrolyte—0.1 M $(C_4H_9)_4NClO_4$; pH 8.8–9.1	quantitative extraction with acetylacetone; iron can be determined in the concentration range 8×10^{-5}–1×10^{-3} M	96

Table 3 (contd.)

Element	Reagent	Object of study	Conditions of extraction-polarographic determination	Remarks	References
Nickel	dimethylglyoxime	sea water	pH 9-10; ammonia buffer solutions; polarographed mixture: toluene—1 M ammonia buffer-ethanol	down to 1×10^{-8} M Ni determined from catalytic hydrogen wave; hundred-fold amounts of Cu and Co in extract do not interfere (oscillographic differential polarography)	85
Indium	4-benzoyl-3-methyl-1-phenyl-5-pyrazolone	doped semiconducting alloys	pH 1.2-1.3; polarographed mixture: chloroform—1 M LiCl or 0.75 M NH_4Br in methanol (1:4)	sensitivity of determination much higher when NH_4Br is used than for LiCl; accompanying elements (Cd, Sb, As) do not affect peak height	94
Indium	8-hydroxyquinoline	–	extractant—fused naphthalene; pH 3-12; supporting electrolyte—0.1 M pyridine + 0.1 M $HClO_4$ in dimethylformamide	i_{lim} proportional to metal concentration in the range 0.7-21.5 $\mu g\ ml^{-1}$; error of determination 1.1% majority of cations and anions do not interfere with determination; complexone III interferes	62
Molybdenum	8-hydroxyquinoline	alloys and other complex materials	extractant—naphthalene; extraction temperature ~ 60 °C; pH 2.25-5.30; supporting electrolyte—0.1 M $NaClO_4$ + 0.1 M $HClO_4$ in DMF	citrates, oxalates, tartrates, $PdCl_2$, and $FeCl_3$ interfere with determination; the majority of ions do not interfere	
Molybdenum	BPHA	steel	Mo extracted from hydrochloric acid solution with 2 ml of 1% BPHA solution in $HClO_4$; LiCl in methanol also added	the majority of metals and complex-forming substances do not interfere with determination	39
Cadmium	α-dibutylphosphinyl-α-hydroxypropionic acid	aluminium alloys	isopentyl extract polarographed in the presence of 0.1 M LiCl in ethanol as supporting electrolyte; pH of aqueous phase 6	minimum measurable amount of cadmium 5.6×10^{-4} mg ml^{-1}	101
Antimony	diantipyrinylmethane	steels	1 M LiCl in ethanol added to extract before oscillopolarographic measurements	linear relation between peak height and Sb^{3+} concentration holds between 1×10^{-7} and 1×10^{-3} M; Cu for a 20:1 ratio, Bi for a 3:1 ratio, and Sn for all ratios interfere with determination; relative error <10%	92
Arsenic	–	steels	As^{3+} extracted from 11.5 *N* HCl with carbon tetrachloride and butanol is added	error +0.4-2.0% (oscillopolarography)	96
Gallium	salicylic acid	metallic aluminium	pH 3; homogeneous mixture; butyl acetate–aqueous 0.5 M LiCl solution and 0.1 M sodium salicylate—ethanol (1:1:2)	range of proportionality of gallium concentration 5.4×10^{-4}-2.2×10^{-3} M	97

*Extraction in the form of halide complexes.

REFERENCES

1. Yu.A.Zolotov and N.M.Kuz'min, "Ekstraktsionnoe Kontsentrirovanie" (Concentration by Extraction), Izd.Khimiya, Moscow, 1971.
2. I.A.Shevchuk, Zhur.Anal.Khim., **29**, 413 (1974).
3. Yu.A.Zolntov, "Tezisy Dokladov XI Mendeleevskogo S'ezda" (Abstracts of Reports at the XIth Mendeleev Congress), Izd.Nauka, Moscow, 1975, p.14.
4. I.P.Alimarin and Yu.A.Zolotov, Zhur.Anal.Khim., **30**, 1253 (1975).
5. "Novye Napravleniya v Polyarograficheskom Metode (Kollektivnaya Monografiya)" [New Trends in the Polarographic Method (Collective Monograph)], Izd. Shtiintsa, Kishinev, 1975, p.130.
6. I.V.Pyatnitskii and R.P.Ruzhanskaya, Zhur.Anal. Khim., **24**, 650 (1969).
7. I.V.Pyatnitskii and R.P.Ruzhanskaya, Zhur.Anal. Khim., **25**, 1063 (1970).
8. I.V.Pyatnitskii and R.P.Ruzhanskaya, Ukrain.Khim. Zhur., **36**, 1154 (1970).
9. I.V.Pyatnitskii and R.P.Ruzhanskaya, Zhur.Anal. Khim., **26**, 1475 (1971).
10. R.P.Katser, Candidate's Thesis, Kiev State University, Kiev, 1972.
11. Yu.A.Karbainov, Candidate's Thesis, Tomsk Polytechnic Institute, 1965.
12. Yu.A.Karbainov, Symposium, "Promyshlennost' Khimicheskikh Reaktivov i Osobo Chistykh Veshchestv" (Industrial Manufacture of Chemical Reagents and Specially Pure Substances), Izd.IREA, Moscow, 1966, No.5, p.126.
13. Yu.A.Karbainov, Izv.Tomsk.Politekh.Inst., **164**, 228 (1967).
14. Yu.A.Karbainov and A.G.Stromberg, Izv.Tomsk. Politekh.Inst., **151**, 7 (1966).
15. L.A.Chernova, Yu.A.Karbainov, E.M.Tsymbalova, and E.A.Zakharova, Symposium, "Uspekhi Polyarografii s Nakopleniem" (Advances in Polarography with Accumulation), Izd.Tomsk.Gos.Univ., Tomsk, 1973, p.114.
16. Yu.A.Zolotov, N.M.Kuz'min, and Yu.A.Karbainov, Trudy Kom.po Anal.Khim., Akad.Nauk SSSR, **17**, 288 (1969).
17. L.A.Chernova, E.A.Zakharova, and Yu.A.Karbainov, Zhur.Anal.Khim., 27, 38 (1972).
18. L.A.Chernova, Yu.A.Karbainov, S.A.Sedova, and E.A.Zakharova, Zhur.Anal.Khim., **28**, 1059 (1973).

19. Yu.A.Zolotov, Yu.A.Karbainov, and N.M.Kuz'min, Symposium, "Uspekhi Polyarografii s Nakopleniem" (Advances in Polarography with Accumulation), Izd. Tomsk.Gos.Univ., Tomsk, 1973, p.50.
20. Yu.A.Karbainov and A.G.Stromberg, Zhur.Anal. Khim., **20**, 769 (1975).
21. A.T.Pilipenko, E.A.Shpak, and A.I.Samchuk, Ukrain.Khim.Zhur., **42**, 972 (1976).
22. L.S.Kopanskaya, B.G.Revenko, and M.G.Shvartsman, Zhur.Anal.Khim., **28**, 1933 (1973).
23. G.K.Budnikov, V.F.Toropova, N.A.Ulakhovich, and I.P.Viter, Zhur.Anal.Khim., **29**, 1204 (1974).
24. G.K.Budnikov, N.A.Ulakhovich, I.P.Viter, and L.V.Kolesnikova, Zhur.Obshch.Khim., **44**, 730 (1974).
25. G.K.Budnikov, N.A.Ulakhovich, and N.K.Shakurova, "Tezisy XII Vsesoyuznogo Chugaevskogo Soveshchanaya po Khimii Kompleksnykh Soedinenii, Novosibirsk" (Abstracts of Reports at the XIIth All-Union Chugaev Conference on the Chemistry of Complex Compounds,, Novosibirsk), Izd.Sibir.Otd.Akad.Nauk SSSR, 1975, p.96.
26. V.F.Toropova, G.K.Budnikov, N.A.Ulakhovich, and N.K.Shakurova, "Tezisy III Vsesoyuznogo Soveshchaniya po Sintezu i Issledovaniyu Neorganicheskikh i Kompleksnykh Soedinenii v Nevodnykh Sredakh, Rostov-na-Donu" (Abstracts of Reports at the IIIrd All-Union Conference on the Synthesis and Study of Inorganic and Complex Compounds in Non-Aqueous Media, Rostov-on-Don), Izd.Rostov.Univ., 1976, p.100.
27. V.F.Toropova, G.K.Budnikov, N.A.Ulakhovich, R.A.Cherkasov, G.A.Kutyrev, and V.V.Ovchinnikov, "Tezisy Dokladov XI Mendeleevskogo S'ezda" (Abstracts of Reports at the XIth Mendeleev Congress), Izd.Nauka, Moscow, 1975, p.21.
28. N.A.Ulakhovich and G.K.Budnikov, Zhur.Obshch. Khim., **47**, 1588 (1977).
29. G.K.Budnikov, N.K.Shakurova, N.A.Ulakhovich, R.A.Cherkasov, V.V.Ovchinnikov, G.A.Kutyrev, and V.F.Toropova, Zhur.Anal.Khim., **32**, 1326 (1977).
30. V.F.Toropova, G.K.Budnikov, and S.G.Zhiyangulova, "Tezisy III Vsesoyuznogo Soveshchaniya po Sintezu i Issledovaniyu Neorganicheskikh i Kompleksnykh Soedinenii v Nevodnykh Sredakh, Rostov-na-Donu" (Abstracts of Reports at the IIIrd All-Union Conference on the Synthesis and Study of Inorganic and Complex Compounds in Non-Aqueous Media, Rostov-on Don), Izd.Rostov.Univ., 1976, Part II, p.99.
31. V.F.Toropova, G.K.Budnikov, S.G.Zhiyangulova, and O.V.Batalova, Zhur.Obshch.Khim., **45**, 5 (1977).
32. L.S.Kopanskaya and V.G.Revenko, Zhur.Anal.Khim., **31**, 1706 (1976).
33. V.Gutmann, "Chemistry of Coordination Compounds in Non-Aqueous Media" (Translated into Russian), Izd.Mir, Moscow, 1971, p.30.
34. V.F.Toropova, Ya.I.Tur'yan, and G.K.Budnikov, Symposium, "Elektrosintez i Makhanizm Organicheskikh Reaktsii (Progress Elektrokhimii Organicheskikh Soedinenii)" [Electrical Synthesis and Mechanisms of Organic Reactions (Progress in the Electrochemistry of Organic Compounds)], Izd.Nauka, Moscow, 1973, p.256.
35. G.K.Budnikov, "Printsipy i Primenenie Voltampernoi Ostsillograficheskoi Polyarografii" (Principles and Applications of Voltage–Current Oscillographic Polarography), Izd.Kazan.Gos.Univ., Kazan, 1975.
36. N.Tanaka, Electrochim.Acta, **21**, 701 (1976).
37. Yu.Ya.Fialkov, A.N.Zhitomirskii, and Yu.I.Tarasenko, "Fizicheskaya Khimiya Nevodnykh Rastvorov" (The Physical Chemistry of Non-Aqueous Solutions), Izd.Khimiya, Leningrad, 1973, p.296.
38. I.D.Kozirod and V.D.Shchukin, Symposium, "Fiziko-Khimicheskie Metody Analiza i Kontrolya Proizvodstva" (Physicochemical Analytical and Industrial Control Methods), Izd.Dagestan.Univ., Makhachkala, 1976, p.57.
39. S.K.Bhowal and F.Umland, Z.anal.Chem., **282**, 197 (1976).
40. L.Ya.Kheifets, N.A.Sobina, and N.A.Romanov, Symposium, "Sovremennye Metody Opredeleniya Mikroelementov (Tezisy Dokladov III Vsesoyuznogo Simpoziuma)" [Modern Methods for the Determination of Microelements (Abstracts of Reports at the IIIrd All-Union Symposium)], Izd.Kishinev.Univ., Kishinev, 1977, p.63.
41. T.Fujinaga and K.Yamashita, Bull.Chem.Soc.Japan, **37**, 989 (1964).
42. T.Fujinaga, K.Izutsu, and K.Yamashita, Rev. Polarogr., **13**, 52 (1965).
43. T.Ishii, H.Einaga, and E.Aoki, Japan Analyst, **14**, 149 (1965); Analyt.Abstr., **13**, 6243 (1966).
44. V.F.Toropova, G.K.Budnikov, and N.A.Ulakhovich, Talanta, **25**, 263 (1978).
45. A.Hulanicki, Talanta, **14**, 1371 (1967).
46. A.Wytlenbach and S.Bajio, Anal.Chem., **47**, 1813 (1978).
47. N.A.Ulakhovich, G.K.Budnikov, and N.K.Shakurova, Zavod.Lav., **44**, 270 (1978).
48. N.A.Ulakhovich, G.K.Budnikov, and L.G.Fomina, Zhur.Anal.Khim., **34**, 241 (1979).
49. Yu.A.Figel'son, V.G.Yakovleva, and E.Ya.Neiman, Zhur.Anal.Khim., **31**, 1904 (1976).
50. G.K.Budnikov, N.A.Ulakhovich, and V.A.Mikhailov, Symposium, "Novosti Polyarografii" (New Developments in Polarography), Izd.Shtiintsa, Kishinev, 1972, p.306.
51. G.K.Budnikov and N.A.Ulakhovich, Zhur.Anal.Khim., **28**, 448 (1973).
52. R.Cordova, A.Oliva, and R.Schrebler, Talanta, **24**, 259 (1977).
53. E.N.Vinogradova, I.I.Drozdova, G.V.Prokhorova, and T.A.Severova, Zhur.Anal.Khim., **25**, 183 (1970).
54. Yu.A.Karbainov et al., Izd.Tomsk.Politekh.Inst., **254**, 110 (1975).
55. G.K.Budnikov et al., Zhur.Anal.Khim., **30**, 2120 (1975).
56. V.F.Toropova et al., Euroanalysis II, Budapest, 1975, p.285.
57. V.F.Toropova, G.K.Budnikov, and N.A.Ulakhovich, Symposium, "Organicheskie Reagenty v Analiticheskoi Khimii" (Organic Reagents in Analytical Chemistry), Izd.Naukova Dumka, Kiev, 1976, p.122.
58. E.V.Medyantseva et al., "Tezisy Dokladov II Vsesoyuznogo Soveshchaniya po Analizu Prirodnykh i Stochnykh Vod" (Abstracts of Reports at the IInd All-Union Conference on the Analysis of Natural and Drainage Waters), Izd.Nauka, Moscow, 1977, p.68.
59. N.A.Ulakhovich, V.K.Budnikov, L.G.Fomina, and V.F.Toropova, Symposium, "Sovremennye Metody Opredeleniya Mikroelementov (Tezisy Dokladov III Vsesoyuznogo Simpoziuma)" [Modern Methods for the Determination of Microelements (Abstracts of Reports at the IIIrd All-Union Symposium)], Izd.Kishinev, Univ., Kishinev, 1977, p.62.

60. V.P.Frolova, G.K.Budnikov, N.A.Ulakhovich, E.P.Medyantseva, and V.F.Toropova, Symposium, "Progressivnye Elektrokhimicheskie Metody Analiticheskogo Kontrolya" (Progressive Electrochemical Analytical Control Methods), Izd.NTO, Kuybishev, 1977, p.112.
61. T.Fujinaga and B.K.Puri, Z.anal.Chem., **269**, 340 (1974).
62. T.Fujinaga and B.K.Puri, Bull.Inst.Chem.Res.Kyoto Univ., **51**, 253 (1973).
63. T.Fujinaga and B.K.Puri, Talanta, **22**, 71 (1975).
64. T.Kitagawa and A.Ichimura, Bunseki Kagaku, **24**, 41 (1975).
65. T.Fujinaga and B.K.Puri, Trans.SAEST, **9**, 116 (1974).
66. T.Fujinaga and H.L.Lee, Rev.Polarogr., **21**, 130 (1975); Ref.Zhur.Khim., 10G135 (1976).
67. E.N.Vinogradova et al., Zhur.Anal.Khim., **25**, 2332 (1970).
68. H.L.Lee et al., Bull.Inst.Chem.Res.Kyoto Univ., **54**, 283 (1976).
69. C.H.Tran and H.T.Nguyen, Tapchi hoa hoc., 19 (1977);
70. D.B.Hudbard and F.Gernon, Anal.Letters, **2**, 657 (1969).
71. A.T.Pilipenko, E.A.Shpak, and A.I.Samchuk, Zhur. Anal.Khim., **30**, 1086 (1975).
72. E.A.Shpak, A.I.Samchuk, and A.T.Pilipenko, Zhur. Anal.Khim., **29**, 938 (1974).
73. A.T.Pilipenko, E.A.Shpak, and A.I.Samchuk, Ukrain.Khim.Zhur., **41**, 195 (1975).
74. A.T.Pilipenko, E.A.Shpak, and A.I.Samchuk, Zhur.Anal.Khim., **30**, 717 (1975).
75. A.T.Pilipenko, E.A.Shpak, and A.I.Samchuk, Ukrain.Khim.Zhur., **40**, 266 (1974).
76. A.T.Pilipenko, E.A.Shpak, and A.I.Samchuk, Zaved.Lab., **40**, 252 (1974).
77. A.T.Pilipenko, E.A.Shpak, and A.I.Samchuk, Symposium, "Tezisy Dokladov Vsesoyuznogo Soveshchaniya po Khimicheskim i Instrumental'nym Metodam Analiza Prirodnykh i Stochnykh Vod" (Abstracts of Reports at the All-Union Conference on Chemical and Instrumental Methods for the Analysis of Natural and Drainage Waters), Izd.Nauka, Moscow, 1973, p.103.
78. A.T.Pilipenko, E.A.Shpak, and A.I.Samchuk, Ukrain.Khim.Zhur., **41**, 734 (1975).
79. A.T.Pilipenko, E.A.Shpak, and A.I.Samchuk, Symposium, "Geokhimicheskie i Analiticheskie Metody Izucheniya Veshchestvennogo Sostava Osadochnykh Porod i Rud" (Geochemical and Analytical Methods for the Investigation of the Material Composition of Sedimentary Rocks and Ores), Izd. Nauka, Moscow, 1974, p.122.
80. A.I.Samchuk, Symposium, "Voprosy Geokhimii i Mineralogii, Petrologii i Rudoobrazovaniya" (Problems of Geochemistry and Mineralogy, Petrology, and Ore Formation), Izd.Naukova Dumka, Kiev, 1974, p.160.
81. A.T.Pilipenko, E.A.Shpak, and A.I.Samchuk, Zhur. Anal.Khim., **31**, 244 (1976).
82. A.T.Pilipenko, E.A.Shpak, and A.I.Samchuk, Ukrain Khim.Zhur., **42**, 972 (1976).
83. P.M.Rao and S.B.Rao, Indian J.Chem., 11, 1160 (1973).
84. P.M.Rao and S.B.Rao, Z.anal.Chem., **272**, 128 (1974).
85. G.V.Prokhorova, E.I.Vinogradova, I.S.Grevneva, and E.M.Skobelkina, Zhur.Anal.Khim., **28**, 123 (1973).
86. A.S.Tilyupo, E.M.Tsygankov, and V.K.Chebotarev, Symposium, "Fiziko-Khimicheskie Metody Kontrolya Proizvodstva" (Physicochemical Industrial Control Methods), Izd.Rostov.Gos.Univ., Rostov-on-Don, 1975, p.23.
87. N.A.Ulakhovich, G.K.Budnikov, and O.Yu.Kargina, "Tezisy VII Vsesoyuznogo Soveshchaniya po Polyarografii" (Abstracts of the VIIth All-Union Conference on Polarography), Izd.Nauka, Moscow, 1978, p.131.
88. N.A.Ulakhovich et al., Zhur.Obshch.Khim., **48**, 2122 (1978).
89. K.N.Bagdasarov et al., Trudy NPI, 312 (1975).
90. L.S.Tilyupo, Candidate's Thesis, Izd.Rostov.Gos. Univ., Rostov-on-Don, 1975.
91. K.N.Bagdasarov, L.S.Tilyupo, E.M.Tsygankov, and V.K.Chebotarev, "Tezisy Dokladov VI Vsesoyuznogo Soveshchaniya po Polyarografii" (Abstracts of Reports at the VIth All-Union Conference on Polarography), Izd.Zinatne, Riga, 1975, p.33.
92. E.N.Ignatenko and E.G.Ignatenko, Symposium, "Fiziko-Khimicheskie Metody Kontrolya Proizvodstva" (Physicochemical Industrial Control Methods), Izd. Rostov.Gos.Univ., Rostov-on-Don, 1975, p.12.
93. E.L.Ignatenko, E.G.Ignatenko, and K.N.Bagdasarov, "Tezisy Dokladov VI Vsesoyuznogo Soveshchaniya po Polyarografii" (Abstracts of Reports at the VIth All-Union Conference on Polarography), Izd.Zinatne, Riga, 1975, p.34.
94. V.G.Revenko et al., Zhur.Anal.Khim., 27, 187 (1972).
95. T.Kitagawa and A.Ichimura, Bunseki Kagaku (Japan Analyst), 22, 1042 (1973); Ref.Zhur.Khim., 2G84 (1974).
96. E.G.Ignatenko et al., Symposium, "Novye Metody Kontrolya Materialov na Ostatochnye Elementy i Mikroelementy" (New Methods for the Monitoring of Residual Elements and Microelements in Materials), Moscow, 1975, p.144.
97. E.N.Vinogradova, K.N.Smirnov, and G.V.Prokhorova, Zhur.Anal.Khim., **25**, 2044 (1970).
98. K.Hasebe, T.Ohtsuki, and T.Kambara, Bull.Chem. Soc.Japan, **48**, 1786 (1975).
99. V.N.Epimakhov et al., Zhur.Anal.Khim., 28, 1476 (1973).
100. T.Kitagawa and A.Ichimura, Rev.Polarogr., 21, 131 (1975); Ref.Zhur.Khim., 10G27 (1976).
101. R.M.Batyrshina, M.G.Zimin, L.A.Eliseeva, and V.F.Toropova, Izv.Vys.Ucheb.Zaved., Khim.i Khim. Tekhnol., **20**, 1635 (1977).
102. V.G.Revenko and V.V.Bagreev, Zavod.Lab., **41**, 267 (1975).
103. L.S.Kopanskaja and A.T.Russu, "Reinstoff in Wissenschaft und Technik", Dresden, DDR, 1975, p.110.
104. Yu.A.Zolotov, "Ekstraktsiya Unutrikompleksnykh Soedinenii" (Extraction of Inner Complexes), Izd. Nauka, Moscow, 1968, p.75.
105. V.I.Kuznetsov and I.V.Seryakova, Zavod.Lab., **23**, 1176 (1957).
106. V.I.Kuznetsov and I.V.Seryakova, Zhur.Anal.Khim., **14**, 161 (1959).
107. F.I.Lobanov, A.G.Buyanovskaya, and I.M.Gibalo, Zhur.Anal.Khim., **26**, 1655 (1971).
108. J.Stary, "The Extraction of Chelates" (Translated into Russian), Izd.Mir, Moscow, 1966, p.230. [This may be a reference to a survey by J.Stary in "Solvent Extraction", Proceedings of International Solvent Extraction Conference, 2, 1120 (1971)(Edited by J.G.Gregory, B.Evans, and P.C.Weston, Soc. Chem.Ind., London (Ed. of Translation)].

109. T.V.Nghi and F.Vydra, J.Electroanalyt.Chem., 71, 325 (1976).
110. T.V.Nghi and F.Vydra, J.Electroanalyt.Chem., 71, 333 (1976).
111. E.L.Ignatenko et al., "The IInd National Conference on Analytical Chemistry with International Participation, Golden Sands, Varna, 1976", p.208.
112. N.S.Odobesku and L.V.Kopanskaya, Symposium, "Progressivnye Elektrokhimicheskie Metody Analiticheskogo Kontrolya" (Progressive Electrochemical Analytical Control Methods), Izd.NTO, Kuybishev, 1977, p.78.
113. A.I.Zemlyanskaya and G.A.Barsukova, "Trudy Instituta Khimii Ural'skogo Nauchnogo Tsentra Akademii Nauk SSSR" (Transactions of the Institute of Chemistry of the Urals Scientific Centre of the USSR Academy of Sciences), Sverdlovsk, 1974, No.2, p.69.
114. S.V.Pilipenko, K.N.Bagdasarov, and E.G.Ignatenko, Symposium, "Fiziko-Khimicheskie Metody Kontrolya Proizvodstva" (Physicochemical Industrial Control Methods), Izd.Rostov.Gos.Univ., Rostov-on-Don, 1975, p.15.
115. S.V.Pilipenko, K.N.Bagdasarov, and E.G.Ignatenko, Symposium, "Fiziko-Khimicheskie Metody Kontrolya Proizvodstva" (Physicochemical Industrial Control Methods), Izd.Rostov.Gos.Univ., Rostov-on-Don, 1975, p.19.
116. K.Lenda and M.Bartusek, Scripta Fac.sci.natur. UJEP Chem., 3, 49 (1973).

Faculty of Chemistry,
Kazan State University

Translated from *Uspekhi Khimii*, **49**, 171-191 (1980) U.D.C. 541.11:543.544

Thermodynamic Treatment of the Polarity and the Selectivity of Sorbents in Gas Chromatography

R.V.Golovnya and T.A.Misharina

Existing methods for assessing the polarity and the selectivity of sorbents in gas chromatography are examined. The recently developed thermodynamic treatment of the polarity and the selectivity of stationary phases is shown to have several advantages over the Rohrschneider-McReynolds system. Attention is paid mainly to the quantitative characterisation of the energy of sorbate-sorbent intermolecular interactions on the basis of retention indices. A universal system is proposed for assessing polarity and selectivity in gas chromatography in terms of the energy of intermolecular interaction.
A list of 83 references is included.

CONTENTS

I. Introduction 88
II. Intermolecular interactions governing retention in gas chromatography 89
III. Thermodynamic treatment of the polarity and selectivity of stationary phases and adsorbents in gas chromatography 90
IV. Universal system for assessing polarity and selectivity of stationary phases 91
V. Calculation of energy contributions by fragments of molecule analysed 96

I. INTRODUCTION

The widespread use of gas-chromatographic methods of analysis in science and technology makes it necessary to assess as fully as possible the properties of stationary phases and adsorbents, which would permit the choice of optimum conditions for analysis. The problem of classifying stationary phases in gas chromatography and assessing their polarity and selectivity has already been the subject of research for more than twenty years. Empirical methods for such assessment have been surveyed[1].

Before passing to a thermodynamic consideration of the problem of polarity and selectivity, we shall briefly consider existing methods of determination. According to Littlewood polarity is determined by the enhanced affinity of the given substance for a polar compound ("the stationary phase is the more polar the longer it retains a polar substance in comparison with the retention of a non-polar substance"[2]). The polarity of a compound is attributed to the presence of a dipole moment; the magnitude of the orientation (dipole–dipole) interaction is regarded as decisive in assessing the polarity of a stationary phase[3,4]. Several attempts have been made to relate polarity to the electrostatic and structural properties of stationary phases and substances analysed. Careful analysis of these results[5-7] has shown that only when both structures are comparatively simple, while the proportion of polar groups in the stationary phase is not too large, do relative retentions clearly depend on polarisability, the dipole moments of the interacting molecules, and the dielectric constant of the stationary phase. It is especially difficult to establish any dependence with stationary phases and compounds whose molecules have no dipole moment but are capable of forming hydrogen bonds (such stationary phases are usually regarded as polar[8,9]). Substances that have no dipole moment but are capable of complex formation are retained better by polar than by non-polar phases. The results that have accumulated have made it necessary to interpret the polarity of stationary phases somewhat more broadly, as the capability of such phases for electron-donor–acceptor interaction with a substance being analysed[10].

Numerous attempts have been made to assess the polarities of stationary phases, adsorbents, and carriers empirically in terms of the retention of polar and non-polar substances. Kovats and Wehrly developed[11,12] the idea of estimating the polarities of stationary phases from the retention indices I of a series of compounds of general formula RX, where R represents an n-alkyl radical containing at least six carbon atoms, and X various functional groups. Selectivity was measured by the difference ΔI between the retention indices for each of the substances RX on the given stationary phase and on Apiezon L. The range of ΔI values was termed the "retention dispersion". Despite the great quantity of information which this parameter gave on the ability of stationary phases to retain substances containing various functional groups, it did not become widely used because of the large amount of experimental work required. Bayer[13] suggested that selectivity could be determined from the relative retention of two substances having similar boiling points, one of these compounds being an n-alkane. Rohrschneider[14] used the relative butane–butadiene retention to assess polarity; he chose squalane and oxy-$\beta\beta'$-dipropionitrile as extreme points of the polarity scale, with that for squalane equated to zero. Later suggestions for determining the polarity of stationary phases have included the use of two[15-19], three[20-23], and five[24] compounds.

The well known Rohrschneider–McReynolds system[25-27] has become the most widely used, in which the main compounds for testing stationary phases are benzene, butanol, pentan-2-one, nitropropane, and pyridine, supplemented by 2-methylpentan-2-ol, 1-iodobutane, oct-2-yne, 1,4-dioxan, and *cis*-hydrindane. The indices I for the first five test compounds serve for the assessment of polarity, and the differences ΔI for assessing the selectivity of stationary phases.

It is interesting that the suggestion has been made repeatedly that the polarity of stationary phases should be assessed from the relative retention of adjacent n-alkane homologues[28-31]. It was first proposed[28] that the polarity should be defined by

$$\lg \alpha = \lg V_{g(n+1)} - \lg V_{gn},$$

where $V_{g(n+1)}$ and V_{gn} are the retention volumes of n-alkanes containing respectively $n+1$ and n carbon atoms. It was assumed that the more polar the stationary phase the shorter the retention time of n-alkanes. The one-sidedness of assessing the polarity of stationary phases with respect to n-alkanes has been stressed[32,33].

The problem of determining the polarity of stationary phases in terms of the differential molar free energy per mole of methylene groups in n-alkanes has been discussed[34-36]. Developing these ideas, Novak suggested[10] that the polarity should be determined from the excess energies of mixing of a mole of methylene groups. He obtained these values by measuring the retention times of acetates forming a homologous series and the vapour pressures of the homologues at the analysis temperature and a pressure of 1 atm. The idea of assessing the polarity of stationary phases solely on the basis of the change in the retention parameters of n-alkanes or their thermodynamic characteristics is somewhat illogical, since this involves an attempt to determine polarity by testing compounds for which polar interactions with stationary phases are uncharacteristic. The decrease in energy of dispersion interaction during analysis on a polar phase is thus assumed to be directly proportional to the capacity of the phase for polar interactions. This hypothesis requires proof: it cannot be assumed *a priori*. In any case the polarity scale based on capacity for dispersion interaction is uninformative. It has been suggested[36,37] that the polarity and the selectivity of stationary phases should be estimated from the differential molar enthalpies of the dissolution of compounds containing a series of functional groups. Enthalpies were determined from the temperature dependence of the specific retention volume of the test substances. However, an approach to the assessment of ability to retain polar substances that disregards the change in entropy is not rigorous. The analysis of polar substances on polar stationary phases involves not only a change in the heat of dissolution but also a decrease in the degree of freedom of the molecule analysed, so that retention is determined by the overall differential molar free energy of dissolution. Neglect of the entropy contribution may lead to erroneous conclusions. The need to allow for the entropy contribution in assessing polarity has been noted[38,39] with the suggestion that the polarity of stationary phases should be estimated from the energy contributions by various functional groups.

A tendency has appeared recently for the concepts of "polarity" and "selectivity" to be equated[40,41], which introduces still greater confusion into an understanding of the physical significance of these terms. Thus the concept of polarity and selectivity in gas chromatography has hitherto remained indeterminate. Inspection of published results reveals ambiguity in the treatment of this concept.

The present Review is concerned mainly with the thermodynamic assessment of polarity and selectivity. These concepts are interpreted in terms of various types of intermolecular interactions governing retention in gas chromatography. Systematic regard for the thermodynamic characteristics of processes involved in the interaction between the sorbent and the substances undergoing analysis enables a simple method to be recommended for the quantitative estimation of polarity and selectivity from thermodynamic quantities.

II. INTERMOLECULAR INTERACTIONS GOVERNING RETENTION IN GAS CHROMATOGRAPHY

Retention in chromatography is determined mainly by the energy of intermolecular interactions between the substances undergoing analysis and the stationary liquid phase or the adsorbent. The differential molar free energy of dissolution or adsorption is the sum of the energies of the intermolecular interactions—non-specific, due to physical forces, and specific electron-donor–acceptor interactions, which are chemical in nature.

Physical forces of interaction between two molecules (van der Waals forces) comprise dispersion, induction, and orientation interactions, the total energy of which is for diatomic molecules 1–3 kcal mole^{-1}.[42] The energy of dispersion interaction to the London approximation E_d is the main component of the physical forces:

$$E_d = -\frac{3}{2}\frac{\pi h}{R^6}\alpha_1\alpha_2\frac{J_1 \cdot J_2}{J_1 + J_2}, \quad (1)$$

where α is the static polarisability of the molecules, the J are their ionisation potentials, and R is the intermolecular distance.

If the molecules have non-zero dipole moments μ_1 and μ_2, the contribution of the energy of orientation interaction E_0 may be very substantial:

$$E_0 = -\frac{2}{3kTR^6}\mu_1^2\mu_2^2, \quad (2)$$

where k is Boltzmann's constant and T K is the temperature. In some cases E_0 may reach 50% of the energy of the physical forces[42-44].

The energy of induction interaction E_i usually introduces a small fraction to the total energy; it is expressed by the Debye formula[43]

$$E_i = -\frac{1}{R^6}(\mu_1^2\alpha_2 + \mu_2^2\alpha_1). \quad (3)$$

Thus the energy of the physical forces of interaction of the molecules depends on their static polarisability α, ionisation potentials J, and dipole moments μ. The polarisability can be calculated by means of the formula[42]

$$\alpha = \frac{3}{4}\frac{MR_\infty}{\pi N} \approx \frac{3}{4}\frac{MR_D}{\pi N}.$$

Since $n_\infty^2 \cong 1.1 n_D^2$, we find that

$$\alpha = \frac{3}{4\pi N}\frac{n_D^2 - 1}{n_D^2 + 2}\tilde{V}_m \quad (4)$$

where MR_D is the molecular refraction for the sodium D-line, MR_∞ the molecular refraction for light of zero frequency[42], i.e. at infinite wavelength, n_D the refractive index for the sodium D-line, N Avogadro's number, and $\tilde{V}_m$ the molar volume. We shall examine the cases encountered in gas chromatography.

1. In the analysis of a non-polar molecule (subscript "T") on a non-polar stationary phase (subscript "Ph") the differential molar free energy of dissolution is determined by the energy of dispersion interaction: i.e. $E = E_d$. Hence the greater the molecular refraction the more strongly will the substance be retained by the column sorbent. This was first verified experimentally by Littlewood[2].

2. In the analysis of a non-polar substance on a polar phase or of a polar substance on a non-polar phase the interaction energy is determined by the sum of the contributions:

$$E = E_d + E_i; \quad (5)$$

in which E_i, calculated by means of Eqn.(3), will have a single component. If the dipole moment of the test substance $\mu_T = 0$, we have

$$E_i = -\frac{1}{R^6}\mu_{Ph}^2\alpha_T; \quad (6)$$

if, however, $\mu_{Ph} = 0$, then

$$E_i = -\frac{1}{R^6}\mu_T^2\alpha_{Ph}. \quad (7)$$

It must be borne in mind that, if the substance is capable of donor–acceptor interaction (DA) with the stationary phase, the energy of such specific interaction is added:

$$E = E_d + E_i + E_{DA}. \quad (8)$$

For example, benzene and *p*-dinitrobenzene have zero dipole moments, but with several polar phases they give π-complexes; the donor–acceptor interaction energy of aromatic hydrocarbons with the ether groups of polyethylene glycols (PEG) reaches ~1.8 kcal mole^{-1},[45] and must be taken into account.

3. In the analysis of a polar substance on a polar stationary phase all types of physical interaction occur, and interactions of chemical nature—complex formation, hydrogen bonding, etc.—are often added. The total interaction energy is

$$E = E_d + E_i + E_o + E_{DA}. \quad (9)$$

The concept of physical interactions has been developed and tested experimentally for diatomic molecules. Applied to gas chromatography, therefore, it merely enables us to understand on what the energy of physical forces of interaction depends, what is the contribution by each component to the total free energy. It makes possible prediction of the sequence in which substances of similar structure are eluted from a column in the absence of specific donor–acceptor interactions with the sorbent. Actually, the interaction energy is considerably greater, and an accurate calculation must take into account the influence on the test molecule of the surrounding medium, the molecular weight, the number of contacts with the stationary phase, etc; an attempt can be made to use for this purpose one of the theories of solutions[46,47]. Experimental data indicate that the energy of interaction of non-specific physical forces in gas–liquid chromatography may reach ~10 kcal mole^{-1}. When the methyl ester of an aliphatic acid containing 24 carbon atoms undergoes analysis on SE-30, for example, the differential molar free energy is 8.34 kcal mole^{-1}.[48]

The differential molar free energy of sorption, which determines the retention of a substance in a column, is in general the sum of energies of both physical and chemical types of interaction; this sum is determined solely by experiment. According to views developed by Zhukhovitskii, furthermore, the free energy probably includes also the energy consumed by the substance in penetrating the stationary phase[3,5,49,50]. The contribution by the energy of donor–acceptor interactions, which are chemical in nature, may be significant in the analysis of polar substances on polar stationary phases. Such interactions probably involve at least partial delocalisation of electrons and the formation of electron-donor–acceptor bonds. The energy of weak donor–acceptor interactions usually varies in the range 1–3 kcal mole^{-1}. In the case of hydrogen bonds it may reach 3–8 kcal mole^{-1}.[51,52]

Experimental investigation of donor–acceptor interactions began at the start of the 1960s. The properties of many such interactions and their energies of formation have been given in a monograph[53]. Several determinations of the energy of weak hydrogen bonds have been made by the methods of infrared spectroscopy and gas chromatography[54,55]. There is no doubt that donor–acceptor interactions occur widely. Published data[56] enable us to assess between what classes of substances they are possible and what is the heat of formation of the complexes. Benzene, for example, is active in forming complexes with aromatic compounds—benzene, phenol, aniline—and also with dioxan and hydrogen cyanide. Complex formation of similar type probably occurs in the analysis of benzene and other aromatic compounds on silicone phases containing phenyl and nitrile groups, as well as on phases containing ether groups (polyethylene glycols, Tritons, Carbowaxes, etc.). Complex formation with alcohols can occur during analysis on stationary phases containing nitrile and ester groups. During gas-chromatographic analysis the energy contribution by donor–acceptor interactions to the free energy may be substantial[45,51–56].

Thus the differential molar free energy of dissolution of a substance in a stationary phase is the sum of non-specific energies of intermolecular interactions amounting to ~1–10 kcal mole^{-1}, due to physical forces, and the energy of specific donor–acceptor interactions of chemical nature, including hydrogen bonding (~1–8 kcal mole^{-1}).

III. THERMODYNAMIC TREATMENT OF THE POLARITY AND SELECTIVITY OF STATIONARY PHASES AND ADSORBENTS IN GAS CHROMATOGRAPHY

It has already been remarked that the concepts of polarity and selectivity are very indefinite in gas chromatography, and are interpreted differently by different investigators[2–40]. In the opinion of the Reviewers gas-chromatographic polarity must be interpreted as *the capacity of a sorbent for various types of intermolecular interactions,* which is assessed from the differential molar free energy respectively of dissolution and of adsorption ΔG and ΔG_A in gas–liquid and gas–adsorption chromatography: the higher is ΔG, the more polar the sorbent. The selectivity of two comparable stationary phases or adsorbents represents *the difference in ability to retain* the compound analysed, and is expressed quantitatively by the difference in excess energies of mixing $\delta(\Delta G^E)$[57]: the greater the value of $\delta(\Delta G^E)_{2,1}$, the greater the selectivity of sorbent *2* in comparison with *1*.

The polarity of a sorbent cannot be assessed by analysing only one substance, since it is impossible to choose a compound capable of all types of intermolecular interactions on contact with the sorbent. A series of test substances must be selected that model possible intermolecular interactions most closely and completely. They should include those that will reveal the capacity of the sorbent for dispersion, orientation (dipole–dipole), and induction interactions, and permit determination of electron-donor–acceptor properties, as well as the ability to form hydrogen bonds.

Determination of the polarity of stationary phases or adsorbents requires the use, not of a single scale for one test substance, but of a set of scales for all the test substances. The reason is that each sorbent has a different capacity for intermolecular interactions during an analysis, and it is advisable to compare all free energies for all test substances. But the sum of the values

$$\sum_1^i \Delta G_i,$$

like the sum[24,58]

$$\sum_{i=1}^{i} \Delta I_i,$$

does not indicate individual features of a sorbent because of possible compensation effects. For example, a stationary phase with a large energy of dispersion interaction and hence a small energy of orientation interaction may have the same sum

$$\sum_{i=1}^{i} \Delta G_i,$$

as a phase having moderate energies of dispersion and electron-donor–acceptor interactions; therefore assessing polarity from the sum of the differential molar free energies of dissolution of all the test substances will not enable the optimum phase to be chosen for separating a specific mixture.

In every case the experimenter who has a mixture of compounds should envisage the intermolecular interactions of which they are capable, and then select a stationary phase or an adsorbent that will realise these possibilities. If, for example, compounds having a large dipole moment, unsaturated or hydroxylated, are to be separated, polarity scales are to be compared on the basis of free-energy values for substances that test the capacity of stationary phases for orientation interaction, π-complex formation, and hydrogen bonding.

The choice and the number of test substances have been the subject of study by many investigators for more than a decade[20-27]. The difficulty is that it is impossible to select test substances capable of only a single type of interaction—orientation, induction, or donor–acceptor interaction—for usually two or more types function simultaneously. Researches to find the necessary and sufficient number of test substances, made by Tacats[59], Hartkops[60], and de Clercq[61] with mathematical assessment of the weighting of each of a long series of proposed substances used to characterise stationary phases, have shown that Rohrschneider and McReynolds' five compounds are quite sufficient to assess the polarity of stationary phases in gas–liquid chromatography. Other substances will give little additional information on the properties of sorbents.

In the Reviewers' opinion the assessment of polarity can usefully be expressed in terms of six parameters[62-64] based on the differential molar free energies of dissolution ΔG^{CH_2} of a methylene unit of an n-alkane (or of a methyl ester of an aliphatic acid) and the five well known test substances[24,27,58]—benzene (x), butan-1-ol (y), pentan-2-one (z), 1-nitropropane (u), and pyridine (s)—which model the chief types of intermolecular interactions with stationary phases during analysis (Table 1). Some changes in this list of test substances may be required to estimate the polarity of adsorbents in gas–adsorption chromatography, but at present this is difficult to verify, since sufficient published data are not available.

If gas-chromatographic polarity is regarded as the capacity of sorbents for various intermolecular interactions (physical and chemical in nature) with substances undergoing analysis, it can be determined numerically from the differential molar free energies of sorption of the test substances. Retention of a compound in a column is always due to intermolecular forces of interaction. On this view there are in gas chromatography no stationary phases or adsorbents that are absolutely incapable of intermolecular interactions. In the old terminology non-polar solvents are those that are capable mainly of dispersion interaction with a substance to be analysed. Such stationary phases include, for example, squalane, Apiezons, Kovats' hydrocarbon, etc. These phases are characterised by large differential molar free energies of dissolution of the methylene group. According to the thermodynamic treatment of polarity they possess a large "dispersion polarity"[62]. Stationary phases and adsorbents that possess a minimal capacity for all types of intermolecular interactions, i.e. that have minimal values of ΔG for all test substances, must be included among non-polar sorbents[63,64].

Thus the thermodynamic interpretation of gas-chromatographic polarity attributes to this term a quite different significance from that accepted hitherto. Such a definition of polarity makes it easy to avoid the ambiguity in understanding the nature of sorption forces in gas chromatography and brings published results into an orderly system, avoiding the confusion that had arisen from a different interpretation of this concept.

The energy of the dispersion, orientation, induction, and donor–acceptor interactions responsible for the retention of a substance in a column depends on the temperature of analysis. Hence the polarity, defined by the energy of intermolecular interaction, will also depend on the temperature. Therefore the polarities of different stationary phases and adsorbents can be compared only under isothermal conditions at the same analysis temperature by comparing values of ΔG or specific retention volumes. It is incorrect to determine the polarities of different sorbents from the retention indices, and the selectivities from ΔI, as is widely done at the present time for stationary phases[58], since the energy value of an index unit changes from one sorbent to another (see Section IV). As a consequence, different sorption energies correspond to the same values of the retention index or of ΔI.

Recent publications have suggested[38,39] that the polarities of stationary phases should be determined from the differential molar free energies of dissolution of functional groups—hydroxyl, formyl, carbonyl, formyloxy, acetoxy, oxy—for homologous series of organic compounds. Firstly the dependence of the specific retention volume on the reciprocal of the temperature is plotted from two or three points, ΔH and ΔS are determined graphically, the total energy of dissolution ΔG is calculated, and then the energy contributions by individual fragments of the molecules, including functional groups, are determined[39]. However, the authors disregard the effect of the position of a functional group in a molecule on its energy contribution. For example, the contribution by a carbonyl group is greater in the homologous series of alkan-2-ones than in alkan-3- and -4-ones[65]; the same applies to the oxy-group, which is analogous to the thio-group[66] in its gas-chromatographic behaviour. Hence the estimation of polarity from the contributions by various functional groups[39] is quite complicated and does not give a true picture because of inaccurate calculation and a simplified treatment of the results.

Thus in the strict thermodynamic sense the capacity of a sorbent for various intermolecular interactions with a substance undergoing analysis (its polarity) is determined by the differential molar free energies of sorption. Selectivity represents a difference in the capacity of comparable sorbents for intermolecular interactions with the substance analysed, and is determined by the quantity $\delta(\Delta G^E)$.

IV. UNIVERSAL SYSTEM FOR ASSESSING POLARITY AND SELECTIVITY OF STATIONARY PHASES

1. Assessment of Polarity

Before considering a universal system for assessing the polarity of sorbents in gas chromatography we can usefully examine in greater detail the Rohrshchneider–McReynolds estimation of the polarity and selectivity of stationary phases[24-27,58], which has been widely used by research workers. By now more than 200 stationary phases have been classified according to this system[27,58], which diminishes the number of experiments in the selection of stationary phases for gas–liquid chromatography.

A detailed account of the principle underlying the characterisation of stationary phases will be found in a review[1]. According to Rohrschneider polarity and selectivity are characterised by five ΔI values, each the difference between the retention indices of a standard test substance x, y, z, u, or s (Section III) on the given stationary phase and on squalane regarded as a phase of "zero polarity".

In order to describe theoretically the relation between the ΔI values and the thermodynamic characteristics of the gas-chromatographic process Rohrschneider suggested the empirical equations[24]

$$\lg V_g = -\Delta G + \text{const}, \qquad (10)$$

$$-\frac{\Delta G^{CH_2}}{100} = B = b/100, \quad (11)$$

$$\Delta I = I_{Ph} - I_{Ph_1} = 100\frac{\Delta G_{Ph} - \Delta G_{Ph_0}}{\Delta G^{CH_2}_{Ph}}, \quad (12)$$

in which b is the coefficient in the dependence of the logarithm of the specific retention volume of an n-alkane on the number of carbon atoms

$$\lg V_{gn} = a + bn, \quad (13)$$

or

$$b = \lg V_{g(n+1)} - \lg V_{gn}; \quad (14)$$

$\Delta G^{CH_2}_{Ph}$ is the differential molar free energy of dissolution of a methylene group of the n-alkane in Ph, the polar phase, I_{Ph} and I_{Ph_1} are the retention indices of the substance on the phases Ph and Ph_1, the latter representing squalane, and ΔG_{Ph_0} is the energy of dissolution in the polar phase Ph of the hypothetical hydrocarbon containing $n = I_{Ph_1}/100$ carbon atoms.

Equation (10) shows the dependence of the specific retention volume V_g on the differential molar free energy of dissolution ΔG. Equation (11) represents the dependence of the differential molar free energy of dissolution of a methylene unit of an n-alkane ΔG^{CH_2} on the coefficient b. According to the fundamental empirical equation (12) the quantity ΔI is directly proportional to the difference between the free energies of dissolution on the given phase Ph and the phase of "zero polarity" Ph_1. Actually, Eqn.(10) is valid only when specific volumes of substances V_g are compared on the same stationary phase at the same temperature. According to other workers[67]

$$\Delta G = -2.3RT \lg \frac{V_g T\rho}{273}, \quad (15)$$

$$\lg V_g = -\frac{\Delta G}{2.3RT} - \lg \frac{T\rho}{273}, \quad (16)$$

where ρ is the density of the stationary phase at the analysis temperature T K. Hence Eqn.(16)—not Eqn.(10) as in Ref.24—must be used to classify different stationary phases.

A rigorous deduction of Eqns.(11) and (12) could be made after the relation between the retention index and the free energy ΔG had been established. In 1971 Golovnya and Arsen'ev showed[68] that

$$\Delta G = -2.3RT\left[\frac{I - 100n}{100}b + \lg\frac{V_{gn}T\rho}{273}\right], \quad (17)$$

which revealed discrepancies in Rohrschneider's thermodynamic treatment of ΔI and also ΔG^{CH_2}. Thus, when we use Eqn.(17) to express the differential molar free energies of dissolution of two n-alkane homologues ΔG_{n+1} and ΔG_n and take their difference, we obtain[62]

$$\Delta G^{CH_2} = -2.3RTb. \quad (18)$$

Hence calculation of the differential molar free energy of dissolution of a methylene unit of an n-alkane, or other homologous compounds in which the difference in the index per methylene unit is 100, requires the use of Eqn.(18), not Eqn.(11), which is not even dimensionally correct.

Use of Eqn.(17) to compare the gas-chromatographic behaviour of a given substance on the two phases Ph and Ph_0 yields for the difference in the differential molar free energies of dissolution the expression[63]

$$\delta(\Delta G)_{Ph,Ph_0} = \Delta G_{Ph} - \Delta G_{Ph_0} = \quad (19)$$
$$= \frac{1}{100}(I_{Ph}\Delta G^{CH_2}_{Ph} - I_{Ph_0}\Delta G^{CH_2}_{Ph_0}) - 2.3RT(a_{Ph} - a_{Ph_0}) + 2.3RT\lg\rho_{Ph}/\rho_{Ph_0},$$

where a_{Ph} and a_{Ph_0} are determined for n-alkanes by the application of Eqn.(13) to analytical results on these phases. Equation (19) shows that the difference in the free energies of dissolution in the two phases is a complicated function of the indices I_{Ph} and I_{Ph_0}, which is not consistent with the empirical equation (12) previously used to assess the polarity and the selectivity of stationary phases[24-27,58]. Analysis of Eqn.(19) reveals that the free-energy difference cannot be directly proportional to ΔI. The same conclusion can be reached by using the well known relation[44,48,69] $\Delta G = A + BI$ to express ΔI. The resulting formula

$$\Delta I_{Ph,Ph_0} = \frac{\Delta G_{Ph} - A_{Ph}}{\Delta G^{CH_2}_{Ph}} - \frac{\Delta G_{Ph_0} - A_{Ph_0}}{\Delta G^{CH_2}_{Ph_0}},$$

is not equivalent to Rohrschneider's equation (12). The Rohrschneider–McReynolds assessment of polarity distorts the real picture more strongly the greater the difference in the gas-chromatographic behaviour of n-alkanes on the stationary phases under comparison, and hence the difference in the quantities $\Delta G^{CH_2}_{Ph}$ and $\Delta G^{CH_2}_{Ph_0}$.

It follows from Eqn.(19) that the energy value of one index unit differs on different stationary phases. Therefore the same index on different stationary phases corresponds to different free energies. The energetic importance of unit retention index on a given stationary phase can be determined by means of Eqn.(18), since ΔG^{CH_2} correspond to 100 index units (i.u.), and $\Delta G_{i.u.} = \Delta G^{CH_2}/100 = -0.023RTb$ cal mole^{-1} is the energy value of one index unit. According to the thermodynamic treatment (Section III) the polarity of a stationary phase must be determined from ΔG values calculated from retention indices by means of Eqn.(17).[63] At the present time it is probably advisable to use the compounds listed in Table 1 as test substances for the assessment of polarity.

Table 1. Test species for assessment of phase polarities.

Species	Type of interaction with sorbent tested*
Methylene in n-alkane or methyl aliphatic ester	dispersion
Benzene	π-complex formation
Butan-1-ol	hydrogen bonding with electron-donor groups
Pentan-2-one (weak electron-donor)	donor–acceptor complex formation
1-Nitropropane	orientation, since dipole moment $\mu = 3.6$; donor–acceptor complex formation
Pyridine (base)	hydrogen bonding with hydrogen donors; donor–acceptor complex formation

*Only the retention of methylene groups is determined by the energy of dispersion interaction. Retention of the remaining test species, unfortunately, depends on the character of the sorbent as a consequence of the total energy of the dispersion, orientation, induction, and donor–acceptor interactions (Section II); the type of interaction which they test is a component of the total energy of sorption.

The capability of a sorbent for dispersion interaction with a substance undergoing analysis is determined from the differential free energy of sorption of a methylene group ΔG^{CH_2} in the homologous series of n-alkanes, or in methyl esters of aliphatic acids in the case of very polar sorbents.

It has recently been established[70] that these esters have a homologous difference of 100 index units per methylene group even on such polar phases as Silar 5CP and Silar 10C,[70] whereas the series of alkyl acetates suggested previously for this purpose[10] exhibits a variation in the homologous difference with the polarity of the phase, as follows from a comparison of the indices for homologues tabulated in Ref.71. Hence acetates cannot be recommended as test substances for the classification of sorbents according to their ΔG^{CH_2} values.

As example of the assessment of dispersion polarity Table 2 lists values of ΔG^{CH_2} for several stationary phases, calculated by means of Eqn.(18).[63] Comparison of the capacities of these phases for dispersion interaction, assessed from the ΔG^{CH_2} values (Table 2) shows that SE-30, which is non-polar in the old terminology, is less capable of dispersion interaction than are the moderately polar OV-17 and Chalcomide M-18 OL, and is close to the more polar Triton X-305. Hence the decrease in the capacity for dispersion interaction is not proportional to the increase in polarity of the stationary phases[62,63]. Maximum dispersion polarity, i.e. capacity for dispersion interaction with a substance, is exhibited by such phases as squalane, the Kovats hydrocarbon $C_{87}H_{176}$,[72] and the Apiezons. The greatest dispersion polarity among the stationary phases in Table 2 is exhibited by squalane, which has the highest free energy of dissolution of n-alkanes.

Table 2. "Dispersion polarity"* of some stationary phases at 120 °C, estimated from the differential molar free energies of dissolution of a methylene unit of an n-alkane ΔG^{CH_2}.[63]

Stationary phase	b	$-\Delta G^{CH_2}$, cal mole^{-1}	Stationary phase	b	$-\Delta G^{CH_2}$, cal mole^{-1}
Squalane	0.2891	520	SE-30	0.2495	449
Dioctyl sebacate	0.2862	514	SE-31	0.2485	447
Chalcomide M-18 OL	0.2844	511	Igepal CO-880	0.2414	434
$C_{87}H_{176}$	0.2841	511	Triton X-305	0.2404	432
Apiezon M	0.2833	510	Pluroonic F-88	0.2362	425
Apiezon L	0.2821	507	Quadrol	9.2353	423
Dioctyl phthalate	0.2792	502	PEG-4000	0.2238	403
Flexol 8N8	0.2733	491	Carbowax-20M	0.2235	402
Castorwax	0.2684	483	PEG-600	0.2180	392
Tritolyl phosphate	0.2630	473	Carbowax-1000	0.2174	391
Ucon LB 1715	0.2603	468	DEGA	0.2105	379
Poly-Tergent J-300	0.2598	467	EGA	0.2091	376
Oronite N1W	0.2576	463	Zonyl-E7	0.2083	375
Diglycerol	0.2568	461	XF-1150	0.2053	369
OV-17	0.2551	459	Silar 10C	0.1960	353
SE-52	0.2548	458	Tris-CEP	0.1787	322

*Results from Ref.63 supplemented by calculations of ΔG^{CH_2} for several stationary phases taken from tables[27,71].

The capacity of stationary phases for other types of intermolecular, including dispersion, interaction is determined from the differential molar free energies of dissolution of the five test substances (Table 1), which are calculated by means of Eqn.(17). Indices of the test substances, specific retention volumes V_{gn} of n-alkanes, and values of the coefficient b, which are required for the calculation, can be taken from Reynolds' tables[27,71]. Density data for stationary phases at the temperature of analysis cannot usually be found in the literature, and must be determined specially. If the density ρ is unknown, values of ΔG can be calculated[63] to within 10% by means of the formula

$$\Delta G + 2.3RT \lg \rho = -2.3RT\left[\frac{I - 100n}{100} b + \lg \frac{V_{gn}T}{273}\right]. \qquad (20)$$

This does not affect the general picture in the estimation of polarity.

Table 3 gives as example the estimation of polarity for several stationary phases from the ΔG values of the five test substances[63]. Comparison of ΔG^{CH_2} and of the five ΔG values permits numerical assessment of the capacity of the stationary phases for intermolecular interactions—dispersion, orientation, induction and donor—acceptor—including hydrogen bonding. The larger the value of ΔG for a given test substance the greater the capacity of the phase for those intermolecular interactions that are tested by this substance (Table 1). Thus in the thermodynamic treatment of polarity the most polar stationary phase will be that exhibiting the highest ΔG values for every test substance among comparable stationary phases, and the most non-polar that with which all five ΔG values are least. Inspection of Table 3 on this basis indicates SE-30 to be the most non-polar, and Oronite N1W the most polar. Table 3 indicates also that each stationary phase has its individual features. For example, the retention of alcohols on Oronite N1W, Poly-Tergent J-300, and Chalcomide M-18 OL, and that of organic bases on Oronite N1W, are greater than on polyethylene glycols. Aromatic compounds are retained most strongly by Oronite N1W, dioctyl sebacate, Chalcomide M-18 OL, Flexol 8N8, and Poly-Tergent J-300 (Table 3). The contribution of dispersion interaction to the total ΔG value can be determined as in Ref.62.

Table 3. Polarities* of some stationary phases at 120 °C.[63]

Stationary phase	$-(\Delta G + 2.3RT \lg \rho)$, cal mole^{-1}				
	benzene	butan-1-ol	pentan-2-one	1-nitropropane	pyridine
Apiezon L	2820	2450	2600	2820	3110
Apiezon M	2820	2460	2610	2810	3100
Dioctyl sebacate	3250	3420	3300	3800	3750
Chalcomide M-18 OL	3220	3870	3360	3980	3840
Dioctyl phthalate	3050	3200	2310	3770	3660
Flexol 8N8	3110	3530	3270	3860	3690
Castorwax	3060	3510	3260	3640	3950
Tritolyl phosphate	2910	3320	3140	3840	3710
Ucon LB 1715	2890	3360	2990	3550	3580
Poly-Tergent J-300	3080	3710	3240	3930	3950
Oronite NIW	3840	4400	3980	4690	4710
Diglycerol	930	2730	1680	2330	3360
SE-52	2580	2470	2610	2870	2950
SE-30	2530	2410	2540	2740	2850
SE-31	2540	2430	2560	2760	2870
Igepal CO-880	2910	3510	3020	3870	3830
Triton X-305	2650	3260	2760	3620	3570
Pluronic F-88	2950	3530	3020	3880	3810
PEG-4000	2860	3520	2960	3890	3830
Carbowax 20M	2870	3470	2950	3870	3810
PEG-600	2810	3670	3020	3910	3990
Carbowax 1000	2860	3630	3030	3940	3980
DEGA	2460	3080	2680	3550	3700
EGA	2450	2980	2650	3510	3540
Zonyl E-7	2220	2500	3040	3440	3300
XF-1150	2450	3000	2960	3780	3440
Quadrol	2380	3620	2870	3460	3730

*Results from Ref.63 supplemented by calculation for stationary phases from Refs.27 and 71.

The system proposed[62-64] for assessing polarity from the ΔG^{CH_2} values and the five ΔG values of the Rohrschneider–McReynolds test substances is universally applicable. It does not require the "zero polarity" phase necessary in other methods for estimating the polarity of stationary phases[24,27,58], and can be extended to determination of the polarity of adsorbents in gas chromatography if values are included for

the differential molar free energies of adsorption ΔG_A of the test substances. The polarity of adsorbents can be calculated by means of the equations[63]

$$\Delta G_A^{CH_2} = -2.3RTb_A = -2.3RT\,[\lg V_{g(n+1)} - \lg V_{gn}], \quad (21)$$

$$\Delta G_A = -2.3RT\left[\frac{I-100n}{100}b + \lg V_{gn} - \lg RTS\right], \quad (22)$$

$$\delta(\Delta G)_{A_1A_2} = \frac{1}{100}(I_{A_1}\Delta G_{A_1}^{CH_2} - I_{A_2}\Delta G_{A_2}^{CH_2}) - 2.3RT\,(a_{A_1} - a_{A_2}) + 2.3RT \lg S_{A_1}/S_{A_2}, \quad (23)$$

in which a is the constant and b the coefficient in the relation $\lg V_{gn} = a + bn$ for n-alkanes analysed on an adsorbent A, where $b_A = \lg V_{g(n+1)} - \lg V_{gn}$, while I_{A_1} and I_{A_2} are the retention indices of the substance on adsorbents A_1 and A_2, with $\Delta G_{A_1}^{CH_2}$ and $\Delta G_{A_2}^{CH_2}$ the differential molar free energies of adsorption of a methylene unit in n-alkanes on these adsorbents, and S_{A_1} and S_{A_2} (in $cm^2\ g^{-1}$) their specific surfaces.

The single method of using free energies of sorption for quantitative assessment of the capability of stationary phases and adsorbents for intermolecular interactions with substances undergoing analysis makes it possible to characterise every sorbent individually.

2. Assessment of Selectivity

The term "selectivity" is widely used in gas chromatography, but it is often applied without regard to its thermodynamic basis, consequently with different and occasionally incorrect interpretations. For example, selectivity and column efficiency have been identified in one book[74]. Several papers regard selectivity as synonymous with polarity[38,40] or as the ability to separate two substances of closely similar boiling points, and distinguish three types of selectivity defined in different ways[75].

Actually the separating ability of a column is a result of its selectivity and efficiency. The former depends solely on the equilibrium characteristics in the sorbent–gas system; it indicates the difference in retention of the substances undergoing analysis, and is assessed in terms of the relative retention. Selectivity can be expressed quantitatively in terms of thermodynamic quantities. Efficiency depends on kinetic processes occurring in the column and influencing the peak widths; it is estimated as the height of a theoretical column H. It follows from van Deemter's rate theory[76] that H depends on the velocity of the carrier gas, diffusion, and resistance to mass exchange. The separation of two substances depends both on the selectivity and on the efficiency of the column, and is measured by the separation factor R,[43] which includes the distance d between the retention times of the substances and the widths w of their peaks:

$$R = 2d/(w_1 + w_2). \quad (24)$$

It is evident from this formula that the larger is d the higher the selectivity, and that the wider the peaks the lower the efficiency and hence the overall separation.

A thermodynamic examination of comparable gas-chromatographic processes will help to introduce complete clarity into an understanding of selectivity, which is used in two cases—to compare the abilities of (i) a given sorbent to retain two substances, and (ii) two sorbents to retain a given substance—as a characteristic of the properties of a sorbent. Both cases have been considered in terms of thermodynamics, and selectivity has been determined quantitatively from differences in differential molar free energy of mixing $\delta(\Delta G^E)$.[57,77]

The selectivity of a stationary phase in the separation of two substances is defined by the factor

$$\alpha_{ij} = \frac{\gamma_j^\infty p_j^0}{\gamma_i^\infty p_i^0} = (e^{\Delta G_j^E/RT}/e^{\Delta G_i^E/RT})\frac{p_j^0}{p_i^0}, \quad (25)$$

in which γ_i^∞ and γ_j^∞ are the activity coefficients of substances i and j at infinite dilution, p_i^0 and p_j^0 are their saturated vapour pressures under 1 atm at the column temperature, and ΔG_i^E and ΔG_j^E their excess free energies of mixing on the given stationary phase. After rearranging Eqn.(25) we obtain a quantitative assessment of the selectivity of a stationary phase in terms of the difference in excess free energies of dissolution of the two substances:

$$\delta(\Delta G^E)_{ij} = \ln \alpha_{ij} = \Delta G_i^E - \Delta G_j^E. \quad (26)$$

Since[68,77–79]

$$\delta(\Delta G^E)_{ij} = 2.3RT \lg \gamma_i/\gamma_j. \quad (27)$$

the selectivity of a given stationary phase with respect to two substances, i.e. the difference in its ability to retain them at a given temperature, is determined by the difference in the excess energies of mixing: it can be found from the polarity expressed in terms of ΔG by means of the equation[63,64]

$$\delta(\Delta G^E)_{ij} = \delta(\Delta G)_{ij} - 2.3RT \lg p_i^0/p_j^0. \quad (28)$$

The calculation of selectivity by means of this formula requires knowledge of the vapour pressures of the pure substances p_i^0 and p_j^0 under 1 atm at the analysis temperature. When the polarity of the phase expressed in free energies is unknown, the first term in Eqn.(28) can be calculated from the difference in the retention indices of i and j by means of the equation[44]

$$\delta(\Delta G)_{ij} = -2.3RTb\frac{\delta I_{ij}}{100}. \quad (29)$$

It follows from (28) and (29) that the selectivity of one stationary phase with respect to substances i and j can be calculated by means of the formula[63,64]

$$\delta(\Delta G^E)_{ij} = -2.3RT\left[b\frac{\delta I_{ij}}{100} + \lg p_i^0/p_j^0\right]. \quad (30)$$

The second case—the selectivity of two stationary phases Ph_2 and Ph_1 with respect to a given substance a—is expressed quantitatively by the formula[77]

$$\delta(\Delta G^E)_{Ph_2Ph_1} = 2.3RT \lg \gamma_{Ph_2}/\gamma_{Ph_1}, \quad (31)$$

in which γ_{Ph_2} and γ_{Ph_1} are the activity coefficients of i at infinite dilution in the two phases. Recently it has been shown[63,64] that selectivity can easily be determined quantitatively from the polarities of the phases expressed in terms of free energies. Thus at a given temperature the excess energy of i on the phases will be given by the classic equations

$$\Delta G_{Ph_2}^E = \Delta G_{Ph_2} + \Delta G_e, \quad (32)$$

$$\Delta G_{Ph_1}^E = \Delta G_{Ph_1} + \Delta G_e, \quad (33)$$

where ΔG_e is the differential molar free energy of evaporation of the pure substance i under 1 atm at the analysis temperature, and ΔG_{Ph_2} and ΔG_{Ph_1} are the differential molar free energies of dissolution of i in the phases Ph_2 and Ph_1. From (33) and (32) we obtain for selectivity the thermodynamic formula

$$\delta(\Delta G^E)_{Ph_2Ph_1} = \Delta G_{Ph_2} - \Delta G_{Ph_1} = \delta(\Delta G)_{Ph_2Ph_1}. \quad (34)$$

Thus the selectivity of two stationary phases towards a substance analysed at a given temperature is determined quantitatively from the difference in its free energies of

dissolution on the phases and can be calculated from a table of estimated polarities of stationary phases (Table 3).

A single system for assessing selectivity can be obtained by selecting one of the stationary phases as reference, which should satisfy certain requirements. According to the thermodynamic treatment of polarity and selectivity the reference phase should have minimal ΔG values for all test substances and minimal differences between them: i.e.it should have minimal selectivity. Furthermore, it should be chemically homogeneous and should withstand high temperatures. These demands are met neither by squalane (whose disadvantages, including irreproducibility of the indices, have been criticised by Ettre[1] and by Supina[80]) nor by the hydrocarbon 24,24-diethyl-19,29-dioctadecylheptatetracontane, proposed by Kovats[72,73] to replace squalane, as is evident from Table 4.

Table 4. Choice of reference phase for assessing the selectivity of stationary phases on the thermodynamic criterion[64] $\delta(\Delta G)_{max}$.

Phase	Retention index for test cpd.*					ΔI_{max}	Energy of 1 i.u., cal mole^{-1}	$-\delta(\Delta G)_{max}$,
	benzene	butan-1-ol	pentan-1-ol	nitropropane	pyridine			
Squalane	653	590	627	652	699	109	—5.20	567
$C_{87}H_{176}$	674	600	630	664	724	124	—5.11	634
SE-30	668	643	671	716	740	97	—4.49	435
Hydrogenated Apiezon-30	671	599	632	667	736	137	—	—

*Underlining denotes indices of compounds for which ΔI_{max} and $\delta(\Delta G)_{max} = -0.023RTb\Delta I_{max}$ have been calculated.

Recently a comparison has been made[73] of the phases—hydrogenated Apiezon M, the hydrocarbon $C_{87}H_{176}$, and SE-30—with respect to their ability to reproduce the retention indices of the five test-substances, with the aim of seeking a null phase for the determination of selectivity by the Rohrschneider–McReynolds method. Prolonged operation over the range 120–200 °C showed that the indices at 120 °C remained almost unchanged for a year on SE-30, in contrast to the Kovats hydrocarbon. Since the reference phase should possess outstanding reproducibility of indices, and also satisfy the thermodynamic criterion, i.e.have a minimal difference in the free energies of dissolution of the test substances, we have made an estimate of ΔG values. Table 4 lists indices of the test substances for the four phases proposed as reference phases[27,72,73], the energy value of one index unit on each of the stationary phases, and values of the differences $\delta(\Delta G)_{max}$ in the free energies of dissolution of two substances, one of which is retained the longest in the column, whereas the other is eluted first from the column. Among the four stationary phases compared the Kovats hydrocarbon has the maximum selectivity and is therefore least suitable as reference phase for the assessment of selectivity. Minimal selectivity is exhibited by SE-30, which is recommended as reference phase[63,64].

A quantitative assessment of the selectivity of a stationary phase for a given test substance is a measure of its specific interaction with the latter in comparison with SE-30. Table 5 shows as example the selectivities of several stationary phases in terms of $\delta(\Delta G^E)_{Ph,SE}$. It includes for comparison selectivity estimates according to McReynolds[27] based on ΔI values†. It is evident that the former method of assessment is far more informative. As example we compare two phases—Triton X-305 and Igepal CO-880—that are identical on the Rohrschneider–McReynolds view, since their ΔI values differ by 20 index units: actually they exhibit differences in practical gas chromatography, which can be clearly traced in the $\delta(\Delta G^E)$ data, for Igepal CO-880 is three times as selective as Triton X-305 towards aromatic compounds, and twice as selective in the separation of carbonyl compounds. Although the Rohrschneider–McReynolds method shows identity of XF-1150 and Carbowax-20M in the separation of aromatic compounds, alcohols, and amines, the $\delta(\Delta G)_{Ph,SE}$ values indicate that the latter phase has an advantage for the separation of all three classes of compounds. The phases EGA and XF-1150 are also identical according to their ΔI values in the analysis of carbonyl compounds and nitroderivatives, whereas the $\delta(\Delta G^E)$ values indicate that XF-1150 is four times as selective towards the former compounds, and 50% more selective towards the latter, which is confirmed by experiment[63]. Another pair—tritolyl phosphate and Poly-Tergent—have the same selectivity in the separation of aromatic compounds and amines according to ΔI data, but differ sharply according to the $\delta(\Delta G^E)$ values. The choice of optimum conditions for gas-chromatographic analysis of a mixture on the basis of the latter type of data has been described in detail[81] for analysis of a mixture of saturated and unsaturated aldehydes and ketones.

Table 5. Comparison of selectivities of stationary phases based on $\delta(\Delta G^E)_{Ph,SE-30}$ values and on McReynolds constants (at 120 °C).[63]

$-\delta(\Delta G^E)_{Ph,SE-30}$, cal mole^{-1}					Stationary phase	$\Delta I_{Ph,squalane}$				
benzene	butan-1-one	pentan-2-one	nitropropane	pyridine		benzene	butan-1-one	pentan-2-one	nitropropane	pyridine
290	40	60	80	260	Apiezon M	31	22	15	30	40
290	50	70	70	250	Apiezon L	32	22	15	32	42
720	1010	760	1060	900	Dioctyl sebacate	72	168	108	180	123
690	1460	820	1240	990	Chalcomide M-18 OL	89	280	143	239	165
520	790	670	1030	810	Dioctyl phthalate	92	186	150	236	167
580	1120	730	1120	840	Flexol 8N8	96	254	164	260	179
530	1100	720	900	1100	Castorwax	108	265	175	229	246
380	910	600	1100	860	Tritolyl phosphate	176	221	250	374	299
360	960	450	810	730	Ucon LB 1715	132	297	180	275	235
550	1300	700	1190	1800	Poly-Tergent J-300	168	366	227	350	308
1310	1990	1440	1950	1860	Oronite N1W	185	370	242	370	327
50	60	70	130	100	SE-52	32	72	65	98	67
10	20	20	20	20	SE-31	16	54	45	65	43
380	1100	480	1130	980	Igepal CO-880	259	461	311	482	426
120	850	220	880	720	Triton X-305	262	467	314	488	430
420	1120	480	1140	960	Pluronic F-88	262	461	306	483	419
330	1110	420	1150	980	PEG-4000	325	551	375	582	520
340	1060	410	1130	960	Carbowax 20M	322	536	368	572	510
280	1260	480	1170	1140	PEG-600	350	631	428	632	605
330	1220	490	1200	1130	Carbowax 1000	347	607	418	629	589
—70	670	140	810	850	DEGA	378	603	460	665	658
—80	570	110	770	690	EGA	372	576	453	655	617
—310	90	500	700	450	Zonyl E-7	223	359	468	549	465
—80	590	420	1040	590	XF-1150	308	520	470	669	528
—150	1210	330	720	880	Quadrol	214	571	357	472	489

†It has already been mentioned that comparison based on values of $\Delta I = I_{Ph} - I_{sql}$ is incorrect because of different energy equivalents of an index unit of different stationary phases (Section IV).

The above results provide clear evidence that the proposed thermodynamic assessment of the selectivity of stationary phases[63,64] is definitely superior to the McReynolds system and reveals most fully the gas-chromatographic possibilities of a sorbent. It can be extended to gas-adsorption chromatography, since Eqns.(30)–(34) for estimating selectivity from $\delta(\Delta G^E)$ data are still valid[63].

Thus the rigorous thermodynamic treatment of polarity and selectivity in gas chromatography and the availability of equations enabling these properties of sorbents to be determined from thermodynamic functions quantitatively in terms of retention indices enable a single, universally applicable system to be constructed, which will make it possible to find the optimum form of gas-chromatographic analysis to solve a specific problem.

V. CALCULATION OF ENERGY CONTRIBUTIONS BY FRAGMENTS OF MOLECULE ANALYSED

The use of retention indices as gas-chromatographic parameters makes it possible for a qualitative analysis to yield also data for thermodynamic calculation of the contributions, by individual groups in the compounds analysed, to the differential molar free energy of dissolution. For this purpose the formula

$$\delta(\Delta G) = -2.3RTb\frac{\delta I_{ij}}{100}, \qquad (35)$$

is used[44], in which δI_{ij} is the difference between the retention indices of two comparable compounds analysed under the same conditions. Equation (35) has been employed in a comparison of the methyl esters of aliphatic and monounsaturated acids i and j to determine the change in free energy of dissolution on introduction of a double bond into the molecule. On the non-polar phase SE-30 the presence of a double bond diminishes this free energy by 80–120 cal mole^{-1}, but on a polar phase (Silar 5CP) an average increase of 80 cal mole^{-1} is evident at 200 °C.[48]

In analogous heteroatomic compounds the replacement of oxygen by sulphur increases the differential molar free energy of dissolution by 1020 ± 30 cal mole^{-1} independently of the character of the stationary phase[44]. Such an increase is observed on passing from aliphatic ethers, furan, oxolan, dioxan, and their substituted derivatives to sulphides, thiophens, thiolans, and dithians[44]. Calculation based on the application of formula (35) to the difference in retention indices between sulphur- and oxygen-containing compounds of analogous structure indicates that on the non-polar Apiezon M and the polar polyethylene glycol 1000 the retention of both types of compounds is a consequence mainly of dispersion interaction[44].

Equation (35) can be used also to determine the contribution by a functional group in metameric compounds, i.e. compounds of the same class containing the same number of carbon atoms but differing in the position of the functional group. This would indicate whether it is legitimate to assume, when the contribution by a functional group to the free energy of dissolution of one homologous series is known, that this contribution will be the same in another homologous series. We have used earlier results on thiatridecane metamers[82] to trace the variation in the energy contribution by the functional thio-group as it moves deep into an unbranched aliphatic chain[84]. If the contributions to the free energy ΔG by fragments of a molecule are additive[10] the metameric sulphides should be described by the single equation

$$\Delta G = 2\Delta G^{CH_3} + (n-2)\Delta G^{CH_2} + \Delta G^{-S-}. \qquad (36)$$

Analysis of the results[82] shows that the energy contributions ΔG^{CH_3} and ΔG^{CH_2} of the metamers are the same, whereas ΔG^{-S-} changes, decreasing as the sulphur atom moves along the chain. This is readily seen from Table 6, which gives the differences in free energy of dissolution of the thiatridecane metamers relative to 2-thiatridecane. As the sulphur atom is displaced from position 2 to position 7 ($K = 2$ and 7 respectively), the differential molar free energy of dissolution diminishes by 234 and 308 cal mole^{-1} on Apiezon M and polyethylene glycol 1000 respectively. Hence additive equations analogous to (36) can be used only for specific homologous series. The position of a functional group in the molecule must be indicated in a statement of the contribution by the group.

Table 6. Retention indices I and free energies of dissolution ΔG of metameric thiatridecanes on Apiezon M and on PEG-1000 at 130 °C.

K*	Apiezon M at 130°C				PEG-1000 at 130°C			
	I metamer	$-\Delta G$ metamer, cal mole^{-1}	$-\delta(\Delta G)_{2,\,K>2}$** cal mole^{-1}	energy per S, cal mole^{-1}	I metamer	$-\Delta G$, metamer cal mole^{-1}	$-\delta(\Delta G)_{2,\,K>2}$* cal mole^{-1}	energy per S, cal mole^{-1}
2	1520	6831	0	—1595	1757	5783	0	—2173
3	1493	6696	135	—1460	1710	5600	183	—1990
4	1481	6636	195	—1400	1692	5530	253	—1920
5	1477	6616	215	—1380	1684	5499	284	—1889
6	1475	6606	225	—1370	1681	5487	296	—1877
7	1473	6597	234	—1360	1678	5475	308	—1865

*Position of sulphur in metameric thiatridecane, $2 \leq K \leq 7$.
**$\delta(\Delta G)$ is the difference in free energies of dissolution between 2-thiatridecane and the metamer in which the position of the sulphur atom is $K > 2$.

Table 7. Contributions per methylene group ΔI^{CH_2} and ΔG^{CH_2} in various homologous series[65,82,83].

Homologues	Phase	T, °C	ΔI^{CH_2}	$-\Delta G^{CH_2}$, cal mole^{-1}
Nonane-octane	Apiezon M	130	100	498
Nonane-octane	PEG-1000	130	100	389
Nonane-octane	Apiezon M	125	100	503
Nonane-octane	PEGA	125	100	375
Nonane-octane	XF-1150	125	100	359
Nonane-octane	oxy-ββ'-dipropionitrile	50	100	449
Nonanal-octanal	Apiezon M	125	100	503
Nonanal-octanal	PEGA	125	100	375
Nonan-2-one-octan-2-one	Apiezon M	125	100	503
Hexane-1,6-dithiol-pentane-1,5-dithiol	Apiezon M	130	103	513
	PEG-1000	130	97	377
Octan-1-ol-heptan-1-ol	PEG-1000	130	108	420
Hept-2-enal-hex-2-enal	XF-1150	125	112	402
Hept-2-enal-hex-2-enal	oxy-ββ'-dipropionitrile	50	84	377
Heptan-2-one-hexan-2-one	oxy-ββ'-dipropionitrile	50	83	373

Previous results[65,82,83] can be used to calculate the energy contribution by a methylene unit in various homologous series analysed under identical conditions. Table 7 shows that $\Delta I^{CH_2} = 100$ does not apply to all homologous series: it is observed only with straight-chain aldehydes and methyl ketones on Apiezon M and PEGA, whose differential molar free energy for dissolution of a methylene group is the same as with n-alkanes. For homologous series in which

$\Delta I^{CH_2} = 100$, Eqn.(35) can be used to calculate the energy contribution due to specific interaction of the functional group with the stationary phase, from the difference between the retention indices of the given substance and the n-alkane containing the same number of carbon atoms. For αβ-unsaturated aldehydes on XF-1150 and on oxy-ββ′-dipropionitrile $\Delta I^{CH_2} \neq 100$ and ΔG^{CH_2} differs substantially from the values obtained for n-alkanes (Table 7). A similar pattern is observed for dithiols and other compounds.

Hence the energy contribution whether of a methylene or of a functional group depends on the homologous series and the character of the stationary phase. It is thus inadvisable to use energetic contributions to the free energy of dissolution of functional groups, to estimate the polarity of a stationary phase[39], in isolation from the total differential molar free energy of dissolution of the test substance.

REFERENCES

1. L.S.Ettre, Chromatographia, 6, 489 (1973); 7, 261, 397 (1974).
2. A.B.Littlewood, J.Gas Chromatog., 1, 16 (1963).
3. V.M.Sakharov, Neftekhimiya, 5, 762 (1965).
4. I.M.Shevchuk et al., Zhur.Anal.Khim., 25, 2018 (1970).
5. B.I.Anvaer et al., in "Gazovaya Khromatografiya" (Gas Chromatography), GOSINTI, Moscow, 1974, p.44.
6. B.I.Anvaer et al., Zhur.Anal.Khim., 19, 178 (1964).
7. A.B.Littlewood and F.W.Willmott, Analyt.Chem., 38, 1031 (1966).
8. A.V.Iogansen and G.A.Kurkchi, "Fiziko-khimicheskoe Primenenie Gazovoi Khromatografii" (Physicochemical Application of Gas Chromatography), Khimiya, Moscow, 1973, Chapter 3, p.122.
9. G.A.Kurkchi and A.V.Iogansen, Zhur.Fiz.Khim., 41, 563 (1967) [Russ.J.Phys.Chem., No.3 (1967)].
10. J.Novak, J.Ruzickova, S.Wicar, and J.Janak, Analyt.Chem., 45, 1365 (1973).
11. A.Wehrly and E.Kovats, Helv.Chim.Acta, 42, 2709 (1959).
12. E.Kovats, Adv.Chromatog., 1, 229 (1965).
13. E.Bayer, Angew.Chem., 71, 299 (1959).
14. L.Rohrschneider, Z.analyt.Chem., 170, 256 (1959).
15. P.Chovin and J.Lebbe, Communication aux Journées internationales d'Étude de Méthodes de Séparation immédiate et de Chromatographie, Paris, 1962.
16. J.Maier and O.C.Karpaty, J.Chromatog., 8, 308 (1962).
17. N.Petsev, J.Chromatog., 59, 21 (1971).
18. V.R.Huebner, Analyt.Chem., 34, 488 (1962).
19. P.Chovin, Bull.Soc.chim.France, 1800 (1964).
20. I.Brown, J.Chromatog., 10, 284 (1963).
21. I.Brown, I.L.Chapman, and G.J.Nicholson, Austral.J.Chem., 21, 1125 (1968).
22. D.Zarazir, P.Chovin, and G.Guiochon, Chromatographia, 3, 180 (1970).
23. L.Rohrschneider, J.Chromatog., 17, 1 (1965).
24. L.Rohrschneider, J.Chromatog., 22, 6 (1966).
25. L.Rohrschneider, J.Chromatog., 39, 383 (1969).
26. W.R.Supina and L.P.Rose, J.Chromatog.Sci., 8, 214 (1970).
27. W.O.McReynolds, J.Chromatog.Sci., 8, 685 (1970).
28. P.Chovin and J.Lebbe, "Séparation Immédiate et Chromatographie 1961", G.A.M.S., Paris, 1961, p.90.
29. P.Chovin, J.Gas Chromatog., 2, 88 (1964).
30. P.Chovin and J.Lebbe, J.Gas Chromatog., 4, 37 (1966).
31. R.I.Sidorov and M.P.Ivanova, Zhur.Anal.Khim., 21, 479 (1966).
32. E.Kovats and P.B.Weizs, Ber.Bunsengesellschaft Phys.Chem., 69, 812 (1962).
33. H.Strickler and E.Kovats, J.Chromatog., 8, 289 (1962).
34. E.Kovats, Chimia, 22, 459 (1968).
35. A.I.Korol', Teor.Eksper.Khim., 4, 234 (1968).
36. T.H.Risby, P.C.Jurs, and B.L.Reinbold, J.Chromatog., 99, 171 (1974).
37. B.L.Reinbold and T.H.Risby, J.Chromatog.Sci., 13, 372 (1975).
38. C.E.Figgins and T.H.Risby, J.Chromatog.Sci., 14, 452 (1976).
39. C.E.Figgins, B.L.Reinbold, and P.C.Jurs, J.Chromatog.Sci., 15, 208 (1977).
40. R.D.Schwartz and R.G.Michews, J.Chromatog., 126, 113 (1976).
41. J.Bonastre and P.Grenier, Bull.Soc.chim.France, 1292 (1968).
42. E.A.Moelwyn-Hughes, "Physical Chemistry" (Translated into Russian), Moscow, 1962, pp.341 and 401.
43. Ya.I.Yashin, "Fiziko-khimicheskie Osnovy Khromatograficheskogo Razdeleniya" (Physicochemical Principles of Chromatographic Separation), Moscow, 1976.
44. R.V.Golovnya and T.A.Misharina, Izv.Akad.Nauk SSSR, Ser.Khim., 1974 (1977).
45. L.D.Belyakova et al., Zhur.Fiz.Khim., 42, 177 (1968) [Russ.J.Phys.Chem., No.1 (1968)].
46. J.H.Hildebrand, "Solubility of Non-electrolytes" (Translated into Russian), GONTI, Moscow, 1938.
47. R.A.Keller, B.L.Karger, and L.R.Snyder, in "Gas Chromatography, 1970", edited by R.Stock and S.G.Perry, Institute of Petroleum, London, 1971, p.125.
48. R.V.Golovnya and T.E.Kusmenko, Chromatographia, 9, 545 (1977).
49. D.E.Martire, Analyt.Chem., 33, 1143 (1961).
50. V.M.Sakharov, Zhur.Fiz.Khim., 41, 1585 (1967) [Russ.J.Phys.Chem., No.7 (1967)].
51. G.C.Pimentel and A.L.McClelland, "The Hydrogen Bond" (Translated into Russian), Mir, Moscow, 1964.
52. N.D.Sokolov, "Vodorodnaya Svyaz'" (The Hydrogen Bond), Nauka, Moscow, 1964.
53. E.N.Gur'yanov, I.P.Gol'dshtein, and I.P.Romm, "Donorno-aktseptornaya Svyaz'" (The Donor–Acceptor Bond), Khimiya, Moscow, 1973.
54. R.S.Milliken, J.Amer.Chem.Soc., 74, 811 (1952).
55. G.A.Kurkchi and A.V.Iogansen, in "Gazovaya Khromatografiya" (Gas Chromatography), NIIITEKhIM, Moscow, 1964, p.50.
56. M.I.Shakhparonov, "Vvedenie v Sovremennuyu Teoriyu Rastvorov" (Introduction to the Modern Theory of Solutions), Moscow, 1976.
57. S.E.Langer and R.J.Sheenan, in "Progress in Gas Chromatography", edited by J.H.Purnell, New York, 1968, p.289.
58. Catalog, Applied Science Laboratories, Inst.State College, Pa (USA), 1976–1977.
59. J.Tacats, Z.Szentirmai, E.B.Molnar, and D.Kralik, J.Chromatog., 65, 121 (1972).
60. A.Hartkops, S.Grunfeld, and R.Delumeya, J. Chromatog.Sci., 12, 119 (1974).
61. H.de Clercq et al., J.Chromatog., 122, 535 (1976).

62. R.V.Golovnya and T.A.Misharina, Chromatographia, **10**, 658 (1977).
63. R.V.Golovnya and T.A.Misharina, Izv.Akad.Nauk SSSR, Ser.Khim., 787 (1979).
64. R.V.Golovnya, Chromatographia, **12**, 533 (1979).
65. V.P.Uralets, Candidate's Thesis, Institute of Hetero-organic Compounds of the USSR Academy of Sciences, Moscow, 1972.
66. R.V.Golovnya and V.G.Garbusov, Chromatographia, **8**, 267 (1975).
67. D.H.Desty and W.T.Swanton, J.Phys.Chem., **65**, 766 (1961).
68. R.V.Golovnya and Yu.N.Arsenyev, Chromatographia, **4**, 250 (1971).
69. S.S.Yufit, Dokl.Akad.Nauk SSSR, **188**, 156 (1969).
70. R.V.Golovnya, V.P.Uralets, and T.E.Kuz'menko, Zhur.Anal.Khim., **32**, 340 (1977).
71. W.O.McReynolds, "Gas Chromatographic Retention Data", Preston Technical Abstract Co., Evanston, I11., 1966.
72. F.Riedo, D.Fritz, G.Tarjan, and E.Kovats, J.Chromatog., **126**, 63 (1976).
73. J.H.Haken and D.K.M.Ho, J.Chromatog., **142**, 203 (1977).
74. H.M.McNair and E.J.Bonelli, "Basic Gas Chromatography" (Translated into Russian), Moscow, 1970.
75. K.A.Gol'tberg and M.S.Vigdergauz, "Kurs Gazovoi Khromatografii" (Course of Gas Chromatography), Moscow, 1974.
76. S.Dal Nogare and R.S.Juvet, Analyt.Chem., **38**, No.5, 61R (1966).
77. M.R.James, J.C.Giddings, and R.A.Keller, J.Gas Chromatog., **3**, 57 (1965).
78. R.V.Golovnya and Yu.N.Arsen'ev, Izv.Akad.Nauk SSSR, Ser.Khim., 1356 (1972).
79. R.V.Golovnya and Yu.N.Arsen'ev, Uspekhi Khim., **42**, 2221 (1973) [Russ.Chem.Rev., No.12 (1973)].
80. W.R.Supina, "The Packed Column in Gas Chromatography" (Translated into Russian), Mir, Moscow, 1977.
81. V.P.Uralets and R.V.Golovnya, Zhur.Anal.Khim., **33**, 782 (1978).
82. R.V.Golovnya et al., Izv.Akad.Nauk SSSR, Ser. Khim., 2266 (1976).
83. R.V.Golovnya, V.G.Garbuzov, and T.A.Misharina, Izv.Akad.Nauk SSSR, Ser.Khim., 103 (1976).
84. Proceedings of the Fourteenth International Symposium "Advances in Chromatography", Lausanne, 1979, p.11.

Institute of Hetero-organic Compounds,
USSR Academy of Sciences, Moscow

RUSSIAN
CHEMICAL
REVIEWS
Uspekhi Khimii

February 1980

Translated from *Uspekhi Khimii*, **49**, 193-222 (1980) U.D.C. 541.124

The Present State of the Problem of the Identification of Kinetic Models

V.V.Kafarov and V.N.Pisarenko

The present state of the problem of the identification of kinetic models and the principal methods of solution are described. The principles of the estimation of the constants for non-linear kinetic models are examined and the properties of the resulting estimates are specified. Methods for the determination of the adequacy of single-response models, the statistical significance of their individual components, and the accuracy of the estimates of kinetic parameters are analysed. The Bayes methods and probability ratios, used in tests of hypotheses concerning the mechanism of a complex chemical reaction, as well as methods for the determination of the causes of a possible inadequacy of kinetic models and procedures for the specific construction of an adequate model are described. The importance of an active design of a kinetic experiment for the effective solution of the problem of the identification of models is demonstrated.
The bibliography includes 80 references.

CONTENTS

I.	Introduction	99
II.	The construction of a system of competing hypotheses concerning the reaction mechanism	100
III.	Estimation of the constants for kinetic models	101
IV.	Test of the adequacy of kinetic models	103
V.	Design of precision experiments	105
VI.	Discrimination between models	108
VII.	Design of discriminating experiments	111

I. INTRODUCTION

The problem of the identification of kinetic models is one of the most important in any branch of chemistry—physical, organic, and biological. The reason for this is, in particular, that the solution of the problem in many respects determines the state and level of development of the theory of reactivity of the chemical compounds, which makes it possible in its turn to predict the course of various processes and to establish pathways for the specific synthesis of new chemical substances with specified properties. The problem of the identification of kinetic models is also of practical importance, because both rapid and effective incorporation of new processes in industry and the planning of individual chemical industries are impossible without the determination of the nature and dynamics of a chemical reaction and, the more detailed the investigation of the kinetics of the chemical reaction, the more precise are the results of all subsequent industrial predictions. However, despite its importance for the determination of the mechanism of the chemical reaction, this problem has still not been ultimately resolved.

At the present time the rapid development of computational mathematics, computer technology, and the cybernetics of chemical engineering processes has led to fundamentally new possibilities for the solution of the problem of the identification of kinetic models. In recent years a number of theoretical studies have been carried out in this field[1-5] on the development of methods for the identification of kinetic models and, particularly, statistical methods for the design and analysis of experiments, tests of hypotheses concerning the mechanism of the given chemical process, the establishment of an adequate kinetic model, and an accurate estimation of its parameters. The application of these methods leads to fundamentally new possibilities for the study of complex physicochemical phenomena, since it becomes possible to discover effectively finer details of the reaction mechanisms than in determinations by traditional classical methods.

To simplify the description of the relevant data, the general solution of the problem of the identification of the kinetic model for a complex chemical reaction has been divided in the present review into four consecutive stages.

1. A system of hypotheses concerning the chemical reaction mechanism, which must be tested against the corresponding experimental data, is put forward. Each hypothetical mechanism is represented by a set of elementary reactions (states).

2. Using the available information about the chemical system investigated, sometimes taking into account the selected criterion of optimum conditions, one constructs a "starting" experimental design; the constants for the kinetic models are estimated from the results of measurements.

3. Estimates of kinetic constants obtained at this stage do not usually satisfy the essential requirements as regards accuracy and are therefore revised with the aid of consecutive methods for experimental design.

4. One constructs a consecutive design for a discriminating experiment in such a way that in each single observation the competing models exist under certain critical conditions (from the standpoint of their descriptive power). The suitability of a particular model is decided on the basis of the agreement with experimental data. This leads to the selection of a single model which reflects the given experiment better than any other; the reaction mechanism corresponding to this kinetic model is assumed to be the most fully representative of the structure of the chemical reaction.

II. THE CONSTRUCTION OF A SYSTEM OF COMPETING HYPOTHESES CONCERNING THE REACTION MECHANISM

The role of the first stage in the overall scheme for the solution of the problem of the identification of kinetic models is exceptionally important. Practice shows that the experimenter cannot as a rule choose correctly, on the basis of intuitive considerations, a sufficiently complete system of competing hypotheses, particularly when one is dealing with multistage reactions.

When a multistage chemical reaction takes place, there are both qualitative and quantitative changes in the compositions of the reactants owing to the redistribution of their constituent atoms and individual molecular structures, which remain unaltered in the process (such atoms and molecular structures are referred to as atomic varieties). All chemical reactants can be represented by integral associations of atomic varieties. In view of the necessity to satisfy the law of conservation of mass in the reacting system, it is possible to develop a formalised method for the construction of a system of competing hypotheses, based on the stoichiometric analysis of the reacting system.

The problem of the stoichiometric analysis of the reacting system can be formulated as follows: it is assumed that the initial reactants, intermediates, and reaction products, which are referred to as molecular varieties $M_i^B (i = 1,2,\ldots,N)$ are known (or postulated) from theoretical considerations and also from physical measurements. It is necessary to determine the possible chemical reactions $\mathscr{R}_r (r = 1,2,\ldots,Q)$, among the N molecular varieties M_i^B and to construct a system of competing hypotheses concerning the reaction mechanism. In order to solve this problem, each of the N chemical reactants M_i^B is brought into correspondence with an M-dimensional vector $\alpha_i = (\alpha_{i1},\ldots,\alpha_{ij},\ldots,\alpha_{iM})T$ and each of the Q reactions $\mathscr{R}_r$ is brought into correspondence with an N-dimensional vector $\beta_r = (\beta_{r1},\ldots,\beta_{ri},\ldots,\beta_{rN})T$ [6-13]:

$$M_i^B = \sum_{j=1}^{M} \alpha_{ij} M_j^A, \tag{1.1}$$

$$\mathscr{R}_r = \sum_{i=1}^{N} \beta_{ri} M_i^B, \tag{1.2}$$

where α_{ij} are non-negative integers, $M_j^A (j = 1,\ldots,M)$ are atomic varieties, and β_{ri} are rational numbers, referred to as stoichiometric coefficients. It is assumed that any molecular variety having a positive stoichiometric coefficient is a reaction product and a molecular variety with a negative stoichiometric coefficient as an initial reactant[7].

To chemical reactions $\mathscr{R}_r = \sum_{i=1}^{N} \beta_{ri} M_i^B = 0$ and $\mathscr{R}_r' = \sum_{i=1}^{N} \gamma \beta_{ri} M_i^B = 0$ are identical for any rational γ. Hence it follows that, for any chemical reaction, the ratio of stoichiometric coefficients is of decisive importance. Among the overall set of reactions $\{\mathscr{R}_r\}$ the reactions $\mathscr{R}_l (l = l_1,\ldots l_R)$ are assumed to be independent, provided that there are no non-zero multipliers $\gamma_l (l = l_1,\ldots,l_R)$ such that

$$\sum_{l=l_1}^{l_R} \gamma_l \mathscr{R}_l = 0.$$

Evidently the total number of independent reactions is determined by the rank of the matrix of stoichiometric coefficients $B = \{\beta_{ri}\}$ for the set of reactions $\{\mathscr{R}_r\}$.

The reaction $\mathscr{R}_{r_1}$, occurring among the molecular varieties $M_1^B,\ldots,M_k^B$, is defined as stoichiometrically simple if no reactions of the specified set $\{\mathscr{R}_r\}$ takes place between the molecular varieties.

A number of useful relations can be derived from Eqns.(1.1) and (1.2). On substituting Eqn.(1.1) into the Eqn.(1.2), we obtain

$$\mathscr{R}_r = \sum_{i=1}^{N} \beta_{ri} \sum_{j=1}^{M} \alpha_{ij} M_j^A = \sum_{j=1}^{M} \left(\sum_{i=1}^{N} \beta_{ri} \alpha_{ij} \right) M_j^A = 0.$$

Consequently

$$\sum_{i=1}^{N} \beta_{ri} \alpha_{ij} = 0 \tag{1.3}$$

for all $r = 1,\ldots,Q$; $j = 1,\ldots,M$. Or in a matrix form, we have

$$BA = 0, \tag{1.4}$$

where $A = \{\alpha_{ij}\}$ is the molecular matrix and $B = \{\beta_{ri}\}$ is the matrix of stoichiometric coefficients. One should note that this system of equations characterises none other that the law of conservation of matter in the reacting system.

Since the elements of the molecular matrix A are known, any of the possible reactions can be obtained by solving the homogeneous linear system of equations (1.3), which is called the fundamental system of equations (FSE); the converse assertion is also valid, namely each solution of the FSE represents a possible reaction. Suppose that the rank of the maxtrix A is u_A. Then the maximum number of independent reactions which can occur in the given reaction system is, according to the Gibbs rule, $u_B = N - u_A$.

In order to calculate the stoichiometric coefficients β_{ri} for the independent reactions, we shall find in the molecular matrix A a minor A of rank u_A and shall correspondingly reindex the columns and rows of the matrices B and A so that the indices of the rows of the minor of A vary from 1 to u_A inclusive. Eqns.(1.3) can then be written in the following form:

$$\sum_{i=1}^{u_A} \beta_{ri}\alpha_{ij} = -\sum_{i=u_A+1}^{N} b_{ri}\alpha_{ij}, \quad \begin{matrix} r = 1, \ldots, u_B; \\ j = 1, \ldots, u_A, \end{matrix} \qquad (1.5)$$

where $\beta_{ri}(i = 1,\ldots,u_A)$ are the required unknowns and b_{ri} are stoichiometric coefficients whose values are specified arbitrarily. Any solution of Eqns.(1.5) is specified to within linear combinations of a parameter b_{ri}. The solution is referred to as a basis solution if the parameters b_{ri} are chosen in the following way.

$$b_{ri} = \delta_{u_A+r,i} = \begin{cases} 0, & \text{if } i \neq u_A + r; \\ 1, & \text{if } i = u_A + r. \end{cases} \qquad (1.6)$$

Eqns.(1.5) are then transformed as follows:

$$\sum_{i=1}^{u_A} \beta_{ri}\alpha_{ij} = \sum_{i=u_A+}^{N} \delta_{u_A+r,i}\alpha_{ij}. \qquad (1.7)$$

It is easy to show that each basis solution of the FSE defines a stoichiometrically simple reaction. Consequently, if all the basis solutions have been determined, all the stoichiometrically simple chemical reactions possible in the given reacting system have been thereby found. In order to find all the basis solutions, it is necessary to solve the FSE subject to the limitations defined by Eqns.(1.6) for each non-singular minor of A rank u_A. Naturally, the stoichiometrically simple reactions determined in this way will be linearly dependent. From the set of stoichiometrically simple reactions obtained, one rejects reactions which are absurd from the standpoint of chemical theory and one introduces individual supplementary elementary reactions, which cannot be determined with the aid of the above procedure without a significant increase in complexity but which evidently follow from the set of stoichiometrically simple reactions (usually the number of such supplementary elementary reactions does not exceed 1–2).

To achieve further clarification, consider the following example. Suppose that one investigates a reaction system in which the following elementary reaction takes place:

$$I_2 + M \rightleftarrows 2I^{\cdot} + M,$$

Where I_2, $I^{\cdot}$, and M are respectively the iodine molecule, the iodine atom (a radical species), and a neutral molecule. The procedure described above defines the stoichiometrically simple reaction

$$I_2 \rightleftarrows 2I^{\cdot}.$$

Knowing that the iodine atom is formed in the gas phase when I_2 collides with a neutral molecule, it is possible to formulate the first reaction on the basis of the second.

One must note that the procedure under consideration is relatively ineffective if the reactants in elementary chemical reactions are isomeric and stereoisomeric molecules.

The determination of the possible mechanisms of the process on the basis of the set of elementary reactions (stages) obtained reduces to the selection of the corresponding sets of stoichiometric numbers[14]. The numerical values of the latter are not arbitrary and are subject to a series of limitations. Thus the sum of the equations for the elementary chemical stages, multiplied by the stoichiometric numbers of the corresponding stages, should yield the overall reaction (the final equation)[15–18]. Consequently if the stoichiometric analysis showed that the S elementary reactions involving I intermediates and P reactants and reaction products, then, for example for a single-pathway reaction there exist S stoichiometric numbers ν_r satisfying Eqns.(1.8) and (1.9):

$$\sum_{r=1}^{S} \beta_{rs}\nu_r = 0, \; s = 1, \ldots, I, \qquad (1.8)$$

$$\sum_{r=1}^{S} \beta_{rs}\nu_r = b_{s'}, \; s' = 1, \ldots, P', \qquad (1.9)$$

where b_s' is the stoichiometric coefficient of the s'th reactant or product in the final equation.

Naturally any set of stoichiometric numbers $\{\nu_r\}$ satisfying Eqns.(1.8) and (1.9) corresponds to a specific reaction mechanism. Since there are usually more stoichiometric numbers than independent linear equations (1.8) and (1.9), there exist large sets of hypothetical single-pathway reaction mechanisms. The necessary limitations can be obtained by resorting to additional *a priori* information about the reaction system, for example, the occurrence of a specific limiting elementary reaction or a sequence of specific stages[19]. The extensions to the case of multipathway reactions are self-evident.

For each hypothetical mechanism of a chemical reaction, one constructs the corresponding kinetic model. The methods of construction of such models have been fairly satisfactorily developed[16,18] and will not therefore be considered in the present review.

III. ESTIMATION OF THE CONSTANTS FOR KINETIC MODELS

The kinetic models obtained, which consist of systems of differential, algebraic, or differential-algebraic equations, contain unknown constants, which must be estimated from experimental data. In those cases where one employs empirical models or theoretical kinetic models linear in terms of the parameters, the methods of linear regression analysis, which have been developed in detail, are used to obtain point and interval estimates of the parameters. The theory of linear regression analysis has been described in a number of monographs[20–24].

However, the vast majority of the models are non-linear in terms of the parameters and the procedure for their estimation is much more complex. We shall consider it in greater detail. Suppose that m kinetic models for each of the m kinetic hypotheses M_j $(j = 1,\ldots,m)$ can be put in the form

$$\frac{d\eta^{(j)}}{dt} = \varphi(x_u, \theta_j); \; y_u^{(j)} = \eta_u^{(j)} + \varepsilon_u \text{ or } y_u^{(j)} = f(x_u, \theta_j) + \varepsilon_u, \qquad (2.1)$$

where $f(x_u, \theta_j) = \eta^{(j)}(0) + \int_{\tau_0}^{\tau} \phi(\bar{x}_u, \theta_j)dt$, t is the reaction time, θ_j the p_j-dimensional vector for the space of unknown parameters, x_u the q-dimensional vector of the space of the controllable variables, ε_u the error in the irreproducibility of the observations, and u the number of the

experiment. For simplicity, we shall confine ourselves initially to the analysis of single-response models; the generalisations required for the multiresponse models are self-evident.

In kinetic studies involving the estimation of unknown parameters for the model, the method of maximum probability is most widely used. When it is employed, one normally assumes in addition that the form of the distribution density of the errors of the observations is known. The unknown parameters of the probability distribution density can then be estimated together with the unknown parameters of the models. However, joint estimation of the parameters as a function of the distribution density and in terms of the kinetic model is significant only for single-, two-, and at most three-response models, since otherwise the search for the estimates of the constants correlated with one another would be prosecuted in the space with a very large number of dimensions, which precludes a solution even with the aid of a third generation computer.

We shall now assume that the estimates of θ_j^+ have been obtained in some way for the model M_j; Eqn.(2.1) can then be written as in the following form:

$$e_u^{(j)} = y_u^{(j)} - f^{(j)}(x_u, \theta_j^+), \tag{2.2}$$

where $e_u^{(j)}$ are estimates of the experimental errors ε_u for the given θ_j^+ and M_j.

Suppose that n experiments have been carried out. We shall denote by $P(\varepsilon_u, \psi)$ the distribution density of the probabilities of a random quantity and by $P(\varepsilon, \psi)$ the joint distribution density of a random vector $\varepsilon = (\varepsilon_1, \ldots, \varepsilon_n)^T$, where ψ is the vector of the space of the distribution density parameters containing, in particular, the mathematical expectations and variances of the reproducibility. The function of the probability of the selection of $L^{(j)}(\theta_j^+, \psi^+)$, obtained as a result of the substitution of $e_u^{(j)}$ from Eqn. (2.2) in the expression for $P(\varepsilon, \psi)$, has the following form:

$$L^{(j)}(\theta_j^+, \psi^+) = P(e^{(j)}, \psi^+). \tag{2.3}$$

For independent random quantities ε_u $(u = 1, \ldots, n)$, we have

$$L^{(j)}(\theta_j^+, \psi^+) = \prod_{u=1}^{n} P(e_u(\theta_j^+), \psi^+). \tag{2.4}$$

According to the method of maximum probability, the best estimates of parameters are those attributing the maximum probabilities to the observations obtained in reality. Consequently, the problem of the estimation of the parameters reduces to the determination of the values of $\theta_j^\times$ and $\psi^\times$, which satisfy the condition

$$L^{(j)}(\theta_j^\times, \psi^\times) = \max_{\theta_j^+, \psi^+} L^{(j)}(\theta_j^+, \psi^+). \tag{2.5}$$

The specific form of the function $L^{(j)}(\theta_j, \psi)$ depends on the distribution density of the probabilities of ε. In particular, if the random quantities ε_u $(u = 1, \ldots, n)$ are independent and normally distributed with a zero average and known variances σ_u^2, then,

$$L^{(j)}(\theta_j^+, \psi^+) = \frac{1}{(2\pi)^{n/2}\left(\prod_{u=1}^{n}\sigma_u^2\right)^{1/2}} \exp\left(-\frac{1}{2}\sum_{u=1}^{n}\frac{(y_u - f^{(j)}(x_u\theta_j^+))^2}{\sigma_u^2}\right). \tag{2.6}$$

Then the estimates obtained using the principle of maximum probability are equivalent to the estimates minimising the weighted sum of squares (the estimates obtained by the method of least squares):

$$\Phi^{(j)}(\theta_j^\times) = \min_{\theta_j^+}\Phi^{(j)}(\theta_j^+) = \min_{\theta_j^+}\sum_{u=1}^{n}\frac{e_u^{(j)}(\theta_j^+)^2}{\sigma_u^2}. \tag{2.7}$$

For unknown but equal variances of the observations, Eqn.(2.7) transforms into

$$F^{(j)}(\theta_j^\times) = \min_{\theta_j^+} F^{(j)}(\theta_j^+) = \min_{\theta_j^+}\sum_{u=1}^{n}[e_u^{(j)}(\theta_j^+)]^2. \tag{2.8}$$

We may note in conclusion that, for normally distributed errors of the observations, the estimates obtained by the methods of maximum probability and least squares θ_j are identical. They have a number of optimum properties if the models $f^{(j)}(\bar{x}, \bar{\theta}_j)$ are linear in terms of the parameters regardless of whether or not the quantities ε_u $(u = 1, \ldots, n)$ are normally distributed[24,25].

For multiresponse kinetic models, the probability function of the selection of $L^{(j)}(\theta_j^+, \psi^+)$ for independent normally distributed errors of the observations can be written as follows:

$$L^{(j)}(\theta_j^+, \psi^+) = \prod_{u=1}^{n} P(e_u^{(j)}(\theta_j^+, \psi^+)) =$$

$$= (2\pi)^{-Qn/2}\det(\Sigma)^{-n/2}\exp\left[-\frac{1}{2}\sum_{k=1}^{Q}\sum_{l=1}^{Q}\sigma^{kl}\sum_{u=1}^{n}e_{uk}^{(j)}e_{ul}^{(j)}\right] = \tag{2.9}$$

$$= (2\pi)^{-Qn/2}\det(\Sigma)^{-n/2}\exp[-{}^1/_2\,\mathrm{Sp}\,(\Sigma^{-1}A(\theta_j^+))],$$

where $e_u^{(j)}(\theta_j^+) = y_u - f^{(j)}(x_u, \theta_j^+) = [e_{u1}^{(j)}(\theta_j^+), \ldots, e_{uQ}^{(j)}(\theta_j^+)]^T$ is a Q-dimensional vector of the measurements, $f^{(j)}(\bar{x}_u, \theta_j^+)$ a Q-dimensional vector function—the kinetic model of the chemical reaction corresponding to the hypothesis M_j, $\Sigma = \{\sigma_{kl}\}$ the variance-covariance matrix of the measurements, T the transposition index, and

$$A(\theta_j^+) = \sum_{u=1}^{n} e^{(j)}(\theta_j^+)\, e_u^{(j)}(\theta_j^+)^T;\ \Sigma^{-1} = \{\sigma^{kl}\}.$$

According to the method of maximum probability, the estimates of $\theta_j^\times$ for known Σ maximise $L^{(j)}(\theta_j^+, \psi^+)$, provided that they minimised quantity

$$SS_1^{(j)}(\theta_j^\times) = \mathrm{Sp}\,(\Sigma^{-1}A(\theta_j^\times)) = \min_{\theta_j^+}\mathrm{Sp}\,[\Sigma^{-1}(A(\theta_j^+))]. \tag{2.10}$$

If the matrix Σ^{-1} is diagonal, then $\mathrm{Sp}[\Sigma^{-1}A(\theta_j^+)]$ is the weighted sum of the squares of the residues. Evidently, for $Q = 1$, Eqn.(2.10) is identical with Eqn.(2.7).

On the other hand, if the variance–covariance matrix of the errors of the observations Σ is unknown *a priori*, then, it has been shown[26] with the aid of the Bayes ion approach to the estimation of the parameters that the estimates of the maximum probability of $\theta_j^\times$ are obtained by minimisation with respect to the parameter $\det A(\theta_j^+)$:

$$SS_2(\theta_j^\times) = \det A(\theta_j^\times) = \min_{\theta_j^+}\det A(\theta_j^+). \tag{2.11}$$

It has been noted[27] that, in order to eliminate the possible errors, one includes in Eqn.(2.11) only responses which are linearly independent. The authors[27] quote the required mathematical procedure for the determination and elimination of linearly dependent responses.

In many instances, particularly for non-normal distributions of errors of observations, the use of the principle of maximum probability leads to relations characterising the closeness of the calculated and experimental data other than Eqns.(2.7), (2.8), (2.10), and (2.11). In particular, if the error has a Laplace distribution, it is necessary to use the method of least moduli for single-response situations and the corresponding relation.

$$SS_3(\theta_j^\times) = \sum_{u=1}^{n}|e_u(\theta_j^\times)| = \min_{\theta_j^+}\sum_{u=1}^{n}|e_u(\theta_j^+)|. \tag{2.12}$$

Evidently, the determination of estimates of the maximum probabilities does not by itself guarantee that an adequate model will be obtained; the latter is tested additionally

against statistical criteria governing the agreement with experimental data[28,29].

IV. TEST OF THE ADEQUACY OF THE KINETIC MODELS

The principal methods for testing the adequacy of kinetic models, most widely used in experimental research, are based largely on the procedures of variance analysis and the analysis of residues.

The variance analysis of models is used to compare the differences $e_u^{(j)} = y_u - f^{(j)}(x_u, \theta_j)$ with the quantities ε_u characterising the error of the measurements. By means of such a comparison, it is possible to establish both the overall adequacy of the model and methods for its further simplification, by rejecting the statistically insignificant individual terms of the model or its kinetic parameters.

For this purpose, one calculates the sums of squares

$$SS(1) = \sum_{u=1}^{n} y_u^2 \text{ and } SS(2) = \sum_{u=1}^{n} \hat{\eta}_u^{(j)2} = \sum_{u=1}^{n} f_u^{(j)2}$$

characterising respectively the scatter of experimental data and the scatter of the responses calculated on the basis of the model. The differences $e_u^{(j)} = y_u - f_u^{(j)}$, called residuals, constitute a measure of the inability of the model to describe accurately the experimental data. Evidently, if the model tested is true, then the residues are in fact the estimates of the errors of the measurements. Hence the overall measure $SS(3)$ of the discrepancy between the model and experimental results can be put in the form

$$SS(3) = \sum_{u=1}^{n} (y_u - f_u^{(j)})^2.$$

In the literature $SS(1)$ is called the overall sum of squares, $SS(2)$ is called the sum of squares due to regression, and $SS(3)$ is referred to as the residual sum of squares. Then

$$SS(1) = SS(2) + SS(3),$$

which is a direct consequence of the properties of the method of least squares.

In variance analysis a single degree of freedom is assigned to each individual measurement of the response. Consequently, when n experiments are set up, the overall sum of squares $SS(1)$ for a single-response situation has n degrees of freedom: $SS(3)$ has $n - p_j$ degrees of freedom and $SS(2)$ has p_j degrees of freedom [p_j is the number of parameters of the model with the aid of which one calculates $SS(2)$].

When several replicate measurements are made for identical experimental conditions, the sum of squares $SS(4) = \sum_{u=1}^{n} (y_u - \bar{y})^2$, where $\bar{y} = \sum_{u=1}^{N} y_u/N$ contains all the necessary information about errors of the measurements, since it is proportional to the variance σ^2_{exp}. The quantity

$$SS(5) = \sum_{u=1}^{n} (y_u - f_u^{(j)})^2 - \sum_{u=1}^{n} (y_u - \bar{y})^2,$$

equal to the difference between $SS(3)$ and $SS(4)$, therefore defines the measure of the inability of the test model to reflect the experimental results, i.e., in other words, the sum of squares $SS(5)$ characterises the degree of inadequacy of the model.

If $\tilde{n}$ replicate experiments have been carried out for each of the q different experimental conditions, then the sum of squares $SS(4)$ has $\tilde{n} - 1$ degrees of freedom (one degree of freedom is used to estimate $\bar{y}$), while the sum of squares $SS(5)$ has $n - p_j - q(\tilde{n} - 1)$ degrees of freedom; the latter number is defined as the difference between the number of degrees of freedom of the residual sum of squares and the sum of squares of the errors of the measurements.

The sums of squares arising from different sources define the average squares after division by the corresponding numbers of degrees of freedom. Since the average square of the error of the measurements is an estimate of the variance of the errors of the measurements, evidently the adequacy of the model can be determined in terms of the ratio of the average square of the inadequacy of the model to the average square of the error of the measurements (the F-statistic). If this ratio is large (at least much greater than unity), there is good reason to suppose that the model tested does not reflect the experimental results.

The F-statistic is defined as the ratio of the sum of squares of independent normal random quantities and the test of the adequacy of kinetic models actually reduces to a test of the validity of the inequality

$$\frac{SS(5)/(n - p_j - q(\tilde{n} - 1))}{SS(4)/(q(\tilde{n} - 1))} < F_\alpha[n - p_j - q(\tilde{n} - 1), q(\tilde{n} - 1)]$$

for a level of significance α specified beforehand. The F statistics for the specified level of significance α and the numbers of degrees of freedom in the numerator and denominator have been tabulated and published[24,29].

To illustrate the application of the procedures of variance analysis in the determination of the adequacy of kinetic models, we shall consider the results of a kinetic study of the isomerisation of pentane[30-32]. The authors tested two reaction mechanisms and obtained two corresponding competing kinetic models. The parameters of the models were estimated from experimental data and variance analysis was carried out to test the adequacy of the models. The principal results of this test are presented in Table 1, which shows, in particular, that the first model reflects adequately the experimental results, while the second is at the "limit of adequacy". The latter does not permit either the adoption of the second model with confidence or its rejection as inadequate. Further statistical tests of the second model are therefore necessary.

The procedure described above for the testing of the adequacy of the model nevertheless does not guarantee a statistical significance of its individual terms. Consequently it is necessary to carry out a more detailed analysis of the components of the model, which is achieved by a direct extension of the methods of variance analysis. For this purpose, one carries out an additional expansion of the sum of squares, due to regression, into a series of components. To simplify the analysis, one then usually calculates the sums of squares due to the general regression model and the simplified model in which one term of a group of terms is rejected. The difference between these two sums of squares is the sum of squares characterising the influence of the tested component of the kinetic model. Since it is known that, for adequate models, the average square of residues characterises the variance of the reproducibility, the condition

$$\overline{SS}(6)/\overline{SS}(5) > F_\alpha(1, n - p_j), \qquad (3.1)$$

where $\overline{SS}(6)$ is the average square due to the tested component of the model and $\overline{SS}(5)$ the average square of the residues, determines the significance of the tested component. Evidently such tests must be carried out for all the terms (components) of the kinetic model[33].

An example of such analysis of the significance of one of the terms of the first kinetic model for the isomerisation of pentane is presented in Table 1, which shows that, in view of the considerable difference between the average squares

of the overall and simplified models, inequality (3.1) holds: consequently the tested term is significant and must be retained in the model.

Table 1. Results of the variance analysis of kinetic models of the isomerisation of pentane.

Source of scattering	Sum of squares	No. of degrees of freedom	Average squares	Ratio of average squares	*F* statistic	
					95%	97,5%
		First model				
Overall	763.54	24	—	—	—	—
Regression	754.29	4	188.6	—	—	—
Deviation from regression equation (for the model)	9.25	20	0.462	—	—	—
Inadequacy of the model	8.58	17	0.528	5.9	8.7	14.3
Deviations of repeated observations	0.27	3	0.090			
Elimination of one constant of the model	123.2	1	123.2	1370	246	985
		Second model				
Overall	28894.0	24	—	—	—	—
Regression	26896.8	4	6724.2	—	—	—
Deviation from regression equation (for the model)	1997.20	20	99.86	—	—	—
Inadequacy of the model	1964.56	17	115.5	10.62	8.7	14.3
Deviations of repeated observations	32.65	3	10.88			

Finally, we may note that the results of the variance analysis permit a conclusion only about the overall suitability of the model or the significance of its individual terms. Nevertheless a model can be inadequate even if criteria such as the Fischer criterion show that the model is consistent with experimental data. It is therefore necessary to carry out a more detailed test on the models by the method involving the analysis of residues.

The residues $e_u = y_u = f^{(j)}(x_u, \theta_j)$, being random quantities, are known to have a fully defined probability distribution function. In the majority of cases encountered in practice this is a normal distribution function with a mathematical expectation of zero and a variance σ^2_{exp}. Evidently the determination of the adequacy of the kinetic model on the basis of any one characteristic of the distribution function (for the Fisher criterion , this characteristic is $\sigma^2_{non\text{-}add}$) cannot give a complete guarantee of the adequacy of the model. In view of the foregoing considerations, in a combined test of the agreement between the kinetic model and experimental data, one must employ either entirely the probability distribution function, which requires a large number of experiments, or its principal characteristics. Among these the following may be noted[24,34–36].

1. Analysis of the normality of the distribution. For this purpose, one plots histograms for the distribution of the normalised appearance frequencies of the residues on a function of their numerical values. Such histograms should correspond approximately to the normal distribution law. The hypothesis of the normality can then be tested in terms of difference statistics. Together with this hypothesis, additional tests are also carried out of the hypothesis that the mathematical expectation of the selective distribution is zero, which is done using both graphical methods and the methods of linear or non-linear regression analysis.

2. Analysis of the absence of non-random components in the residues. The first stage of such analysis is carried out by plotting and investigating the graphical dependence of the residues on the predicted responses, which makes it possible to establish a correspondence between the model and experimental data. In particular, the results of variance analysis carried out for the first kinetic model of the isomerisation of pentane, indicate a complete adequacy of the model, while the plot of the residues (Fig.1) shows clearly that the overall adequacy of the model is achieved as a result of the balancing of the residue e_u for low and large responses when the latter vary consistently, with increase of their values. Consequently the first model must be rejected as inadequate.

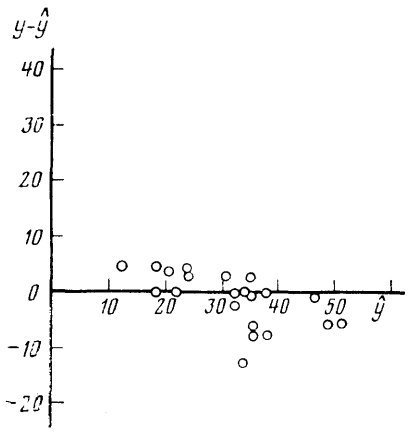


Figure 1. Dependence of the residuals on the predicted response.

Analysis of the graphical dependence of the residues on the predicted responses makes it also possible to obtain additional information about the validity of a number of initial statistical postulates in terms of the characteristics of the errors of the measurements, particularly in terms of the validity of the condition of a constant reproducibility variance in the selected experimental region (Fig.2). If, for example, the scatter of the residues in such plots increases or decreases monotonically, then evidently the variance of the reproducibility error is a variable quantity. In this case the parameters of the models must be estimated by the method of least squares with variable weighting factors or, in order to maintain the constancy of the variance σ^2, the dependent variable $\eta = f^{(j)}(x, \theta_j)$ must be transformed.

Plots of the residues against the controllable variables and time and of the estimated parameters against the controllable variables make it impossible to obtain similarly important information about the possible latent inadequacies in the model, which are established by observing trends in the residues relative to the levels of independent controllable variables. A detailed study of such relations permits a

qualitative analysis of the agreement between the competing models and experimental data and enables one to outline ways for the elimination of possible inadequacies.

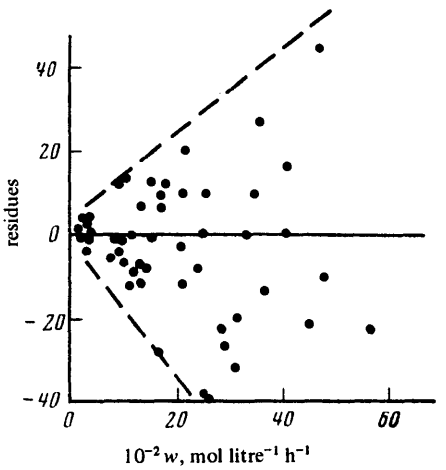


Figure 2. Dependence of the residuals on the predicted reaction rate w.

The establishment of the adequacy of multiresponse models involves a more complex procedure and requires the use of a large amount of experimental information, because, in contrast to the case of the single-response model, one has to test the hypothesis of the equality of two covariance matrices Σ_1 and Σ and not the equality of two variances. Here $\Sigma_1 = A(\theta_j)/(n - p_j)$, where n is the total number of measurements, p_j the minimum number of experiments necessary for the estimation of the kinetic parameters, $A(\theta_j = \sum_{u=1}^{n} e_u(\theta_j)e_u(\theta_j)^T$, and $\Sigma = \sum_{u=1}^{n_2} (y_u-\bar{y})(y_u-\bar{y})^T/(n_2-1) = A_2/(n_2-1)$ is the selective covariance matrix of the measurements, where $y_1,\ldots,y_{n_2}$ represent the reselection of the volume n_2 and $\bar{y} = \sum_{u=1}^{n_2} y_u/n_2$.

To test the hypothesis that

$$\Sigma_1 = \Sigma$$

use is made of the T_4 statistic[28]:

$$T_4 = \frac{1}{2}\left\{(n-p_j)\,\mathrm{Sp}\left[\Sigma_1\left(\frac{A(\theta_j)+A_2}{n-p_j+n_2-1}\right)^{-1} - I\right]^2 + n_2\,\mathrm{Sp}\left[\Sigma\left(\frac{A(\theta_j)+A_2}{n-p_j+n_2-1}\right)^{-1} - I\right]^2\right\}, \quad (3.2)$$

where I is a unit matrix with dimensions $Q \times Q$ and Q is the dimension of the observations vector $y_u (u = 1,\ldots,n_2)$.

Assuming that the hypothesis is correct, the distribution of the T_4 statistic, expressed as a linear combination of χ^2 distributions with different degrees of freedom, assumes the following form for large selections:

$$P(T_4 \leqslant x) = P_f + m^{-1}\left[\frac{1}{12}\{\tilde{\rho}Q(4Q^2+9Q+4) - 12Q(Q+1)^2 + 4Q(Q^2+3Q+4)\}P_{f+2} + \frac{1}{8}\{-\tilde{\rho}Q(6Q^2+13Q+9) + 16Q(Q+1)^2 + 3Q(2Q^2+5Q+5)\}P_{f+4} + \frac{1}{4}(2\tilde{\rho}+2)Q(Q+1)^2 P_{f+2} + \frac{1}{24}(1-\tilde{\rho})Q(2Q^2+3Q-1)P_f + O(n^{-2}), \quad (3.3)$$

where

$$\tilde{\rho} = \frac{n+n_2-p_j-1}{n-p_j}\cdot\frac{n+n_2-p_j-1}{n_2-1},\quad m = n+n_2-p_j-1,\quad P_f = P(\chi_f^2 \leqslant x)$$

with $f = Q(Q+1)$ degrees of freedom.

Consequently, if the observed quantity T_4, treated as a measure of the deviation from the zeroth hypothesis, is not significant according to distribution (3.3), one adopts the hypothesis that $\Sigma_1 = \Sigma$.

V. DESIGN OF PRECISION EXPERIMENTS

The estimation of the parameters of kinetic models must usually satisfy the essential requirements of accuracy in order that the model constructed should have a sufficient predictive power making it suitable for the design, optimisation, and control of processes. It is therefore as a rule necessary to carry out an additional consecutively designed experiment in order to revise the parameters. Numerous studies of this problem[37,38] have been limited mainly to linear models; much less attention has been devoted to non-linear models. It is therefore quite natural that the problem of experimental design for the estimation of the parameters of non-linear models has so far not been ultimately investigated and the methods employed for its solution constitute in essence a generalisation of experimental design methods for linear models.

The procedure used to devise a strategy for consecutive experimentation is determined by the specific tasks of the kinetic study at the given stage. Among these, the following are the most important: (1) estimation with a specified accuracy of the single parameter or subvector of the space of parameters, which is necessary, for example, to confirm the reaction mechanism or to characterise the individual stages of the chemical reaction; (2) the minimisation of the correlation coefficients between two parameters or a group of parameters. The correlation coefficients have an appreciable influence on the rate of convergence of the iterative methods for the estimation of parameters and on the extrapolated properties of the models obtained; (3) estimation of the vector of the space of parameters in the models.

For the solution of such problems, it is sufficient to analyse certain functionals of the information matrix as well as its individual elements and submatrices. Thus it is suggested that the determinant of the information matrix $\Delta = \det X^T X$, whose square root is inversely proportional to the volume $V_{c.e.}$ of the confidence ellipsoid, be used as a functional characterising the accuracy of the estimates of the parameters of single-response models[39]. Indeed,

$$V_{c.e.} = C\prod_{i=1}^{p}\left(\frac{\beta}{\lambda_i}\right)^{1/2} = C\frac{\beta^{p/2}}{(\det X^T X)^{1/2}}, \quad (4.1)$$

where $\lambda_i (i = 1,\ldots,p)$ are the eigenvalues of the matrix X^TX:

$$X_{nxp} = \{x_{ul}\} = \left\{\frac{\partial f(x_u, \theta)}{\partial \theta_l}\right\};$$

C is a constant which depends on the dimension p of the space of parameters, and β a constant which depends on the reproducibility variance σ^2, the number of degrees of freedom $n - p$, and the level of significance α.

The problem of experimental design in the selection of the statistic Δ involves a consecutive determination of experimental conditions such that the maximum decrease of the volume of the confidence region (and the corresponding maximum increase of det X^TX) is observed. The experimental design cycle is continued until the parameters reach the required degree of accuracy. Naturally, since the model is non-linear in terms of the parameters, they must be re-estimated after each new experiment.

There have been numerous modifications of the Box-Lucas criterion for various practical situations, in particular:

(a) For multiresponse models in the absence of *a priori* information about the parameters[40]:

$$\Delta = \sum_{i=1}^{Q}\sum_{j=1}^{Q} \sigma^{ij} (X^{(i)})^T X^{(j)}, \qquad (4.2)$$

where Δ is the information matrix of the Q- response system;

$$X^{(i)} = \{x_{ul}^{(i)}\} = \left\{\frac{\partial f^{(i)}(x_u, \theta_l)}{\partial \theta_l}\right\} \quad (i = 1, \ldots Q;\ l = 1, \ldots p);$$

i, l, and u are indices which determine the number of the response, the parameter, and the experiment.

(b) For multiresponse models in the presence of *a priori* information about the parameters[41]:

$$\Delta_k = \sum_{i=1}^{Q}\sum_{j=1}^{Q} \sigma^{ij} (X^{(i)})^T X^{(j)} + \Omega^{-1}, \qquad (4.3)$$

where Ω is the covariance matrix of the estimates of the para-parameters, known beforehand before the formulation of the refining experiments:

(c) For the estimation of the specified subset of parameters[42]:

$$\Delta_s = \det (Y_{11} - Y_{12}Y_{22}^{-1}Y_{21}), \qquad X^TX = \begin{bmatrix} Y_{11} & Y_{21} \\ Y_{12} & Y_{22} \end{bmatrix}, \qquad (4.4)$$

where Y_{11} is a submatrix with dimensions $s \times s$ of the matrix X^TX with dimensions $p \times p$ and s is the number of estimated parameters ($s < p$).

Further generalisations have been made[43,44] for discontinuous measurements, for the simultaneous design of models of m ($m > 1$) experiments, and for the design of an experiment characterised by a variance matrix, which depends on the experimental conditions.

Criteria of type (4.2)–(4.4) are known as determinant criteria. Box[45] analysed the principal advantages and disadvantages of determinant criteria and discussed many of their properties. Their practical employment, particularly for the estimation of parameters in multiresponse models and in carrying out a small number of experiments, has demonstrated their exceptional effectiveness even in fairly complex cases[46].

However, the structure of kinetic models is as a rule such that the estimates of kinetic parameters are highly correlated with one another, as a result of which the functions characterising the agreement between experimental and calculated data show the presence of "ravines" in the space of parameters in the vicinity of the minimum, which hinder point estimates of the constants. The determinant criteria greatly decrease the volume of the confidence ellipsoid without, however, altering the correlation coefficients and hence without correcting the "ravine" situation.

In this respect the shape criteria†, maximising the minimum eigenvalue of the information matrix X^TX, are preferable, since they tend to impart a greater sphericity to the confidence region by minimising the length of the major half-axis of the confidence ellipsoid. One should also note that the practical employment of the shape criterion makes it possible also to achieve an increase of the determinant of the information matrix because

$$\det X^TX = \prod_{i=1}^{p} \lambda_i, \qquad (4.5)$$

where $\lambda_i (i = 1,\ldots,p)$ are the eigenvalues of X^TX; an increase of the minimum eigenvalue entails an increase of det X^TX. Consequently the two statistics are not entirely independent.

The efficiences of the above criteria have been compared[47,48]. It has been shown for a number of examples that the determinant criterion decreases the volume of the confidence region mainly as a result of its compression along the minor half-axes of the hyperellipsoid, which are significantly smaller, as regards order of magnitude, than the major half-axes. On the other hand, the shape criterion tends to make the joint confidence region spherical. However, a true sphericity cannot be attained, mainly owing to the different sensitivities of the model to a change in the parameters and the limited dimensions of the experimental region.

Table 2. The results of the design of a refining experiment.

Constants to be estimated	Estimates of the constants	Standard deviation $\sqrt{\sigma_{k_l}^2}$	Determinant criterion: estimates of constants	Determinant criterion: standard deviation $\sqrt{\sigma_{k_l}^2}$	Shape criterion: estimates of constants	Shape criterion: standard deviation $\sqrt{\sigma_{k_l}^2}$
	After the starting experiment		After 23 refining experiments			
k_1	4.61	1.16	2.89	0.09	2.97	0.06
k_2	92.29	24.41	57.47	1.94	58.94	1.56
k_3	16.04	4.22	9.23	0.54	9.24	1.07
k_4	33.89	8.58	18.88	0.86	21.24	1.50
Correlation matrices of the estimates	1 0.99 0.98 0.99 0.99 1 0.97 0.99 0.98 0.97 1 0.37 0.99 0.99 0.37 1		1 0.98 0.56 0.66 0.98 1 0.48 0.60 0.56 0.48 1 0.46 0.66 0.60 0.46 1		1 0.96 0.13 0.11 0.96 1 0.06 0.02 0.13 0.06 1 0.01 0.11 0.02 0.01 1	

To illustrate the foregoing considerations, we shall examine the following example[47]. In the study of the enzymatic hydrolysis of sucrose[14] a kinetic equation [Eqn.(4.6)] was obtained in which the kinetic constants were estimated:

$$R_s^{iw} = -\frac{k_1 k_2 c_s}{1 + k_2 c_s + k_3 c_g + k_4 c_f}, \qquad (4.6)$$

† The shape criterion is referred to in the literature as the *E*-criterion of the optimum nature of the design and the determinant criterion is referred to as the *D*-criterion.

where R_S^W is the rate of consumption of sucrose and c_s, c_g, and c_f are the concentrations of sucrose, glucose, and fructose respectively. Their initial concentrations were used as independent controllable variables. Fig.3 illustrates the starting experimental design as well as the conditions of 23 experiments designed additionally on the basis of the determinant and shape criteria. The results of the interpretation of these experiments are presented in Table 2, which shows that the shape criterion makes it possible to estimate more accurately the constants k_1 and k_2 than k_3 and k_4.

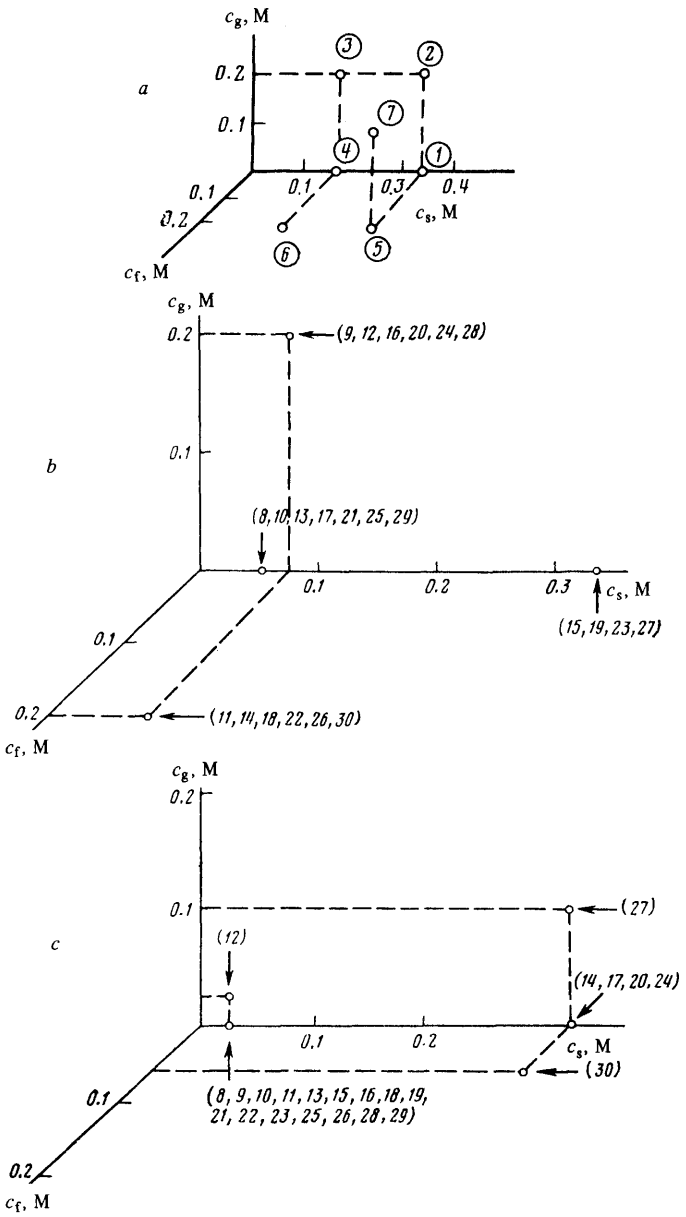


Figure 3. The starting experimental design (*a*) and the conditions of additional planned experiments determined from the determinant criterion (*b*) and the shape criterion (*c*). The coordinates of the points in Figs.3*a*–3*c* correspond to the initial concentrations of fructose, sucrose, and glucose (c_f, c_s, and c_g) in the periodic action reactor. The numerals in brackets are the ordinal numbers of repeated experiments carried out under the conditions indicated by the arrow.

This is apparently because, among the set of the constants estimated, k_1 and k_2 exhibit a greater parametric sensitivity. On the other hand, analysis of the pair correlations of the estimates shows that the correlations are significantly greater in absolute magnitude for the determinant criteria. Consequently, overall, when one considers a given specific example, the shape criteria is preferable.

The results of the comparison of these criteria[47] are not general and one should not expect to obtain analogous results in all cases. The results depend greatly on the type of kinetic model, on the specific numerical estimates of the constants and their parametric sensitivity, and on the length of the intervals corresponding to the variation of different controllable variables. The choice of a particular criterion is therefore determined by the aim of the kinetic study and also by the overall balance of the time allowed for the experiments and for the necessary computer calculations.

Naturally the experimental design which is optimum in relation to a given criterion may be significantly non-optimum in relation to any other. It is therefore useful to characterise the optimum properties of the design using not one criterion but a broad class of fundamental criteria. It is frequently convenient, by analogy with statistical theory of acceptable solutions, to allow a diminution of the optimum properties of the design in relation to the selected criterion, improving significantly at the same time the optimum properties of designs estimated on the basis of other criteria. Consequently, instead of using specific criteria, it is desirable to devise a single complex criterion.

Kiefer[49] suggested that the family of functionals of the information matrix be used to estimate the extent to which the designs approach an optimum:

$$\Phi_k(\xi) = \{p^{-1}\,\mathrm{Sp}\,[\Delta^{-k}(\xi)]\}^{1/k} = \left\{p\sum_{i=1}^{p}\lambda_i^{-k}\right\}^{1/k},$$
$$\Phi_0(\xi) = \lim_{k\to+0}\Phi_k(\xi) = \{\det\Delta(\xi)\}, \qquad (4.7)$$
$$\Phi_\infty(\xi) = \lim_{k\to+\infty}\Phi_k(\xi) = \max\{\lambda_i^{-1}\},$$

which include three of the most general criteria of an optimum, A, D, and E, obtained, in particular, when $k = 1, 0,$ or ∞. The properties of the family of functionals (4.7) have been analysed in detail by Kiefer; he interprets many of them as different characteristics of the dimensions of the confidence ellipsoid.

There are self-evident examples where the family of functionals Φ_k ($k = 0,1,\ldots\infty$) may not correct particular disadvantages of the design procedures. However, the employment of Φ_k is undoubtedly useful in most cases in characterising the properties of designs. Here one should note that the efficiency of the procedure used to design the refining (precision) experiment for models non-linear in terms of parameters will depend also on the initial parameters being estimated, which need to be refined, and hence also on the starting experimental design.

Practice has shown that, as a rule, the intuitively selected starting experiments in the possible region of experimentation lead to unsatisfactory (degenerate or almost degenerate) experimental designs; we may note that a virtually degenerate experimental design# can lead in many instances to incorrect results. It is known[50,51] that the strategy for the

A non-degenerate experimental design is understood to be one whose information matrix determinant is significantly non-zero.

starting experimentation depends both on the specific type of model and on the numerical values of its parameters. The dependence of the strategy on the first factor is significantly greater, so that the design of starting experiments is desirable even in those cases where the experimenter has *a priori* extremely approximate estimates of the model parameters. Naturally, in the complete absence of *a priori* information about the parameters, the traditional approach, in which the experiment is designed intuitively, is the only one possible.

We shall consider the situation where there is some *a priori* information about the parameters and the cost of a single observation is fairly high, so that one needs to construct an exact D-optimum experimental design for a number of experiments N, specified beforehand, which exceeds only slightly the number of parameters p to be estimated. In the latter case the theorem of equivalence for locally optimum exact designs does not hold and only the following system of inequalities is valid:

$$\det(x, \varepsilon'_N) \leqslant \det(x, \varepsilon_N) \leqslant \frac{Np}{N+1-p}, \qquad (4.8)$$

where ε'_N and ε_N are respectively the experimental designs minimising the response variance $d(x, \varepsilon_N)$ and maximising the determinant of the information matrix $M(\varepsilon_N)$. Under these conditions, the procedure used to construct locally optimum exact designs for single-response models can be carried out in the following particular way:

(1) p kinetic parameters θ are specified for the kinetic model being tested;

(2) the design $\varepsilon_N^{(1)} = (x_1, \ldots, x_N)$ with $\det M(\varepsilon_N) \neq 0$ is chosen in the experimentation region G.

(3) the conditions for the $(N+1)$th experiment, maximising $d_N(x, \varepsilon_N^{(1)})$, are calculated;

(4) the design $\varepsilon_{N+1}^{(1)} = \varepsilon_N^{(1)} \cup x_{N+1}$ is formulated;

(5) on the basis of the $\varepsilon_{N+1}^{(1)}$ design, the $\varepsilon_N^{(1)}$ design, for which the determinant of the information matrix is a maximum, is found by consecutive sorting in the $(N+1)$th N-point design.

In the sth step of the construction of the exact design the inequality

$$\det\{M(\varepsilon_N^{(s)})\} > \det\{M(\varepsilon_N^{(s-1)})\} \qquad (4.9)$$

always holds, provided that

$$\sup_{x \in G} d(x, \varepsilon_N^{(s)}) = d(\varepsilon_N^{(s)}) > \frac{Np}{N+1-p}. \qquad (4.10)$$

The construction of the design is repeated until it is found that, for a specified value of δ at some step,

$$d(\varepsilon_N^{(k)}) \leqslant \frac{Np}{N+1-p} + \delta$$

for all $k > s$.

The procedure examined above converges fairly rapidly to the exact locally optimum design. Thus five interactions are usually sufficient for the construction of the exact design.

One should note that the most significant factor determining the optimum strategy for the starting (and subsequent refining) experiments involves the determination of the number of constants in the kinetic model capable of being estimated. To a first approximation, it is equal to the rank of the information matrix $M(\varepsilon_N)$ of the ε_N design; the rank depends both on the numerical values of θ and on the experimental design ε_N. The number of constants capable of being estimated is then usually less than the total number of parameters of the model, because some of them are determined in the form of certain combinations, for example, because of the use of approximations postulating a quasi-stationary reaction or a quasi-equilibrium in the rapid stages. The total number of parameters does not include those whose statistical insignificance has been established by methods of variance analysis in testing the adequacy of the kinetic models.

In the consecutive design of refining experiments one must maximise, together with the selected criterion for an optimum design, also the rank of the information matrix in order not to lose information about the numerical parameters and in order not to reach incorrect conclusions in selecting a kinetic model adequate for the process.

VI. DISCRIMINATION BETWEEN MODELS

Before the concluding stage of the determination of the probable mechanism of a chemical reaction, it is usually found that several kinetic models are consistent with the available experimental data and the problem of discrimination between them therefore arises. There exist two main methods for testing kinetic models—the method of the probability ratio and Bayes' method. Although they are in many respects similar, nevertheless there are fundamental differences.

The method of the probability ratio[52] is effective in testing kinetic hypotheses, particularly when the probability function is know, i.e. when the density of the distribution of the errors of the measurements and the numerical parameters of both the kinetic models and of the distribution function are known. The probability ratio

$$u_{ij} = L_i / L_j \qquad (5.1)$$

then serves as a measure of the advantage of the ith model compared with the jth model. Evidently, if $u_{ij} > 1$, then $L_i > L_j$ and the experimental results are therefore better reflected by the ith model than by the jth model. For $u_{ij} > 10$ and even more so for $u_{ij} > 100$, there exists sufficient evidence in support of the ith model.

However, the parameters θi and θj, on which the probability ratio $u_{ij}(\theta_i, \theta_j)$ depends, are usually unknown. One of the possible ways of eliminating "interfering" parameters consists in the employment of estimates of maximum probability as a function of the probability ratio

$$u_{ij}(\theta_i^{\times}, \theta_j^{\times}) = \max_{\theta_i} L_i(\theta_i) / \max_{\theta_j} L_j(\theta_j). \qquad (5.2)$$

In this case $u_{ij}(\theta_i^{\times}, \theta_j^{\times})$ represents the ratio of the probabilities for two individually best models. When the parameters estimated from the experimental data are not known beforehand, interpretation of the probability ratio and a decision in favour of a particular model become much more arbitrary. For the same number of parameters of the models, the probability ratio $u_{ij}(\theta_i, \theta_j)$, for which preference is given to the ith model compared with the jth model, is selected in the range from 10 to 100.

If $u_{ij}(\theta_i, \theta_j)$ includes the vectors θ_i and θj of different dimensions, the model containing a greater number of parameters is usually found to be superior in the test. This finding must be taken into account in testing kinetic hypotheses.

If the number of tested hypotheses is greater than two $(m > 2)$, they are checked in pairs for all possible pairs. However, it is better to employ the general probability ratio[53]

$$u_j = \frac{L_j(\theta_j)}{\left(\prod_{k=1}^{m} L_k(\theta_k)\right)^{1/m}}. \qquad (5.3)$$

as the criterion. As described above, in this case the pth model is thought to have been proved best in the tests if the values of u_j ($j = 1,\ldots,p-1, p+1,\ldots,m$) do not exceed $0.01-0.1$; here it is assumed that $u_p > 0.1$.

It is nevertheless most useful to employ the criterion (5.3) in a consecutive procedure for the determination of the best kinetic model, the essential features of which are as follows. The experiment is carried out consecutively until the probability ratio for one of the models, for example the lth model, is in the range $0.01-0.1$; the lth model is then discarded and the number of models is reduced by unity. Tests are continued until only one model remains and is adopted as most consistent with the experimental data.

The Bayes ion approach to the solution of the problem of discrimination between models is based on the Bayes theorem and a subjective interpretation of the *a priori* information. In the Bayes ion approach the solution of the discrimination problem begins with the determination of the *a priori* distribution density of the probabilities $P(M_j)$, $j = 1,\ldots,m$, constructed for a set of m competing hypotheses M_j. It is specified on the basis of previous experimental studies or literature data and constitutes a subjective interpretation of the available information by the investigator. The distribution density of the probabilities $P(M_j)$ is usually discrete in view of the finite nature of the set of tested hypotheses and its form has no influence on the result of the final solution of the test of the hypotheses although both the duration of the discrimination procedure and the number of necessary experiments depend on its selection.

Since it is difficult to construct the loss function corresponding to the adoption of an incorrect solution, one usually maximises the *a posteriori* distribution density of $P(M_j|y)$, which is determined from the results of the experiment y and from the *a priori* distribution density of $P(M_j)$ on the basis of Bayes' theory:

$$P(M_l|\mathbf{y}) = \frac{P(\mathbf{y}|M_j)P(M_j)}{P(\mathbf{y})} = \gamma P(\mathbf{y}|M_l)P(M_l), \qquad (5.4)$$

where $P(\mathbf{y}|M_j)$ is the distribution density of the selection obtained on the assumption that the hypothesis is valid and $P(\mathbf{y})$ is the partial distribution density of the selection. The proportionality constant γ in Eqn.(5.4) is determined from the condition that the sum of the *a posteriori* probabilities is equal to unity for all the models.

If the probability function $P(\mathbf{y}|\theta_j, M_j)$ contains "interfering" parameters θ_j, the latter must be excluded from consideration by averaging the function $P(\mathbf{y}|\theta_j, M_j)$ over all possible values of θ_j:

$$P(\mathbf{y}|M_l) = \gamma \int P(\mathbf{y}|\theta_j, M_j)\,P(\theta_j|M_j)\,\mathrm{d}\theta_j, \qquad (5.5)$$

where $P(\theta_j|M_j)$ is the *a priori* distribution density of the parameters θ_j. Similarly $P(M_j)$ is selected from the available information about the values of θ_j.

We may note that, when the Bayes ion approach to the problem of discrimination between the hypotheses is used, the parameters θ_j are regarded as random quantities with a certain probability distribution density.

There exist several ways of achieving the Bayes ion approximation in practice for the solution of the problem of discrimination between models which are non-linear in terms of the parameters. The most general is based on the expansion of non-linear models in Taylor's series in the space of parameters in the vicinity of earlier estimates of θ_j. Restricting the treatment to only the first terms of the expansion, we then have

$$\mathbf{d}_j = X_j(\theta_j - \theta_j^+) + \varepsilon, \qquad (5.6)$$

where $\mathbf{d}_j = (d_{j1},\ldots,d_{jn})^{\mathrm{T}}$, $d_{ju} = y_u - f^{(j)}(x_u, \theta_j^+)$, and $u = 1,\ldots,n$ are indices characterising the number of the experiment. $\theta_j = (\theta_{j1},\ldots,\theta_{jpj})$ is the vector of the space of parameters with the dimensions $pj \times 1$, $\varepsilon = (\varepsilon_1,\ldots,\varepsilon_n)^{\mathrm{T}}$ for the vector of the reproducibility errors, and $X_j = \{x_{ul}^{(j)}\}$ a matrix with the dimensions $n \times p_j$ whose u, l-th element can be put in the form

$$x_{ul}^{(j)} = \left\{\frac{\partial f^{(j)}(x_u, \theta_j)}{\partial \theta_{jl}}\right\}_{\theta_j = \theta_j^+}. \qquad (5.7)$$

It is assumed in addition that (1) the vector of the reproducibility error ε is a normal random vector with a zero vector of mathematical expectations and a covariance matrix Σ, i.e. $\varepsilon \cong N(0,\Sigma)$, and (2) the *a priori* distribution density of the probabilities of Θ_j is also normal with the vector of means $\tilde{\theta}_j$ and a known covariance matrix Ω_j with the dimensions $p_j \times p_j$.

It is readily seen that, for the given assumptions, the random vector d_j is distributed normally with $\mathrm{E}\,d_j = X_j(\theta_j - \theta_j^+)$ and the covariance matrix $D\,d_j = X_j\Omega_j X_j^{\mathrm{T}} + \Sigma$, where E is a symbol representing the mathematical expectation. Eqn.(5.5) then becomes

$$P(\mathbf{y}|M_j) = \frac{\exp\left\{-\frac{1}{2}[\mathbf{d}_j - X_j(\tilde{\theta}_j - \theta_j^+)]^{\mathrm{T}}(X_j\Omega_j X_j^{\mathrm{T}} + \Sigma)^{-1}[\mathbf{d}_j - X_j(\tilde{\theta}_j - \theta_j^+)]\right\}}{(2\pi)^{n/2}[\det(X_j\Omega_j X_j^{\mathrm{T}} + \Sigma)]^{1/2}}. \qquad (5.8)$$

Although Eqn.(5.8) was derived without using Eqn.(5.5), it is fully equivalent to the latter[52].

The *a posteriori* probabilities of the validity of the hypotheses are calculated from Eqn.(5.4). Consequently, we have

$$P(M_j|\mathbf{y}) = \frac{P(M_j)P(\mathbf{y}|M_j)}{\sum_{k=1}^{m} P(M_k)P(\mathbf{y}|M_k)}. \qquad (5.9)$$

At a specific step in the experimentation process one assumes that the lth model has withstood best the tests among the set of competing models if $P(M_l|\mathbf{y})$ assumes values fairly close to unity.

Analogously the Bayes method of selecting the best solutions can be used to estimate the kinetic parameters. In this case the *a posteriori* distribution of the parameter θ is also determined from the Bayes theorem:

$$P(\theta_j|y) = \frac{P(\mathbf{y}|\theta_j)P(\theta_j)}{\int_{\Omega} P(\mathbf{y}|\theta_j)P(\theta_j)\,\mathrm{d}\theta_j} = \frac{P(\mathbf{y}|\theta_j)P(\theta_j)}{P(\mathbf{y})}, \qquad (5.10)$$

where $P(\mathbf{y})$ and $P(\theta_j)$ are the partial distribution densities of the random vectors $\mathbf{y}$ and θ_j. As before, $P(\theta_j)$ contains the initial information about the values of θ_j. If $P(\mathbf{y}|\theta_j)$ and $P(\theta_j)$ are the normal distribution densities of the probabilities, then $P(\theta_j|\mathbf{y})$ is the conventional *a posteriori* distribution density of the parameters θ_j, which is also normal with

$$E(\theta_j) = (X_j^{\mathrm{T}}\Sigma^{-1}X_j + \Omega_j^{-1})(X_j^{\mathrm{T}}\Sigma^{-1}X_j\theta_j^+ + \Omega_j^{-1}\tilde{\theta}_j) \qquad (5.11)$$

and with the covariance matrix

$$D(\theta_j) = [(X_j^{\mathrm{T}}\Sigma^{-1}X_j + \Omega_j^{-1})]^{-1}.$$

In kinetic studies on complex chemical systems the confirmation of the reaction mechanism frequently requires the estimation with a specified accuracy of only some of the constants in the overall set, for example, in order to be able to compare subsequently their values with the constants

obtained from earlier independent measurements. Consequently, one has to estimate only a subvector of the vector of the parameters θ_j, the *a posteriori* distribution density of which is equal to the partial *a posteriori* distribution density of the subvector of the parameters relevant to the given case. For normal $p(\theta_j|y)$, the latter is also normal with the vector of mathematical expectations equal to the corresponding subvector of the specified parameters of the vector $E(\theta_j)$ and with a covariance matrix made up of the elements $D(\theta_j)$ located at the intersections of the columns and rows of the corresponding specified parameters.

We may also note that the use of the *a posteriori* distribution density of the kinetic parameters as a characteristic of the accuracy of their estimates yields incomparably more information about the parameters than the point and interval estimates, which is a characteristic advantage of the Bayesion approach.

The Bayesion procedure for testing kinetic hypotheses, discussed above, which provides for the linearisation of the kinetic models with respect to parameters, is correct only when the models tested for consistency with experimental results are linear in terms of the parameters and the fundamental statistical postulates, concerning the nature of the distribution density of the errors of the measurements and the validity of the employment of the methods of regression analysis, are correct. The application of such procedures in order to discriminate between models which are significantly non-linear in terms of the parameters is legitimate only when the non-linear models can be fitted fairly satisfactorily by linearised models.

In order to improve the reliability of the Bayes methods, which involves the linearisation of the kinetic models, it is necessary to improve in the first place the linearisation procedure itself. This can be achieved, in particular, by a suitable selection of the estimates of θ_j^+ in the vicinity of which the models can be fitted by a truncated Taylor series. It is usually desirable to employ as such estimates the estimates of the maximum probability or estimates which are respectively equal to the vector of the mathematical expectations of the *a posteriori* distribution density of the parameters.

Another method for improving the linearisation procedure consists in a preliminary reparametrisation of the models and their reduction to a form which no longer involves a significant non-linearity. The kinetic models transformed in this way are more covenient for subsequent linearisation. Thus it has been shown in relation to a number of examples[54] that the direct application of Bayes discrimination methods to non-parametrised models leads to contradictory results, while preliminary reparametrisation of the competing models eliminates the possible errors. The algorithms proposed for the reparametrisation of kinetic models were in many respects analogous to the algorithms of Box et al.[55] and Box and Tidwell[56], which were developed to replace dependent and independent variables in regression equations.

One should note that reparametrisation makes it possible to increase appreciably not only the reliability of the Bayes procedures for discrimination between models but also the accuracy of the calculation of the variance matrices and hence the confidence intervals and confidence regions for the estimation of the parameters[57].

A method for the testing of kinetic hypotheses, which does not involve a procedure for the linearisation of models and employs the kinetic models as such in the selection of solutions, has been proposed[58]. In this method the continuous region of parametric space for each competing model, in which the best estimates of the model parameters are sought, is covered by a finite set of discrete points equidistant from one another. An *a priori* probability $P(\theta_j|M_i)$ is assigned to each l_j-th parametric point θ_j and the expression for the *a posteriori* probabilities of acceptable hypotheses (5.9) is replaced by its discrete analogue

$$P(M_j|\mathbf{y}) = \frac{P(M_j)\sum_{l=1}^{s_l} P(\theta_{l_j}|M_j)P(\mathbf{y}|\theta_{l_j}, M_j)}{\sum_{i=1}^{m} P(M_i)\sum_{l=1}^{s_i} P(\theta_{l_i}|M_i)P(\mathbf{y}|\theta_{l_i}, M_i)}, \quad (5.12)$$

where s_i is the total number of parametric points θ_{li} covering the region of the parametric space for the ith model.

The *a posteriori* probabilities

$$P(\theta_{l_j}|\mathbf{y}) = \frac{P(\theta_{l_j}|M_j)P(\mathbf{y}|\theta_{l_j}, M_j)}{\sum_{i=1}^{m}\sum_{l=1}^{s_i} P(\theta_{l_i}|M_i)P(\mathbf{y}|\theta_{l_i}, M_i)}. \quad (5.13)$$

are estimated from the selected y and the *a priori* probabilities $P(\theta_{li}|M_j)$. In the next step of the test of competing kinetic models, i.e. before setting up a new series of experiments and before a new selection of y, the *a posteriori* probabilities $P(\theta_{lj}|y)$ and $P(M_j|y)$ are assumed to be *a priori* probabilities and the cycle of investigations is repeated until the *a posteriori* probability $P(M_k|y)$ of a kth model is close to unity; the kth model is assumed to be most consistent with the experimental results.

The practical application of the method proposed by Hsiang and Reilly[58] presupposes the obligatory use of modern high speed computers with a large memory. Indeed, if, for example, the kinetic model contains five parameters and each parameter has ten discrete values, then 10^5 values of the probability function must be stored in the computer memory. Consequently the method[58] is effective, owing to the so called "dimensional curse", only in those cases where the number of parameters in the competing models is small and the preliminary estimates are known with a sufficiently high accuracy, which makes it possible to select a fairly narrow range of the possible variation of the parameters and in testing the hypotheses one can confine the treatment to a small number of discrete values of the kinetic parameters.

In conclusion we shall examine a useful discrimination method based on the χ_c^2 criterion[59]; the method cannot be in essence classified as a Bayes method or as a probability ratio method. The fundamental idea of the method under consideration is that the ratio of the weighted sum of the squares of the residues to the corresponding number of degrees of freedom for single-response models is an undisplaced estimate of the reproducibility error only for the true kinetic model; for all the remaining models the estimate is displaced. The method tests the homogeneity of the estimates of the reproducibility variances for all the competing models using the Bartlett distribution:

$$\chi_c^2 = \frac{(\ln \bar{s})^2 \sum_{i=1}^{m} p_{s_i} - \sum_{i=1}^{m} p_{s_i} \ln s_i^2}{1 + \frac{1}{3(m-1)}\left[\sum_{i=1}^{m}\frac{1}{p_{s_i}} - \frac{1}{\sum_{i=1}^{m} p_{s_i}}\right]}, \quad (5.14)$$

where m is the number of competing models, s_i^2 the estimates of the reproducibility variances calculated for the ith model, p_{s_i} the number of degrees of freedom of the estimate, and $\bar{s}^2$ the average estimate of the reproducibility error. If, on testing m hypotheses, it is found that χ_c^2 exceeds the tabulated value, the model yielding the maximum variance of the

reproducibility error is rejected. The number of hypotheses is reduced by unity and χ_c^2 is recalculated.

When this criterion is used to solve the problem of discrimination between hypotheses, one should bear in mind that χ_c^2 is extremely sensitive to the deviation of the data from normality and requires the statistical independence of the estimates of the variance against which the hypothesis of homogeneity is tested. It is frequently impossible to establish to what extent such hypotheses hold. However, practical examples of the use of the χ_c^2 criterion in chemical research have demonstrated its effectiveness and reliability[59].

VII. DESIGN OF DISCRIMINATING EXPERIMENTS

In the procedures described above tests of kinetic hypotheses were used to discriminate between models in relation to the results of an experiment, particularly a passive experiment. However, the efficiency of testing procedures greatly increases if the experiment is carried out actively. The problem of the design of discriminating experiments, in contrast to that of the design of precision experiments, is characterised by the absence of uniformity in the criteria employed.

However, they can be subdivided into two categories: the first includes criteria based on various measures of information and the second includes empirical criteria[60,63].

In kinetic experimental studies the entropic criterion, used as a measure of the information entropy S, is most frequently employed among the criteria of the first category. The information entropy can be defined as follows for all $P(M_j) \neq 0$ $(j = 1,\ldots,m)$:

$$S = -\sum_{j=1}^{m} P(M_j) \ln P(M_j), \qquad (6.1)$$

where $P(M_j)$ is the *a priori* probability of the suitability of the M_j-th hypothesis. If $P(M_i) = 0$ for a certain value of i, the product $P(M_i) \ln P(M_i)$ is set equal to zero.

Evidently, if $P(M_k) = 1$ for the kth model, then $P(M_j) = 0$ for $j = 1,\ldots, k-1, k+1,\ldots,m$. Then the entropy S assumes the smallest of the possible values, which is zero. On the other hand, for equal $P(M_j) = 1/m$ $(j = 1,\ldots,m)$, the value of S reaches a maximum. Consequently S characterises a measure of the information obtained about the test system and an increase of the amount of information is accompanied by an obligatory decrease of entropy.

Since in research it is desirable to reduce to the maximum extent the degree of uncertainty in the ideas about the chemical system, one should endeavour to pass from a non-informative situation [$P(M_j) = 1/m$, $j = 1,\ldots,m$; the information is scanty and it is impossible to give preference to any one model] to the most informative situation [$P(M_k) = 1$, $j = 1,\ldots, k-1,\ldots, k+1,\ldots,m$; there is sufficient information to demonstrate in the "statistical sense" the validity of the kth model]. For this purpose, in the region G, corresponding to the experimental conditions, one must carry out only experiments which reduce the entropy S to the maximum extent.

In order to establish the conditions for such experiments, Box and Hill[60] proposed two single-response models based on the criteria $D(\boldsymbol{x})$, which determine the upper limit of the expected decrease of entropy in the design and formulation of the experiment at point $\boldsymbol{x}$ in the experimental region G:

$$D(\boldsymbol{x}) = \frac{1}{2}\sum_{j=1}^{m}\sum_{i=j+1}^{m} P(M_i)P(M_j)\left\{\frac{(\sigma_i^2-\sigma_j^2)}{(\sigma^2+\sigma_i^2)(\sigma^2+\sigma_j^2)}\times \right.$$
$$\left.\times [\hat{\eta}_i(\boldsymbol{x}) - \hat{\eta}_j(\boldsymbol{x})]^2\left(\frac{1}{\sigma^2+\sigma_i^2}+\frac{1}{\sigma^2+\sigma_j^2}\right)\right\}, \qquad (6.2)$$

where $\boldsymbol{x}$ is the vector of the space of independent controllable variables, $\hat{\eta}_i(\boldsymbol{x})$ the response at point $\boldsymbol{x}$ predicted on the basis of the ith model, σ^2 the variance of the reproducibility error, and σ_i^2 the variance of the predicted response i.

In terms of the $D(\boldsymbol{x})$ criterion, an experiment $\boldsymbol{x}^{\times}$ which maximises $D(\boldsymbol{x})$ i.e. for which the conditon

$$D(\boldsymbol{x}^{\times}) = \max_{\boldsymbol{x}\in G} D(\boldsymbol{x}). \qquad (6.3)$$

holds, is most convenient. The entropic criterion[60] has been extended[5] to multiresponse models. Subsequently Reilly[52] again improved the $D(\boldsymbol{x})$ criteria by divising an algorithm for the direct calculation of the expected decrease of the entropy S.

Another important measure of information used in discrimination between models is a function of the general probability ratio. In this case the equality of the generalised probability ratios corresponds to the minimum amount of information about the system of hypotheses, while the maximum difference between them corresponds to the maximum amount of information. Hence it follows directly that, for the attainment in the course of the selection of the solution corresponding to the most favourable informative situation, one must design the experiment in such a way that the expected average increment in the sum of the logarithms of the general probability ratios from experiment to experiment is maximised[12,53]:

$$\Delta L(\boldsymbol{x}_{N+1}) = \sum_{j=1}^{m}\int_{-\infty}^{+\infty}[\ln u_j(N+1) - \ln u_j(N)]\,P_j(y_{N+1}|\,\boldsymbol{x})\,\mathrm{d}\,\boldsymbol{y}_{N+1} =$$
$$= \frac{1}{2m}\left\{\sum_{j=1}^{m}\sum_{k=1}^{m}\mathrm{Sp}\,(\Sigma+S_j)(\Sigma+S_k)^{-1} - m\,\mathrm{Sp}\,I + \right.$$
$$\left. + \sum_{j=1}^{m}\sum_{k=1}^{m}(\hat{\eta}_{N+1}^{(k)} - \hat{\eta}_{N+1}^{(j)})^{\mathrm{T}}[(\Sigma+S_j)^{-1}(\hat{\eta}_{N+1}^{(k)} - \hat{\eta}_{N+1}^{(j)})]\right\}, \qquad (6.4)$$

where $D_j(N)$ is the covariance matrix of the estimates of the constants of the jth model calculated on the basis of N experiments, $P_j(y_{N+1}|x_{N+1})$ is the distribution density of the $(N+1)$th result of the measurement of the response at the point $\boldsymbol{x}_{N+1}$ predicted on the basis of the jth model, $L_j(N)$ the general probability function given by

$$L_j(N) = \frac{\det \Sigma^{-N/2}\det D_j(N)^{1/2}}{(2\pi)^{nN/2-p_j/2}}\cdot\exp\left\{-\frac{1}{2}\left[\sum_{r=1}^{n}\sum_{s=1}^{n}\sigma^{rs}\sum_{l=1}^{N}\times\right.\right.$$
$$\left.\left.\times(y_{rl}^{(j)} - \hat{\eta}_{rl}^{(j)})(y_{sl}^{(j)} - \hat{\eta}_{sl}^{(j)})\right]\right\};$$
$$u_j(N) = \frac{L_j(N)}{\left(\prod_{k=1}^{m} L_k(N)\right)^{1/m}},$$

$S_j = X_j D_j(N) X_j^{\mathrm{T}}$, X_j an $n \times p_j$ matrix with a general element of the type $x_{ri}^{(j)} = \partial\eta_{r,N+1}^{(j)}/\partial\theta_i^{(j)}$, $\hat{\eta}^{(j)}$ the $n \times 1$ vector of the predicted values of the response based on the jth model, $\Sigma = \{\sigma_{ij}\}$ the covariance matrix of the measurements, $\Sigma^{-1} = \{\sigma^{rs}\}$, and the indices j, i, and r characterise respectively the numbers of the model, the parameter, and the response.

Application of criterion (6.4) to the solution of a number of practical problems in chemical kinetics demonstrated its effectiveness and reliability[64,65]. In particular, the use of criterion (6.4) in tests for consistency with experiment of two competing hypotheses about the mechanism of the toluene disproportionation reaction on zeolite catalysts showed that

two consecutive experimental designs are sufficient to demonstrate the superiority of one hypothesis. A similar situation arises in discrimination between multiresponse models, while for single-response models the necessary number of discriminating experiments is usually significantly greater.

Fig. 4 illustrates graphically the function of the general probability ratio ΔL obtained in calculations of the conditions for the first discriminating experiment. The large number of extrema and "ravines" in the plot of the function ΔL against controllable variables indicates computational difficulties in the solution of problems involving discrimination between multiresponse models non-linear in terms of parameters. One should note that discriminating experiments are usually located at the boundary of the region of possible experimentation.

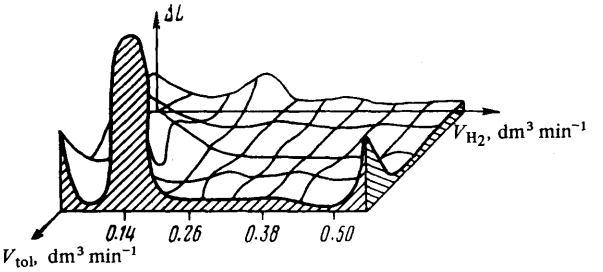


Figure 4. Variation of the response surface of the function of the probability ratio ΔL with controllable variables—the volume flow rates of hydrogen and toluene; the volume flow rate of benzene was constant at 0.05 dm^3 min^{-1}.

Other criteria for the design of discriminating experiments, based on other measures of information, are also known. Thus it has been suggested[66] that the Kullbakov measure be employed, while Borth[67] suggested that one use the increment in the maximum *a posteriori* probability of the suitability of models. The criteria have been compared and their efficiences estimated[68]. However, in practical kinetic research the criteria proposed in the above investigations[66,67] have not so far been used.

All the criteria examined above[69] make it possible to formulate experiments in the experimentation region which permit the establishment of competing models under critical conditions from the standpoint of their descriptive power. One then as a rule takes into account the uncertainty in the predicted responses; preference can be given to experimental conditions characterised by small discrepancies in the predicted responses with small error corridors compared with conditions accompanied by large discrepancies between the predicted responses with large error corridors.

In practice the variances of the predicted responses are calculated with much difficulty and in devising empirical criteria they are therefore as a rule neglected. The $C(x)$ criterion is most widely used[67]:

$$C(x) = \sum_{i=1}^{m} \sum_{j=i+1}^{m} |\hat{\eta}_i(x) - \hat{\eta}_j(x)| , \qquad (6.5)$$

as well as the $B(x)$ criterion[58]:

$$B(x) = \sum_{i=1}^{m} \sum_{j=i+1}^{m} |P(M_i) + P(M_j)| \cdot |\hat{\eta}_i(x) - \hat{\eta}_j(x)|. \qquad (6.6)$$

In applying criteria (6.5) and (6.6) the discriminating experiments are usually located in a single adequately bounded subregion of the experimentation region G. A complex criterion, which provides, together with the maximisation of $C(x)$, also for the maximisation of the distance between the new discriminating point produced by the design and all the remaining points of the design found previously, has therefore been proposed[70]. This principle has been realised in practice[70].

There are now already numerous publications in which the methods for the design and analysis of kinetic precision and discriminating experiments have found practical applications. Most of them describe real practical situations[61–63,71–78], while others deal solely with situations simulated on computers. These publications describe mainly the results of comparisons of different criteria and give estimates of their efficiencies[76–80].

REFERENCES

1. N.M.Emanuel' and D.G.Knorre, "Kurs Khimicheskoi Kinetiki" (A Course of Chemical Kinetics), Izd. Vysshaya Shkola, Moscow, 1974.
2. G.K.Boreskov, Vestnik Akad.Nauk SSSR, 5, 47 (1965).
3. V.V.Karfarov, "Metody Kibernetiki v Khimii i Khimicheskoi Tekhnologii" (Cybernetic Methods in Chemistry and Chemical Engineering), Izd. Khimiya, Moscow, 1976.
4. V.V.Nalimov, "Teoriya Eksperimenta" (Theory of Experiments), Izd.Nauka, Moscow, 1971.
5. D.M.Himmelblau, "Process Analysis by Statistical Methods" (Translated into Russian), Izd.Mir, Moscow, 1973.
6. V.N.Pisarenko and A.G.Pogorelov, "Planirovanie Kineticheskikh Issledovanii" (Design of Kinetic Studies), Izd.Nauka, Moscow, 1969.
7. R.Aris and R.Mah, Ind.Eng.Chem.Fund., 2, 90 (1963).
8. A.Petho, Chem.Eng.Sci., 20, 791 (1965).
9. G.J.Pings and E.B.Nebeker, Ind.Eng.Chem.Fund., 4, 376 (1965).
10. D.A.Frank-Kamenetskii, Uspekhi Khim., 10, 373 (1941).
11. V.V.Kafarov, V.N.Pisarenko, L.A.Mascheva, and O.N.Smirnova, Dokl.Akad.Nauk SSSR, 216, 342 (1974).
12. V.V.Kafarov, V.N.Pisarenko, T.B.Zhukova, and L.A.Mascheva, "Sbornik Dokladov IV Vsesoyuznoi Konferentsii po Planirovaniyu i Avtomatizatsii Eksperimenta v Nauchnykh Issledovaniyakh" (Collected Reports at the IVth All-Union Conference on the Design and Automation of Experiments in Scientific Research), Izd.Sov.Radio, Moscow, 1974.
13. N.N.Semenoff, J.Chem.Phys., 7, 683 (1939).
14. J.Horiuti, J.Res.Inst Catalysis, Hokkaido Univ., 5, No.1, 1 (1957).
15. M.I.Temkin, Dokl.Akad.Nauk SSSR, 152, 156 (1963).
16. M.I.Temkin, Symposium, "Mekhanizm i Kinetika Slozhnykh Kataliticheskikh Reaktsii" (The Mechanisms and Kinetics of Complex Catalytic Reactions), Izd. Nauka, Moscow, 1970, p.57.
17. E.Christiansen, Symposium , "Kataliz.Issledovanie Geterogennykh Protsessoy" (Catalysis. The Study of Heterogeneous Processes) (Translated into Russian Russian), Inostr.Lit., Moscow, 1956, p.193.

18. Yu.S.Snagovskii and G.M.Ostrovskii, "Modelirovanie Kinetiki Geterogennykh Kataliticheskikh Reaktsii" (The Modelling of the Kinetics of Heterogeneous Catalytic Reactions), Izd.Khimiya, Moscow, 1976.
19. A.I.Kuz'michev, B.P.Gusev, V.N.Pisarenko, and V.V.Kafarov, Izv.Akad.Nauk SSSR, Ser.Khim., 1393 (1974).
20. V.V.Nalimov and N.A.Chernova, "Statisticheskie Metody Planirovaniya Ekstremal'nykh Eksperimentov" (Statistical Methods for the Design of Extreme Experiments), Izd.Nauka, Moscow, 1965.
21. C.Daniel and F.S.Wood, "Fitting Equations to Data", Wiley, New York, 1971.
22. O.L.Davies, "The Design and Analysis of Industrial Experiments", Oliver and Boyd, New York, 1956.
23. R.L.Plackett, "Principles of Regression Analysis", Wiley, Oxford, 1960.
24. N.Dreiner and G.Smith, [tentative spelling (Ed. of Translation)] "Applied Regression Analysis" (Translated into Russian), Izd.Statistika, Moscow, 1973.
25. S.Sachs [tentative spelling (Ed. of Translation)], "Theory of Statistical Conclusions" (Translated into Russian), Izd.Mir, Moscow, 1975.
26. G.E.P.Box and N.R.Draper, Biometrika, **52**, 355 (1965).
27. G.E.P.Box, W.G.Hunter, McGregor, and J.Erjavec, Technometrics, 15, 33 (1973).
28. H.Nagao, Annalen Stat, 1, 400 (1973).
29. O.L.Davies, "Statistical Methods in Research and Production", Hafner, New York, 1960.
30. N.L.Corr, Ind.Eng.Chem., **52**, 391 (1960).
31. R.A.Johnson, N.A.Standel, and R.Mezaki, Ind. Eng.Chem.Fund., 7, 181 (1968).
32. J.R.Kittrel and J.Erjavec, Ind.Eng.Chem.Proc. Design Develop., 7, No.3, 321 (1966).
33. R.L.Kabel and L.N.Johanson, Amer.Inst.Chem. Engineers J., **8**, 621 (1962).
34. F.J.Anscombe, Proc.Berkely Symp.Math.Statist. Probability, 4-th, 1, 19 (1963).
35. F.J.Anscombe and J.W.Tukey, Technometrics, **5**, 141 (1963).
36. G.E.P.Box, Annalen New York, Acad.Sci., **86**, 792 (1960).
37. R.W.Anderson and T.A.Bacroft, "Statistical Theory in Research", New York, 1952.
38. T.W.Anderson, Annalen Math.Stat., **33**, 266 (1962).
39. G.E.P.Box and H.Lucas, Biometrika, **46**, 77 (1959).
40. N.R.Draper and W.G.Hunter, Biometrika, **53**, 525 (1966).
41. N.R.Draper and W.G.Hunter, Biometrika, **54**, 147 (1967).
42. W.G.Hunter, W.J.Hill, and T.L.Henson, Canad.J. Chem.Eng., **47**, 76 (1969).
43. A.C.Atkinson and W.F.Hunter, Technometrics, **10**, 271 (1968).
44. M.J.Box, "The Future of Statistics", Acad.Press, New York, 1968.
45. M.J.Box, Technometrics, **12**, 569 (1979).
46. G.F.Froment and R.Mezaki, Chem.Eng.Sci., **25**, 293 (1970).
47. L.H.Hosten, Chem.Eng.Sci., **29**, 2247 (1974).
48. L.H.Hosten and G.Emig, Chem.Eng.Sci., **30**, 1357 (1975).
49. J.Kiefer, Biometrika, **62**, 277 (1975).
50. V.V.Kafarov, V.N.Pisarenko, T.B.Zhukova, and A.V.Solokhin, "Sbornik II Konferentsii po Kinetika Kataliticheskikh Reaktsii" (Collected Reports at the IInd Conference on the Kinetics of Catalytic Reactions), Izd.Sibir.Otd.Akad.Nauk SSSR, Novosibirsk, 1975, Vol.2, p.137.
51. V.N.Pisarenko, V.V.Kafarov, A.V.Solokhin, and T.B.Zhukova, "Trudy MKhTI, Neorganicheskie Materialy, Protsessy i Apparaty, Kibernetika Khimicheskikh Protsessov" (Transactions of the Moscow Institute of Chemical Engineering. Inorganic Materials, Processes, and Apparatus. Cybernetics of Chemical Processes), 1975, No.85, p.172.
52. P.M.Reilly, Canad.J.Chem.Eng., **48**, 168 (1970).
53. V.V.Kafarov, V.N.Pisarenko, and T.V.Zhukova, Dokl.Akad.Nauk SSSR, **218**, 386 (1974).
54. J.Beamer and G.E.Blau, "Statistical Technique Applied to Catalytic Reaction Model Identification", AIChE Meeting, San Francisco, 1971.
55. G.E.P.Box, D.R.Cox, and J.Roy, Stat.Soc., Ser. B, **26**, 211 (1964).
56. G.E.P.Box and P.W.Tidwell, Technometrics, **4**, 531 (1962).
57. E.M.Beale and J.Roy, Stat.Soc., Ser.B, 22, 41 (1960).
58. T.Hsiang and P.M.Reilly, Canad.J.Chem.Eng., **49**, 865 (1971).
59. L.H.Hosten, "Proc.4-th Internat.Symp.on Chemical Reaction Engineering, Heidelberg, 1976".
60. G.E.P.Box and W.J.Hill, Technometrics, **9**, 57 (1967).
61. V.V.Nalimov and G.I.Golikova, "Logicheskie Osnovaniya Planirovaniya Eksperimenta" (Logical Principles of Experimental Design), Izd.Metallurgiya, Moscow, 1976.
62. V.V.Fedorov, "Teoriya Optimal'nogo Eksperimenta" (Theory of The Optimum Experiment), Izd.Nauka, Moscow, 1972.
63. V.G.Gorskii, Symposium, "Voprosy Kibernetiki" (Problems of Cybernetics), Izd.VINITI, Moscow, 1972, p.103.
64. A.I.Kuz'michev, R.F.Merzhanova, L.A.Mascheva, T.B.Zhukova, V.N.Pisarenko, V.V.Kafarov, and N.F.Kononov, Zavod.Lab., 41, 1235 (1975).
65. V.V.Kafarov, B.S.Mortikov, V.N.Pisarenko, and Kh.M.Minachev, "Sbornik Vsesoyuznoi Konferentsii po Mekhanizmu Geterogenno-Katalicheskikh Reaktsii" (Collected Reports at the All-Union Conference on the Mechanisms of Heterogeneous-Catalytic Reactions), Izd.Kartolitografiya, Moscow, 1974, Preprint 48.
66. H.Chernoff, Annalen Math.Stat., **30**, 755 (1959).
67. B.M.Borth, Ph.D.Thesis, University of Waterloo, 1972.
68. D.Meeter , W.Piril, and W.Blot, Technometrics, **12**, 307 (1965).
69. V.V.Nalimov, Zavod.Lab.,No.3, 325 (1978).
70. J.D.Shaw, T.W.Hoffman, and P.M.Reilly, C.E.P. Symp.Ser., **40**, 118 (1974).
71. R.Mezaki and J.Happel, Catalysis Rev., **3**, 241 (1969).
72. L.H.Hosten, G.F.Froment, Ind.Eng.Chem.Proc. Des.Dev., **10**, 280 (1971).
73. V.V.Zinov'ev, V.I.Timoshchenko, E.G.Malygin, M.G.Slin'ko, and D.G.Knorre, Mol.Biol., 7, 82 (1973).
74. V.N.Bibin and B.I.Popov, "Sbornik Vsesoyuznoi Konferentsii po Kinetike Kataliticheskie Reaktsii" (Collected Reports at the All-Union Conference on the Kinetics of Catalytic Reactions), 1975, Vol.2, p.184.

75. H.Nagao, J.Sci.Horoshima Univ,SerA-1, **34**, 153 (1970).
76. N.Sigiura and H.Nagao, Annalen Math.Stat., **39**, 1686 (1968).
77. G.F.Froment and R.Mezeki, Chem.Eng.Sci., **25**, 293 (19709.
78. P.P.Sane, J.M.Woods, and R.E.Eckert, Chem.Eng. Sci., **28**, 1609 (1973).
79. D.J.Pritchard and D.W.Bacon, Canad.J.Chem. Eng., **52**, 103 (1974).
80. R.Bajramovic and P.M.Reilly, Canad.J.Chem.Eng., **55**, 82 (1977).

Mendeleev Moscow Institute of
Chemical Engineering

Translated from *Uspekhi Khimii*, 49, 223-251 (1980) U.D.C. 541.49

The Basicity of Transition Metal Complexes in Reactions with Aprotic Acids

B.V.Lokshin, A.G.Ginzburg, and E.B.Nazarova

Data for the interaction of transition metal complexes (TMC) with aprotic acids, in which the TMC play the role of bases, are examined and reactions, in which the centre of the basicity of the TMC is the transition metal atom, and the ligands are discussed. The influence on the basicity of the central atom of its position in the Periodic System and of its ligand environment as well as the influence of the structure of the complex and the nature of the aprotic acid and the medium on the formation of donor-acceptor complexes between TMC and electron acceptors are considered. A systematic account is given of data for the interaction of TMC with various classes of acceptors: metal and non-metal halides, halogens, alkyl halides, metal cations, π-acids, and one-electron oxidants.
The bibliography includes 136 references.

CONTENTS

I. Introduction 115
II. Interaction via the metal atom 116
III. Interaction of Lewis acids with transition metal complexes via the ligands 118
IV. Competitive coordination 119
V. Reactions of transition metal complexes with acceptors of different types 120
VI. Conclusion 127

I. INTRODUCTION

It is well known that many transition metal complexes (TMC) have nucleophilic properties and can play the role of bases in an acid–base interaction. The metal in such complexes is in a low oxidation state and can be attacked by various electrophiles. The basic properties of TMC were demonstrated for the first time in 1955 when the reversible protonation of π-complexes at the transition metal atom was discovered[1]. Studies in this field subsequently developed greatly and the infrared spectroscopic and NMR methods played a decisive role in the study of protonation[2-6].

The study of protonation yielded important data on the basicity of the metal atom and complexes, since the basicity of the central metal atom can be inferred qualitatively from the ease of protonation. In particular, a relation has been established between the ease of protonation and the position of the metal in the Periodic System. In series of isostructural compounds with the same ligands, differing only in the central transition metal atom, the basicity of the latter increases with increase of its atomic number within the limits of a single Group. In this sense, transition metal compounds differ sharply from bases containing elements of the main groups of the Periodic System, whose basicity diminishes on passing to heavier atoms within the limits of the same Group. The reason for this is in the difference between the properties of the orbitals involved in the formation of the donor–acceptor bonds. For main Group elements, the lone pair of n electrons of the sp^2- or sp^3-hybridised heteroatoms is involved in the interaction, i.e. the corresponding compounds are n-bases. For TMC, the highest occupied molecular orbital is a virtually pure d orbital of the metal and is occupied by d electrons, i.e. these complexes behave as d-bases.

The basic properties of TMC are shown not only in protonation reactions but also in reactions with many aprotic acids. The basicity of TMC can be shown in two aspects of their reactivity: (a) the interaction with an acceptor suitable as regards the symmetry and energy of the vacant orbital, leading to the formation of a new donor–acceptor chemical bond; (b) oxidation of the TMC involving the abstraction of one electron from the highest occupied molecular orbital without the formation of a new chemical bond. Such oxidation can proceed both chemically under the influence of a suitable oxidant (Ag^+, NO^+) and electrochemically. The study of these reactions greatly extends the scope of research into the basicity of TMC. These data are also important for the understanding of the mechanisms of many reactions of TMC, for example, reactions in the presence of Lewis acids and oxidative addition reactions.

In the present review an attempt is made to achieve a systematic arrangement of the extensive experimental data, which are available for the interaction with aprotic acids, from the standpoint of the basicity of the TMC. In this case we understand by basicity the ability of the TMC to form donor–acceptor (D–A) complexes (adducts) with electron acceptors involving an increase of the coordination number (C.N.) of the donor atoms. The possibility of the formation of an adduct depends not only on the properties of the donor molecules but also on the type of acceptor used. The strength of the D–A bond is determined by the relative energies and symmetries of the D and A orbitals involved in the formation of the bond and also by steric factors. The properties of the same TMC as a base can therefore be different in relation to different acceptors. The interactions of TMC with the following classes of electron acceptors have been considered: aprotic acids—metal and non-metal halides; halogens and alkyl halides; metal cations; π-acids; one-electron oxidants.

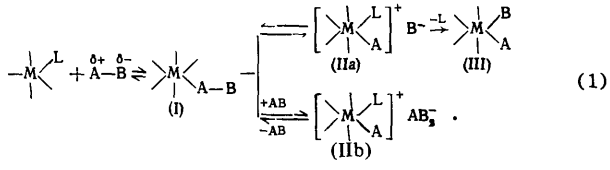
There are several possible basicity centres in the molecules of the TMC considered to which attack by the electrophile can be directed: the central metal atom, the O, S, or N atoms or ligands such as CO, CS, NO, N_2 or CN, halogen ligands, and finally π-ligands. It is shown below that the reactions with aprotic acids can lead to the formation of adducts not only via the metal atom but also via the ligand and that, depending on the type of complex, the aprotic acid, and the reaction conditions, the complexes can behave as d-bases, n-bases, or π-bases. Sometimes these possibilities are realised simultaneously.

A number of reviews devoted to the basicity of transition metal complexes have already been published, but some of these[6,7] cover only the literature up to 1970 and one[8] is concerned mainly with the basicity of carbonyl ligands and is incomplete.

Reactions via the central metal atom and via the ligand will be considered separately below.

II. INTERACTION VIA THE METAL ATOM

For five-ccordinate and six-coordinate complexes, the reactions via the metal atom can be represented by the following mechanism, where A–B is a conventional representation of a molecule of the Lewis acid:



(1)

The electron acceptor can add to the metal to give a neutral adduct (I), which can then be converted into an ionic compound (IIa) or (IIb) with dissociation of the A–B bond. The latter compounds should be electrically conducting in solutions. However, in the majority of cases the structure of the adduct cannot be establsihed exactly in solution, since conductimetric data are not always reliable or are not available. Owing to the reversibility of the formation reactions of compounds (I) and (II), an equilibrium is established in the solution as a result of which the observed conductivities can be low.

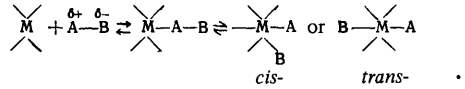
Adducts with two or several molecules of the Lewis acid frequently contain involved complex anions (for example, $SnCl_5^-$, $HgCl_3^-$, $Hg_2Cl_5^-$, etc.). The structure of the adduct in solution and in the crystal can be various. Thus polar solvents promote the conversion of adducts of type (I) into compounds of type (II).

The structure of complexes with Lewis acids has not always been established with sufficient reliability. For solid adducts, X-ray diffraction data are available in many instances, but the evidence for the structure has usually been reached solely on the basis of spectroscopic data. The equilibrium between the adduct and the initial compounds in solutions has been studied even less. The equilibrium position can be inferred, at least qualitatively, from such data for the relative basicities of the complexes. In other cases, the relative basicities of series of complexes can be established in accordance with the occurrence or non-occurrence of an interaction with a standard Lewis acid under identical conditions.

In the absence of structural data, the main criterion of the formation of adducts via the metal is provided by spectroscopic measurements. Complexes containing the CO ligand have been most widely investigated, because the CO stretching vibration frequencies are extremely sensitive to changes in the formal oxidation state of the metal. The interaction of the acceptor molecule with the central metal atom leads to an increase of the stretching vibration frequencies of the CO groups, which is associated with the decrease of the electron density at the metal atom and this entails a weakening of the $d_\pi(M) \rightarrow p_{\pi^*}(CO)$ dative bonds and an increase of the CO bond orders in the complex $\overline{M}-C\equiv\overset{+}{O}\leftrightarrows M=C=\ddot{O}:$. As in protonation involving the metal atom, such a frequency shift is believed to be a characteristic feature of the involvement of the metal atom in coordination to the Lewis acid. As will be shown below, other types of coordination of the acceptor lead to quite different changes in the spectra. It is not always possible to state with confidence which type of adduct has been obtained—(I) or (II). It is usually assumed that, in the formation of type (II) adducts, the formal positive charge on the metal atom increases by unity and the CO frequency shift should be the same as in protonation (100–150 cm^{-1}).

The electron density on the metal atom in adduct (I) should also be reduced but to a smaller extent; consequently the observed hypsochromic shift should be smaller. For example, complexes of the type $L_2Fe(CO)_2$ form 1:1 or 1:2 adducts with $HgCl_2$. The ν(CO) frequency shift is 70–80 cm^{-1} for the first type and 100–120 cm^{-1} for the second. Accordingly, the structures $L_2(CO)_3Fe \rightarrow HgCl_2$ and $[L_2(CO)_3FeHgCl]^+HgCl_3^-$ have been attributed to these adducts[9], which has been confirmed by conductimetric measurements.

The final product (III) of reaction (1) is formed by the elimination of a neutral ligand molecule, usually CO (the so-called oxidative elimination). This stage of the reaction is irreversible. In the present review reactions of this type will not be considered in detail (see the previous reviews[10,11]). In the case of tetracoordinate complexes reactions can proceed without the elimination of ligands, involving an expansion of the coordination sphere and an increase of the coordination number by two (oxidative addition reactions):



(2)

We may note that the basicity of the central metal atom is one of the main factors which determine the course of such reactions. This can be seen from the following reaction as an example[12]:

$$(bipy)M(CO)_4 + 2HgCl_2 \rightleftharpoons (bipy)M(CO)_4 \cdot 2HgCl_2 \xrightarrow{-CO} (bipy)M(CO)_3Cl(HgCl) + HgCl_2$$

(M = Mo or W; bipy = 2,2'-bipyridyl).

For M = W, it is possible to isolate an unstable intermediate adduct $(bipy)W(CO)_4.2HgX_2$ (X = Cl or Br), which rapidly evolves CO and gives rise to the stable tricarbonyl derivative $(bipy)W(CO)_3X(HgX)$. For the corresponding molybdenum complex, the intermediate adduct is so unstable that one obtains immediately the tricarbonyl derivative $(bipy)Mo(CO)_3X(HgX)$. The reaction with $SnCl_4$ yields in both cases the oxidative addition product $(bipy)M(CO)_3.Cl(SnCl_3)$, where M = Mo or W.[12,13]

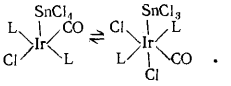
The interaction of phosphine derivatives $(diphos)M(CO)_4$ (diphos = $Ph_2PCH_2CH_2PPh_2$) with $HgCl_2$ proceeds without the evolution of CO and the adducts $(diphos)M(CO)_4.HgCl_2$ are formed[12]. The infrared spectra of these adducts in solution contain the ν(CO) bands of the initial complexes and in addition higher-frequency bands, corresponding to an increase of the oxidation state of the metal atom, appear, i.e. the adducts are in equilibrium with the initial substances in solution. The conductances Λ_M of solutions of the adducts in acetonitrile are low, but the addition of an excess of $HgCl_2$ lowers the degree of dissociation of the adduct and increases Λ_M. On this basis, it is postulated that the adducts have the structure $[(diphos)M(CO)_4.HgCl]^+Cl^-$.

It is seen from the examples presented that, depending on the nature of the reactants, reaction (1) can give rise to different products.

The interaction with aprotic acids is extremely characteristic of square planar rhodium and iridium complexes. Here there is a possibility of a donor–acceptor adduct (C.N. = 5

for M) or of oxidative addition (C,N. = 6).[6,14] For example, *trans*-$L_2Ir(CO)Cl$ ($L = PPh_3$) reacts with HgX_2 to give the oxidative addition products $L_2(CO)ClIr\begin{matrix}\nearrow X\\ \searrow HgX\end{matrix}$.[15] The same complex forms 1:1 and 1:2 adducts with BF_3 in solution. The 1:1 adduct[16] is a simple adduct with an Ir–B donor-acceptor bond whose (CO) frequency has been increased by 100 cm^{-1} compared with the carbonyl frequency of the initial complex. For the 1:2 adduct, ν(CO) does not differ appreciably from the value for the 1:1 adduct. The structure of the 1:2 adduct is obscure. It has been suggested that its second BF_3 molecule is not linked to the Ir atom but is connected to the first BF_3 group via a bridge of fluorine atoms[5].

The reaction of *trans*-$L_2Ir(CO)Cl$ with $SnCl_4$, leading to the formation of $L_2(CO)ClIr.SnCl_4$, is extremely interesting[17]. The resulting complex is monomeric and non-conducting. The infrared spectrum shows two bands in the carbonyl region, at 2080 and 2020 cm^{-1} in the solid state and at 2080 and 2041 cm^{-1} in chloroform. The presence of the two ν(CO) bands can be explained by the presence of isomers which undergo a rapid interconversion:



This is an unusual type of isomerism involving a change in the formal oxidation state of the central metal atom. The higher-frequency band corresponds to the oxidative addition product and the lower-frequency band is associated with the donor–acceptor adduct.

Thus the acid–base interaction of the metal atom in the complex L_nM with the aprotic acid AB can lead to several types of compounds: neutral adducts $L_nM \rightarrow AB$ and salt-like compounds $[L_nM-A]^+B^-$ or $[L_nM-A]^+AB_2^-$. The mode of reaction depends on a number of factors: the nature of the metal, the nature of the ligands surrounding it, the type of Lewis acid, and the solvent. Although the available data are non-systematic, they nevertheless make it possible to trace a number of regularities.

1. The Influence of the Nature of the Central Metal Atom

The dependence of the basicity of the complex on the nature of the central metal atom can be established by comparing the behaviour of complexes differing solely by the central atom in reactions with the same electron acceptor.

It was already noted above that, on treatment with BF_3, the complex $L_2Ir(CO)Cl$ ($L = PPh_3$) forms adducts via the metal atom, which contain the $Ir \rightarrow B$ bond.[16] The analogous rhodium complex $L_2Rh(CO)Cl$ does not form adducts with BF_3, which leads to the conclusion that the Ir atom is more basic than the Rh atom. In contrast to the rhodium complex, the iridium complex is also capable of forming a compound with O_2.[14] Thus, atoms with a higher atomic number proved to be more basic in the given Group of the Periodic System. This behaviour, which agrees with that found in the study of protonation[3–5,18–21], is extremely general; it holds also in other Groups of the Periodic System.

Thus cyclopentadienyltricarbonylmanganese $CpMn(CO)_3$ (CTM) does not interact with $TiCl_4$, while the addition of $TiCl_4$ to the corresponding rhenium complex $CpRe(CO)_3$ (CTR) in CH_2Cl_2 gives rise to a spectrum, where, apart from the ν(CO) bands of the initial substance, there are also bands of the adducts displaced towards higher wavenumbers by more than 100 cm^{-1},[22] which is characteristic of adducts formed via the metal atom.

After the addition of an excess of $SnCl_4$ in CH_2Cl_2, the infrared spectrum of the phosphite derivative of CTM, i.e. $CpMn(CO)_2P(OPh)_3$, contains the ν(CO) frequencies of both the initial complex and the adduct[23]. For $CpRe(CO)_2P(OPh)_3$ under the same conditions, the equilibrium is almost wholly displaced towards the formation of the adduct[22]. These data indicate more pronounced basic properties of rhenium compared with manganese.

The arene complexes of Group VI transition metals behave similarly. Thus $MsCr(CO)_3$ (Ms = mesitylene) is in equilibrium with the addition product in CH_2Cl_2 in the presence of an excess of $SnCl_4$. The equilibrium involving the corresponding Mo and W compounds is wholly displaced towards the adduct. Analysis of the available data shows[22] that the basicity of the metal increases in the sequence Cr < Mo < W. An analogous conclusion was reached for the triad Co < Rh < Ir.[14,24]

2. The Influence of the Ligand Environment on the Basicity of the Metal in the Complex

The basicity of the transition metal atom in the complex depends very markedly on the nature of the surrounding ligands. The replacement of ligands by species with more marked electron-donating properties, for example, tertiary phosphines, leads to an increase of basicity and, conversely, the introduction of electron-accepting ligands suppresses basicity.

CTM does not interact with $SnCl_4$ in solutions[23], but the addition of five electron-donating ethyl groups in the Cp ring enables the complex $(Et_5C_5)Mn(CO)_3$ to form an adduct with $SnCl_4$ in solution, although the equilibrium is in this case displaced towards the formation of the initial substances. The replacement of one CO group by a phosphine ligand PR_3, with more pronounced electron-donating properties, increases the basicity of the Mn atom to an even greater extent. The basicity then depends on the electron-donating properties of the group R in the ligand PR_3, increasing sharply in the sequence OPh ≪ Ph < alkyl. Like CTM, CTR does not interact with $SnCl_4$, but the replacement of CO by PR_3 sharply increases the basicity and makes the complex capable of forming adducts; the reaction proceeds readily in solution and goes almost to completion[22].

The complex $MsCr(CO)_3$ (Ms = mesitylene) is in equilibrium with the adduct molecules in the presence of an excess of $SnCl_4$. The phosphine derivative $MsCr(CO)_2PPh_3$ is almost completely converted into an adduct in the presence of an excess of $SnCl_4$.[22]

The substitution of two CO groups in $CpMn(CO)_3$ by two phosphine ligands is accompanied by an even greater increase of the basicity of the manganese atom. Diphosphine complexes of the type $CpMn(CO)L_2$ [$L_2 = (PPh_3)_2$ or the bidentate diphosphines $Ph_2P(CH_2)_nPPh_2$ ($n = 1–3$)] react in solution not only with $SnCl_4$ but also with weaker aprotic acids $SbCl_3$, $HgCl_2$, and $GeCl_4$.[23] In all cases the single ν(CO) frequency then increases by 100–110 cm^{-1} and, depending on the ratio of the amounts of the initial reactants, the spectrum contains the bands of both forms or only of the adducts. In the presence of an excess of $SnCl_4$, $SbCl_3$, or $HgCl_2$ only the bands of the adducts were observed in the infrared spectrum of the solution. For $GeCl_4$, both bands were observed even when the compound was present in a large excess in solution, and their intensity ratio indicates a shift of the equilibrium towards the initial compound.

3. Dependence of the Nature of the Interaction on the Aprotic Acid

The mode of reaction of TMC in many respects depends on the type of acceptor molecule. Certain Lewis acids are capable of interacting with complexes not only via the metal atom but also via the ligands. These instances will be examined separately below. This section deals solely with interactions via the metal.

The higher the basicity of the metal atom in the complex, the greater the range of aprotic acids with which it can interact. Thus $(Ph_3P)_2Rh(CO)Cl$ does not interact with BF_3 but does so with BCl_3 and BBr_3, the adduct with BBr_3 being most stable[25,26], which agrees with the usual sequence based on the variation of the Lewis acidity: $BF_3 < BCl_3 < BBr_3$.[27] The complex $CpMn(CO)_2PPh_3$ forms adducts with $SnCl_4$, but does not react with the weaker aprotic acids $GeCl_4$ and $SbCl_3$. The complexes $CpMn(CO)L_2$, where $L_2 = (Ph_3P)_2$ or bidentate diphosphine ligands, form adducts with weak Lewis acids, and the latter can be arranged in the following sequence in terms of the ease of interaction: $SnCl_4 \gg SbCl_3 \cong HgCl_2 > GeCl_4$.[23] The sequence $TiCl_4 > SnCl_4 > SnBr_4$ has been established for $CpRe(CO)_2L$.[22]

$AlCl_3$, which is capable of forming adducts via both the metal and the ligands (see below), occupies a special place among Lewis acids.

III. INTERACTION OF LEWIS ACIDS WITH TRANSITION METAL COMPLEXES VIA THE LIGANDS

Another type of interaction of Lewis acids with TMC involves the formation of adducts with participation of the lone electron pair of one of the ligand atoms. This can be the oxygen atom in the CO and NO groups, the sulphur atom in CS, the nitrogen atom in the N_2 and CN ligands, and a halogen atom.

For complexes containing halogen or nitrile ligands at the transition metal atom, the reaction with Lewis acids proceeds as a rule via an *n*-electron pair of the ligand. If the complex contains, together with halogen or nitrile ligands, carbonyl or nitrosyl ligands, then the shift of the vibration frequencies of the latter can be a sign of the formation of donor–acceptor adducts. The coordination of Lewis acids (A) to halogen or nitrile ligands (X) $(O\equiv C-\overset{\frown}{M}-\overset{\curvearrowright}{X}: \rightarrow A)$ leads to a slight increase of the ν(CO) or ν(NO) frequency—by 15–25 cm^{-1}. Such interaction entails a weakening of the M–CO dative bonds and correspondingly, within the framework of the mechanism $M^- - C\equiv O^+ \leftrightarrow M=C=O$, an increase of the CO bond orders. However, this influence of the acceptor is significantly weaker than in the direct interaction with the metal atom: $O\equiv C-\overset{\frown}{M}\rightarrow A$ [$\Delta\nu$(CO) ≅ 100–150 cm^{-1}. As an example[28] one can quote the ν(CO) frequencies (cm^{-1}) in the spectra of the complexes $CpRe(CO)_2Br_2$ (2005, 2068), $CpRe(CO)_2Br(Br \rightarrow AlCl_3)$ (2022, 2083), and $CpRe(CO)_2 .Br(Br \rightarrow AlCl_3)$ (2022, 2083), and $CpRe(CO)_2(Br \rightarrow AlCl_3)_2$ (2031, 2096).

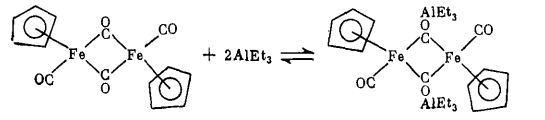
The donor–acceptor interaction of Lewis acids with the CN group leads to an increase of the stretching vibration frequency of the latter. The CN group behaves analogously in any nitrile and not only in transition metal complexes. It is believed that the increase of the ν(CN) frequency on coordination is associated with the increase of the force constant of the CN bond and with the change in the mechanism of the vibrations of the molecule when it is bound in a complex[29–31].

When the complex $CpFe(CO)_2(CN)$ is coordinated to Lewis acids ER_3 (E = Al or Ga; R = Me or Cl) or BX_3 (X = H, F, Cl, Br, or Me), the stretching vibration frequencies of all three groups (two CO groups and one CN group) increase[32]. The frequency shifts (Table 1) lead to the conclusion that the acceptor is coordinated to the CN group.

Table 1. The stretching vibration frequencies of the CN and CO groups in the adducts of $CpFe(CO)_2(CN)$ with Lewis acids.

Complex	ν_{CN}, cm^{-1}	ν_{CO}, cm^{-1}
$CpFe(CO)_2(CN)$	2120	2055 2007
$CpFe(CO)_2(CN\rightarrow AlCl_3)$	2168	2068 2026
$CpFe(CO)_2(CN\rightarrow BF_3)$	2201	2073 2031

The interaction of the complex with the carbonyl ligand is characteristic of the strongest Lewis acids—boron and aluminium derivatives. The possibility of the addition of a Lewis acid to the oxygen atom of the carbonyl ligand in the complex was first observed for bridging CO groups in the dimeric complex $[CpFe(CO)_2]_2$, which forms an adduct with two $AlEt_3$ molecules[33,34]:



The structure of the adduct was established by X-ray diffraction[33]. Its formation leads to an appreciable decrease of the ν(CO) frequencies of the bridging groups involved in the interaction with aluminium and to an increase of the stretching vibration frequencies of the terminal carbonyl ligands. The decrease of the stretching vibration frequencies of the CO groups linked to aluminium is caused by the weakening of the CO bonds owing to the shift of electron density towards the acceptor molecule. This entails a strengthening of the $M \rightarrow C$ dative bonds in the $MCO \rightarrow Al$ fragments and their weakening for the CO groups not coordinated to aluminium, which leads in its turn to an increase of the terminal CO bond orders and an increase of their vibration frequencies.

The study of the interaction of complexes containing both bridging and terminal CO groups with Lewis acids derived from aluminium showed that the bridging carbonyl groups are more basic and that the basicity of the oxygen atom in the CO groups increases in the following sequence: terminal groups < double bridge groups < triple bridge groups[8]. The difference between the basicity of the bridging and terminal CO groups can be used to displace the equilibrium and to convert terminal groups into bridging groups, for example[35,36]:

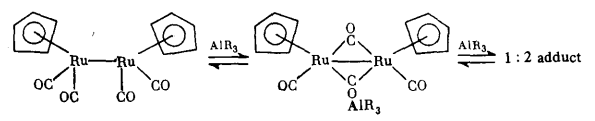
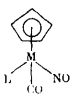
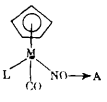
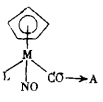
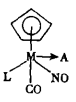
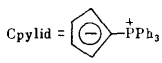


Table 2. The stretching vibration frequencies of the CO and NO groups (cm^{-1}, in CH_2Cl_2) of the complexes $CpM(CO)_2NO$ and $CpM(CO)(NO)PPh_3$ (M = Mo or W) and their adducts with Lewis acids[22].

Complex								
	ν(NO)	ν(CO)	ν(NO)	ν(CO)	ν(NO)	ν(CO)	ν(NO)	ν(CO)
$CpMo(CO)_2NO$	1670 s.	1942 s. 2021 s.	—	—	—	—	—	—
$CpMo(CO)_2NO+SnCl_4$	1670 s.	1945 s. 2020 s.	—	—	—	—	—	—
$CpMo(CO)_2NO+TiCl_4$	1666 s.	1941 s. 2020 s.	1486 m.	2003 sh. 2065 m.	—	—	—	—
$CpMo(CO)_2NO+AlCl_3$	1670 s.	1950 s. 2025 v.s.	1450 s.	2025 v.s. 2087 v.s.	1710 m.	1735 sh. 2065 m.		
$CpW(CO)_2NO$	1660 s.	1929 s. 2011 s.	—	—	—	—	—	—
$CpW(CO)_2NO+SnCl_4$	1658 s.	1929 s. 2011 v.s.	1481 m.	1981 m. 2051 m	—	—	—	—
$CpW(CO)_2NO+AlCl_3$	1655 s.	1930 s. 2010 v.s.	1450 s.	2010 v.s. 2055 s.	—	—	—	—
$CpMo(CO)(NO)PPh_3$	1606 s.	1941 s.	—	—	—	—	—	—
$CpMo(CO)(NO)PPh_3+SnCl_4$	—		—	—	—	—	1747 s.	2070 s.
$CpMo(CO)(NO)PPh_3+AlCl_3$	—		1390 s.	1991 s.	—	—	1722 s.	2070 s.
$CpW(CO)(NO)PPh_3$	1595 s.	1900 s.	—	—	—	—	—	—
$CpW(CO)(NO)PPh_3+SnCl_4$	—	—	—	—	—	—	1740 s.	2050 s.
$CpW(CO)(NO)PPh_3+AlCl_3$	1590 m.	1900 m.	1400 s.	1975 s.	—	—	1713 m.	2070 m.

Note. v.s = very strong (intense), s = strong, m = medium, and sh = shoulder.

Interaction with CO, N_2, and NO terminal ligands leads, as for the coordination with bridging CO groups, to a significant decrease of the stretching vibration frequency of the coordinated group and to an increase of the stretching vibration frequencies of ligands not linked to the aprotic acid. For example[37], the ν(CO) frequencies are 1904, 1808, and 1791 cm^{-1} for $CpylidMo(CO)_3$ and 1932, 1845, and 1665 cm^{-1} for $CpylidMo(CO)_2(CO \rightarrow AlMe_3)$:



The same transition metal complexes with different Lewis acids can react in different ways—either via the metal atom or via the ligands (CO, NO). For example, $CpylidMo(CO)_3$ interacts with H^+, BF_3, $TiCl_4$, and $AlCl_3$ via the Mo atom and with $AlMe_3$ via the CO group[19,22,37].

The simultaneous formation in solution of adducts both via the metal atom and via the terminal CO or NO groups has been observed in some cases. Section IV deals in detail with factors influencing the mode of reaction in competitive coordination.

IV. COMPETITIVE COORDINATION

As shown above, transition metal complexes can react with aprotic acids to form adducts via both the metal and via the ligands. The mode of reaction depends on the relative basicities of the metal atom and the lone electron pairs of the ligands and on the nature of the acceptor and the solvent. Depending on these factors, the same complex can interact differently with different Lewis acids and sometimes there is a possibility of the simultaneous formation of adducts of different types.

This is clearly seen from the example of the complexes $CpM(CO)_2(NO)$ and $CpM(CO)(NO)(PPh_3)$ (M = Mo or W).[22] They are capable of forming three different types of adducts: via the metal and via the oxygen atoms of the carbonyl or nitrosyl ligand. The most basic centre in the $CpM(CO)_2(NO)$ molecule is the nitrosyl oxygen atom. Thus the formation of adducts via the NO groups with complexes of the type Cp_3Ln, where Ln = lanthanide, has been described[38]. $TiCl_4$ and $SnCl_4$, which usually interact with *d*-bases and are coordinated to the metal atom, in this case also interact with the oxygen atom of the NO group[22]. Under these conditions, $SnCl_4$ does not interact with $CpMo(CO)_2(NO)$, but forms an adduct with $CpW(CO)_2(NO)$. The higher basicity of the nitrosyl oxygen atom in the tungsten derivative compared with the molybdenum compound is caused by the more marked shift of electron density from the W atom ($d_\pi - p_\pi$ interaction); an analogous conclusion follows from spectroscopic data[39].

The phosphine derivatives $CpM(CO)(NO)(PPh_3)$, in which the basicity of the M atom is greatly enhanced, form adducts with $SnCl_4$ via the metal atom. The differences between the reactions can be clearly followed on the basis of the infrared spectra. In the adducts via the NO group the ν(NO) frequencies are reduced by more than 200 cm^{-1} compared with the initial comlexes, while the ν(CO) frequencies are increased by 40–70 cm^{-1}. In the adducts formed via the metal atom, both ν(CO) and ν(NO) are displaced towards higher frequencies by ~150 cm^{-1} (Table 2). The increase of the basicity of the central atom after the introduction of the phosphine ligand makes complex formation via the metal atom energetically more favourable than coordination via the nitrosyl group.

The complex $CpW(CO)_2(NO)$ forms an adduct with $AlCl_3$ in CH_2Cl_2 via the oxygen atom of the NO ligand. The behaviour of the molybdenum compound $CpMo(CO)_2(NO)$ in relation to $AlCl_3$ is interesting. The somewhat reduced basicity of the nitrosyl oxygen atom, compared with the corresponding tungsten complex, leads to competition between the oxygen atoms of the carbonyl and nitrosyl groups, although here coordination via the nitrosyl group predominates (Table 1).

In the triphenylphosphine derivatives $CpM(CO)(NO)(PPh_3)$ (M = Mo or W) the basicity of the metal atom is increased, which leads to competition between the metal and the nitrosyl

oxygen atom in the reaction with $AlCl_3$. The tungsten complex forms adducts via both the nitrosyl group and the metal atom. Whereas coordination to the metal only is observed in the interaction with $SnCl_4$, in the interaction with $AlCl_3$ the formation of an adduct via the oxygen atom of the nitrosyl group predominates, which is indicated by the ratio of the intensities of the corresponding infrared bands (Table 2). The situation is similar for the molybdenum complex, but the content of the adduct formed via the metal atom is increased relative to the tungsten complex, which may be associated with a somewhat lower basicity of the nitrosyl oxygen atom in the molybdenum derivative.

Thus, depending on the relative basicities of the metal and the carbonyl and nitrosyl oxygen atom and also on the nature of the acceptor, there is a possibility of donor–acceptor interactions of different types for carbonyl nitrosyl complexes: with participation of the transition metal atom as the centre of basicity, with participation of the oxygen atom of the carbonyl or nitrosyl ligand, or with the simultaneous formation of both types of adducts.

The influence of the solvent on the nature of the donor–acceptor interaction has been observed in the study of the reaction of $CpMn(CO)_3$ with $AlCl_3$.[28] It has been shown by infrared spectroscopy that in benzene the Lewis acid is coordinated to the carbonyl group, while in CH_2Cl_2 an adduct is formed via the metal atom, i.e. $Cp(CO)_3Mn \rightarrow AlCl_3$, in addition to the adduct $CpMn(CO)_2.(CO \rightarrow AlCl_3)$. The introduction of donor ligands facilitates the interaction via the metal. In benzene the complex $CpMn(CO)_2(PPh)_3$ gives rise to a mixture of adducts via the oxygen atom of the CO group and via the manganese atom; in CH_2Cl_2 the formation of an adduct via the metal atom only was observed. Other complexes behave analogously in their reactions with $AlCl_3$ (see below). Examples of different types of reactions as a function of the acceptor are presented in Table 3.

Table 3. Dependence of the mode of coordination of the Lewis acid to the transition metal complex on the nature of the acid.

Transition metal complex base	Acceptor	
	bond with M atom	bond with ligand*
$(Ph_3P^+—C_5H_4^-)Mo(CO)_3$	H^+, BF_3, $TiCl_4$, $AlCl_3$	$AlMe_3$
$CpW(CO)_3^-$	H^+, $InPh_3$	$AlPh_3$, $MgPy_4^{2+}$, $Al(THF)_3^{3+}$
$CpM(CO)(NO)(PPh_3)$ (M = Mo, W)	$SnCl_4$, $AlCl_3$	$AlCl_3$
$CpRe(CO)_3$	$TiCl_4$, $AlCl_3$	$AlCl_3$
Arene $M(CO)_3$ (M = Cr, Mo, W)	H^+, $HgCl_2$, $TiCl_4$, $SnCl_4$, $AlCl_3$	$AlCl_3$
$[CpFe(CO)_2]_2$	H^+	AlR_3, BCl_3, BBr_3

*Py = pyridine.

On the other hand, the same Lewis acid can interact in different ways with the complex depending on its structure. Thus $SnCl_4$ is coordinated via the metal atom to the complexes $AreneM(CO)_3$† (M = Cr, Mo, or W), $CpM(CO)(NO)PPh_3$ (M = Mo or W), $CpM(CO)_2L$ (M = Mn or Re; L = PR_3), *trans*-$IrCl(CO)(PPh_3)_2$, and Cp_2Ru. However, one should note that the coordination of $CpW(CO)_2(NO)$ involves the nitrosyl oxygen atom and that of $CpCr(NO)_2Cl$ involves the chlorine atom. Compounds of the type AlR_3 form adducts via the metal atom with the complexes $CpM(CO)_nL_{3-n}$ (M = Mn, $n = 1–3$; M = Re, $n = 2, 3$; L = PR_3), $AreneM(CO)_3$ (M = Cr, Mo, or W), $(C_6H_6)Cr(CO)_2PPh_3$, $CpM(CO)_4$ (M = V or Nb), $CpV(CO)_3PPh_3$, $Fe(CO)_n(PPh_3)_{5-n}$ ($n = 3, 4$), CpReH, and Cp_2WH. In the case of $[CpFe(CO)_2]_2$ and a number of other complexes with bridging carbonyl ligands the coordination involves the oxygen atom of the bridging CO groups. The compounds $CpM(CO)_3$ (M = Mn or Re), $CpMn(CO)_2PPh_3$, $AreneM(CO)_3$ (M = Cr, Mo, or W), $CpV(CO)_n(PPh_3)_{4-n}$ ($n = 3, 4$), and $Mo(phen)(PPh_3)_2(CO)_2$ react with AlR_3 via the terminal CO groups, $CpM(CO)_n.(NO)L_{2-n}$ (M = Mo or W; $n = 1, 2$) are coordinated via the oxygen of the NO ligand, $CpRe(CO)_2Br_2$ and $CpCr(NO)_2Cl$ are coordinated via the halogen atom, and $CpFe(CO)_2CN$ is coordinated via the nitrogen atom of the cyano-group.

†Here and henceforth Arene = η^6-C_6H_6 and its homologues (mesitylene and hexamethylbenzene).

V. REACTIONS OF TRANSITION METAL COMPLEXES WITH ACCEPTORS OF DIFFERENT TYPES

1. Reactions with Derivatives of Group I–V Elements

(*a*) *Derivatives of Group I elements (Cu and Ag) as acceptors.* There are few examples of the interaction of TMC with acceptors derived from Group I elements. Thus $(diphos)_2.W(CO)(CS)$ reacts with $AgBF_4$ to form the product $\{[(diphos)_2W(CO)CS]_2Ag\}^+BF_4^-$, in which the acceptor is coordinated to the S atom of the CS ligand[40]. The compound $CpCoL_2$ interacts with $[L_2CuCl]_2$ via the metal atom, forming $CpL_2Co \rightarrow CuL_2Cl$ (L = PMe_3).[41]

(*b*) *Group II metal (Zn and Hg) halides.* Data for the interaction of EX_2 (E = Zn or Hg; X = halogen) with different complexes are presented in Table 4. There are no examples of coordination via the lone electron pairs of ligands such as CO, NO, N_2, CN or halogen for mercury or zinc derivatives, but coordination of HgX_2 to the sulphur atom of the CS ligand is known[40].

The Lewis acids HgX_2 are capable of forming adducts of different compositions (ranging from 1:1 to 1:7), and this behaviour is in fact extremely characteristic of these compounds. As mentioned above, 1:1 adducts can be either donor–acceptor complexes with $M \rightarrow HgX_2$ linkages or salts $[M–HgX]^+X^-$. In the solid state additional acceptor molecules sometimes occupy sites in the crystal lattice without forming a direct bond with the donor molecule but participating in intermolecular coordination. This is particularly characteristic of the adducts with HgX_2. For example, the crystal lattice of $Cp_2Ru.3HgCl_2$[42] contains the $Cp_2Ru \rightarrow HgCl_2$, $[Cp_2RuHgCl]^+Cl^-$, and $HgCl_2$ molecules.

X-Ray diffraction analysis of the complexes $CpCo(CO)_2.HgCl_2$[43,44] and $Cp_2Ru.HgX_2$ (X = Cl or Br)[45] indicates the formation of a metal–metal covalent bond. The Co → Hg bond length in the donor–acceptor adduct is 2.578 Å; the formation of this adduct increases ν(CO) by 75 cm^{-1}.[44,46] According to X-ray diffraction data, the 1:3 adduct has a CO–Hg bond with a length of 2.504 Å, i.e. shorter than in the 1:1 adduct. A crystal of the 1:3 complex contains the $[CpCo(CO)_2HgCl]^+$ cations, Cl^- anions, and two $HgCl_2$ molecules[47]. The formation of this complex causes a large shift of ν(CO) (by 90 cm^{-1}). The frequency shifts agree with the values quoted above for the adducts $L_2Fe(CO)_3.HgX_2$.[9]

Together with an intense ν(Cp–Ru)(symm.) line, yet another intense line appears in the Raman spectra of the adducts $Cp_2Ru.HgX_2$ (X = Cl or Br),[45] whose intensity does not change significantly on passing from the $HgCl_2$ adduct to the $HgBr_2$ adduct. This line (137 cm^{-1} for Cl and 130 cm^{-1} for Br) has been assigned to the vibration of the Ru–Hg bond. The Cp–Ru–Cp stretching vibration bands change slightly on coordination to a Lewis acid (by +5 cm^{-1}). The interaction of HgX_2 with Cp_2Ru has apparently little influence on the bonds between ruthenium and Cp rings, since the ruthenium atom uses non-bonding d electrons in the formation of a donor–acceptor bond with HgX_2.

Table 4. The interaction of transition metal complexes with Group II metal halides.

Initial substances	Compn. of adduct	Proposed structure	Refs.
$(Me_3C_6H_3)$ Cr $(CO)_3$ + $HgCl_2$	1:2	$(Me_3C_6H_3)$ Cr $(CO)_3 \cdot 2HgCl_2$	12
$(Me_3C_6H_3)$ Mo $(CO)_3$ + HgX_2 (X = Cl, Br)	1:1	$(Me_3C_6H_3)$ $(CO)_3$Mo—HgX_2	12
Ditto	1:2	$[(Me_3C_6H_3)$ $(CO)_3MoHgX]^+HgX_3^-$	12
(1, 3, 5-C_7H_8) Mo $(CO)_3$ + HgX_2 (X = Cl, Br)	1:1	(1, 3, 5-C_7H_8) $(CO)_3$Mo—HgX_2	12
(bipy) $W(CO_4$ + HgX_2 (X = Cl or Br; bipy = 2,2-bipyridyl)	1:2	bipy $(CO)_4W \cdot 2HgCl_2$	12
Ditto	--	bipy $(CO)_3WX$ (HgX)	12
(bipy) Mo $(CO)_4$ + HgX_2 (X = Cl, Br)	—	bipy $(CO)_3$MoX (HgX)	12
(diphos) M $(CO)_4$ + HgX_2 (M = Mo, W; X = Cl, Br)		[(diphos) M $(CO)_4HgX]^+X^-$	12
$(diphos)_2$M $(CO)_2$ + HgX_2 (M = Mo, W; X = Cl, Br, I)	1:2	$[(diphos)_2(CO)_2$ M (HgX)$]^+HgX_3^-$	12
(C_6H_6) Cr $(CO)_{3-n}L_n$(L = PPh_3, $n = 0,1$)	1:2; 1:3	—	51, 52
CpM $(CO)_2L$ + $HgCl_2$ (M = Mn, Re; L = PPh_3, $AsPh_3$, $SbPh_3$)	1:4—5	Cp $(CO)_2$LMn·n$HgCl_2$	53
Fe $(CO)_5$ + $HgCl_2$	1:1; 1:2	—	54
Ditto	--	Fe $(CO)_4(HgCl)_2$	54
(PPh_3) Fe $(CO)_4$ + $HgCl_2$	1:2	—	12
$(EPh_3)_2$Fe $(CO)_3$ + HgX (E = P, As, Sb; X = Cl, Br)	1:1	$(EPh_3)_2(CO)_3$—HgX_2	55
[P $(OPh)_3]_2$Fe $(CO)_3$ + HgX_2 (X = Cl, Br)	1:2	$[P(OPh)_3]_2(CO)_3$Fe—HgX_2	55
Cp_2Fe + HgX_2 (X = Cl, Br)	1:7	red—adduct, blue—Cp_2Fe^+ salt	45
(RC_6H_4) Fe (C_6H_4R') + HgX_2	1:6—7	—	56
$(Ph_2PC_6H_4)_2$Fe + HgX_2 (X = Cl, Br)	1:1; 1:2	—	56
trans-$(PPh_3)_2$M (CO_3) + HgX_2 (M = Ru, Os; X = Cl, Br, I)	1:2	$[(PPh_3)_2$ M $(CO)_3(HgX)]^+$ HgX_3^-	57
Cp_2Ru + HgX_2 (X = Cl, Br)	1:1*	Cp_2Ru—$HgBr_2$	45
Ditto	1:3*	$[Cp_2Ru—HgCl_2]$ $[Cp_2Ru—HgCl]^+$ $Cl^- \cdot [HgCl_2]$	42
Cp_2Os + $HgCl_2$	1:2	Cp_2Os—$HgCl_2$	58
CpCo $(CO)_2$ + HgX_2 (X = Cl, Br)	1:1*	Cp $(CO)_2$Co—HgX_2	43, 44, 46
Ditto	1:3*	$[CpCo(CO)_2(HgX)]^+X^-$ + $2HgX_2$	47
$CpCoL_2$ + $HgCl_2$(L = PMe_3)	1:1	CpL_2Co—$HgCl_2$	41
$CpCoL_2$ + $ZnCl_2$ + (L = PMe_3)	1:1	CpL_2Co—$ZnLCl_2$	41
CpIr (CO) (PPh_3) + $HgCl_2$	1:1	Cp (CO) (PPh_3) Ir—$HgCl_2$	59
CpIr (CO) (PPh_3) + $ZnBr_2$	1:1	Cp (CO) (PPh_3) Ir—$ZnBr_2$	59

*The structure of the reaction product was established by X-ray diffraction.

In contrast to ruthenocene, the interaction of ferrocene with mercury halides is more complex. Regardless of the reactant ratio, the same product, having the 1:7 composition, has been obtained for mercury(II) chloride[45]. A red precipitate is formed initially, turning blue on standing.

The red compound formed with $HgBr_2$ has not been isolated. The red compound $Cp_2Fe.7HgCl_2$ is diamagnetic at room temperature, while the blue compound is paramagnetic and has a magnetic moment close to that for ferrocenium salts. On heating, the red product becomes blue. On the basis of these data, it has been suggested that the red compound contains the Fe–Hg bond and is an adduct of Cp_2Fe with $HgCl_2$, while the blue compound consists of $CpFe^+$ and a complex anion. The above structure of the blue product is also supported by the finding that, after the addition of NH_4PF_6 to its aqueous solution, $[Cp_2Fe]^+PF_6^-$ is formed as a result of anion exchange. Thus the reaction of Cp_2Fe with HgX_2 (X = Cl or Br) ultimately involves the oxidation of ferrocene, in contrast to ruthenocene, which forms adducts with HgX_2.

When π-complexes with aromatic ligands are acted upon by HgX_2 salts, there is also a possibility of the mercuration of the π-ligand with formation of the C–HgX bond, which is characteristic of ferrocene[48] and $CpM(CO)_3$ (M = Mn or Re).[49,50]

(c) *Derivatives of Group III elements* EX_3 (*E = B, Al, Ga, In, or Tl; X = halogen or organic group*). Examples of the interaction of Lewis acids derived from Group III elements with transition metal complexes via both the metal and via the ligands (bridging and terminal CO groups, N_2, NO, CN and halogens) are known. The interaction with the oxygen atoms of the briding ligands is more characteristic of aluminium derivatives than of other Lewis acids. This leads to interesting features of the behaviour of transition metal complexes in reactions with aluminium compounds, which will be discussed below.

Numerous reactions of transition metal complexes, containing bridging carbonyl groups, with Lewis acids have been investigated: $[CpFe(CO)_2]_2$ with BX_3 (X = Cl or Br);[35] $[CpFe(CO)]_4$ with $AlBr_4$ and BX_3 (X = F, Cl, or Br);[35] $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Co_2(CO)_8$, and $Ru_3(CO)_{12}$ with $AlBr_3$;[35,60] $[CpNi(CO)]_2$ and $Cp_3Ni_3(CO)_2$ with AlR_3 (R = Et or iso-C_3H_7) and BF_3.[7,35] It has been shown by infrared spectroscopy and in a number of instances also by X-ray diffraction that the bond in the resulting donor–acceptor adducts is formed via the bridging CO groups. The American chemist Schriver, whose studies have been surveyed in a review[8], has made a considerable contribution to the study of the basicity of bridging carbonyl groups.

Table 5. The stretching vibration frequencies of the CO groups [ν(CO), cm^{-1}] in the adducts of $[CpFe(CO)_2]_2$ with Lewis acids[35]

Complex	Terminal CO groups	Bridging CO groups	
		free	coordinated
$[CpFe(CO)_2]_2$	1971; 1930	1797; 1765	—
$[CpFe(CO)_2]_2AlEt_3$	1993; 1985	1828	1682
$[CpFe(CO)_2]_2 \cdot BCl_3$	2038; 2020	1845	1463

It is noteworthy that, when Lewis acids are coordinated to bridging CO groups, the shifts of the ν(CO) stretching vibration frequencies are significantly different for adducts with different Lewis acids (Table 5).[35] Apparently the difference in the frequency shifts reflects qualitatively the strength of the donor–acceptor bond formed. The greater the degree of charge transfer and correspondingly the more stable the complex formed, the greater should be the changes in the vibration frequencies of the CO groups resulting from coordination to the Lewis acid.

However, estimation of the strength of the donor–acceptor interaction solely from the vibration frequency shifts is not always legitimate. The vibration frequencies can be influenced significantly also by other factors, which have no direct bearing on the change in the electronic structure of the donor molecules as a result of charge transfer on coordination. Thus an increase in vibration frequency can be caused also by kinematic factors. For carbonyl compounds, where coordination takes place via the oxygen atom of the CO group, estimation of the strength of the donor–acceptor bond from the ν(CO) frequency shifts can constitute a fair approximation, since the stretching vibrations of the carbonyl groups are highly localised and the changes in the vibration frequencies are predominantly caused by charge transfer from the oxygen atom to the acceptor molecule, i.e. by electronic effects.

Thus, according to infrared spectroscopic data, the compounds BX_3 are stronger acceptors than AlX_3. The replacement of the halogen in Al derivatives by electron-donating organic groups (Me, Et, Ph) weakens the acid properties. The observed regular variation of the ν(CO) and $\nu(N_2)$ frequency shifts in the spectra of the complexes *trans*-$ReClL_4X$ (X = CO or N_2) on coordination to aluminium derivatives as a function of R in AlR_3 is consistent with this observation[61]:

Complex	ν(CO), cm^{-1}	$\Delta\nu$(CO), cm^{-1}
trans-ReCl(CO)($Ph_2PCH_2CH_2PPh_2$)$_2$	1803	—
trans-ReCl($Ph_2PCH_2CH_2PPh_2$)$_2$(CO → $AlMe_3$)	1677	−126
trans-ReCl($Ph_2PCH_2CH_2PPh_2$)$_2$(CO → $AlPh_3$)	1653	−150
trans-ReCl($Ph_2PCH_2CH_2PPh_2$)$_2$(CO → $AlCl_3$)	1630	−173

Thus the shift increases with enhancement of the electron-accepting properties of the Lewis acid.

There are many examples in the literature indicating the possibility of the coordination of the terminal CO, N_2, and NO ligands in transition metal complexes to aluminium derivatives: *trans*-$ReClL_4X$ (X = CO or N_2) with AlR_3 (R = Me, Ph, or Cl);[61] ML_4X_2 (X = CO or N_2; M = Mo or W) with AlR_3 (R = Me, Et, or Ph) and $GaMe_3$;[61–63] $OsCl_2L_3(N_2)$ with $AlMe_3$ [61] (L = phosphine ligands; L_2 = chelating diphosphine ligands); (π-$Ph_3P^+-C_5H_4^-$)Mo(CO)$_3$ with $AlMe_3$;[37] $[CpW(CO)_3]^-Na^+$ with $AlPh_3$;[64] $W(CO)_5L$ (L = PPh_3, $P(OPh)_3$, or $P(n\text{-}C_4H_9)_3$] with $AlEtCl_2$ in the presence of O_2;[65] CpM(CO)(NO)L (M = Mo or W; L = CO or PPh_3) with $AlCl_3$;[22] $CpM(CO)_3$ (M = Mn or Re), π-AreneM(CO)$_3$ (M = Cr, Mo, or W), $CpV(CO)_4$, and some of their derivatives with $AlCl_3$.[25]

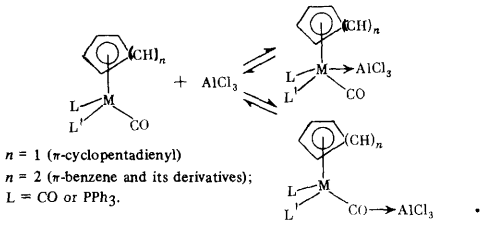
The study of the basicity of the atom Y or the coordinated ligand XY (CO or N_2) in the complexes *trans*-ReCl(XY)L_4 (L = PMe_2Ph) [61] relative to $AlMe_3$ solution in benzene showed that the N_2 ligand is more basic than the CO ligand in these compounds. Comparison of the equilibrium constants for the reactions

$$AlMe_3 \cdot Et_2O + ReCl(XY)L_4 \underset{80°}{\overset{C_6H_6}{\rightleftharpoons}} Et_2O + ReCl(XY \rightarrow AlMe_3)L_4$$

led to this conclusion.

The complexes CpIr(CO)(PPh_3) with $TlCl_3$,[59] Cp_2MH_2 (M = Mo or W) with BX_3 (X = F or Cl) and AlR_3 (R = Me, Et, or Ph),[66,68] Cp_2ReH with BF_3 [66] and $AlMe_3$,[67] and Cp_2Ti with $AlEt_3$ [69] give rise to 1:1 adducts, in which the presence of M–M′ bonds is postulated.

Lokshin et al.[28] made the first systematic study of the interaction of a large number of carbonyl π-complexes of Group V–VII transition metals with $AlCl_3$. Investigation of a series of complexes of the same metal with different ligands or of isotypical complexes with different central metal atoms made it possible to determine the influence of the nature of the ligands and the central metal atom in the complex or the reactivity and the mode of reaction with $AlCl_3$. It has been shown that, depending on the nature of the complex itself and on the solvent, $AlCl_3$ can be coordinated either via the metal atom or via the CO group, or via both centres simultaneously:



n = 1 (π-cyclopentadienyl)
n = 2 (π-benzene and its derivatives);
L = CO or PPh_3.

This leads to completely different changes in the carbonyl region of the infrared spectrum, so that the formation of adducts of a particular type can be deduced spectroscopically. For example[28], the ν(CO) frequencies are 1931 and 2027 cm^{-1} for $CpRe(CO)_3$, 1740, 1991, and 2054 cm^{-1} for $CpRe(CO)_2$(CO → $AlCl_3$), and 2055, 2074, and 2130 cm^{-1} for $Cp(CO)_3Re \rightarrow AlCl_3$.

As mentioned above (Section IV), the mode of reaction depends on the solvent employed. Coordination via the metal atom and via the CO group was promoted by carrying out the reaction in CH_2Cl_2 and in benzene respectively. Thus the formation of adducts via the CO group in CH_2Cl_2 solution was observed only for $CpM(CO)_3$ (M = Mn or Re) and ring-substituted CTM derivatives: $(PhCH_2C_5H_4)Mn(CO)_3$ and $(Et_5C_5)Mn(CO)_3$. Apart from these complexes, in benzene solutions simultaneous interaction via both the oxygen atom of the CO ligand and the metal atom was observed also for $CpMn(CO)_2PPh_3$, $(Et_5C_5)Mn(CO)_2PPh_3$, $(C_6H_6)Cr(CO)_3$, $(1,3,5\text{-}Me_3C_6H_3)Cr(CO)_3$, $(Me_6C_6)Cr(CO)_3$, $(C_6H_6)W(CO)_3$, $CpV(CO)_4$, and $CpV(CO)_3PPh_3$.[28]

Competition between these two reactions is probably determined by the relative basicities of the metal and the oxygen in the complex and the relative strengths of the resulting bonds, the difference between the energies being evidently small. The weaker the basic properties of the metal atom in the complex the greater the predominance of the coordination via the CO group and, conversely, the more basic the metal atom, the more characteristic is the interaction via this centre. Complexes in which the metal atom is most basic do not give rise to adducts via the CO ligand in either CH_2Cl_2 or in benzene: CpMn(CO)(diphos), $CpRe(CO)_2PPh_3$, $CpNb(CO)_4$, $(C_6H_6)Cr(CO)_2PPh_3$, $Fe(CO)_4PPh_3$, and $Fe(CO)_3(PPh_3)_2$.[28]

The interaction of the cyanide complexes $K_4[Fe(CN)_6]$, $K_2[Ni(CN)_4]$, $Fe(phen)_2(CN)_2$ (phen = 1,10-phenanthroline), and $Fe(CNR)_4(CN)_2$ (R = H, Me, or Et) with boron halides has been investigated[70,71] and it has been shown that the adducts formed contain cyanide bridges between the transition metal and BX_3 (for example, $-\overset{|}{\underset{|}{Ni}}-C\equiv N-BF_3$), each CN group being linked to the Lewis acid.

A complex pattern in the carbonyl region of the spectrum (Table 6) is observed for the interaction of *trans*-RhX(CO).$(EPh_3)_2$ with BX_3 (X = halogen; E = P or As).[25,26] As mentioned above, different cases are possible, involving the formation of a donor–acceptor adduct or oxidative addition; nor can one rule out the possibility of interaction via the halogen ligand. In all these cases, the spectral changes in the region of the vibrations of the CO group are different. The most marked changes in ν(CO) apparently occur in oxidative addition and smaller changes correspond to the formation of a donor–acceptor adduct. The hypsochromic

shifts of the signal frequencies on coordination to a halogen are usually small (15–20 cm^{-1}).

It is believed that *trans*-$RhCl(CO)(PPh_3)_2$ forms a donor–acceptor adduct with BCl_3 via the rhodium atom[26]. However, $\nu(CO)$ for the adduct is displaced only by 23 cm^{-1} (Table 6); for such a small shift, coordination of the acid to a chlorine atom is more probable.

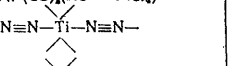
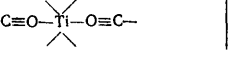
Table 6. Infrared spectra (in the region of the stretching vibrations of the CO group) of the adducts of the complexes *trans*-$[RhCl(CO)(EPh_3)_2]$ with BX_3.

Complex	Lewis acid	Compn. of adduct	ν(CO), cm^{-1}	$\Delta\nu$(CO), cm^{-1}
trans-$[RhCl(CO)(PPh_3)_2]$	—	—	1968	—
Ditto	BCl_3	1:1	1991	+23
	BBr_3	1:1	2098 w, 1990 s	+130, +22
trans-$[RhBr(CO)(PPh_3)_2]$	—	—	1969	—
Ditto	BBr_3	1:1	2102 w, 2049 m, 1998 w, 1985 s	+133, +80, +29, +16
trans-$[RhCl(CO)(AsPh_3)_2]$	—	—	1967	—
Ditto	BBr_3	1:1	2101 m, 2047 s	+130, +80

The infrared spectra of other adducts of rhodium complexes with BX_3 contain two or more bands in the region of the CO vibrations. There is apparently a possibility of the formation of different products simultaneously. Judging from the infrared spectra, the adduct *trans*-$RhBr(CO)(PPh_3)_2$ can contain molecules of the rhodium complex coordinated to the Lewis acid via the halogen ligand (1998, 1985 cm^{-1}), a donor–acceptor adduct (2049 cm^{-1}), and the oxidative addition product (2102 cm^{-1}).[25,26]

As mentioned above, the corresponding iridium complex *trans*-$IrCl(CO)(PPh_3)_2$ interacts with BF_3 via the metal atom, as shown by the hypsochromic shift of $\nu(CO)$ by 100 cm^{-1} (from 1967 to 2067 cm^{-1}).[16] The interaction of the same complex with $AlMe_3$ leads to an increase of the stretching vibration frequency of the CO group by 12 cm^{-1}. The formation of an adduct via the iridium atom has been postulated[61]. However, the above value of $\Delta\nu(CO)$ is more likely to indicate the coordination of $AlMe_3$ via the chlorine atom. The interaction of the same complex with $SnCl_4$ (see above, Section II). leads to $\Delta\nu(CO)$ or 113 cm^{-1} for the oxidative addition product and 74 cm^{-1} for the donor–acceptor adduct[17].

Table 7. Adducts formed via the ligands of transition metal complexes with Lewis acids of the type MX_4.

Complex	Lewis acid	Adduct	Refs.
$CpCr(NO)_2Cl$	$SnCl_4$	$CpCr(NO)_2(Cl \rightarrow SnCl_4)$	22
$CpMo(CO)_2(NO)$	$TiCl_4$	$CpMo(CO)_2(NO \rightarrow TiCl_4)$	22
$CpW(CO)_2(NO)$	$SnCl_4$	$CpW(CO)_2(NO \rightarrow SnCl_4)$	22
trans-$(Me_2PhP)_4ReCl(N_2)$	$TiCl_4$		79
trans-$(Me_2PhP)_4ReCl(CO)$	$TiCl_4$		79

Complexes containing halogen ligands as a rule react with Lewis acids via the halogen atom. Adducts of this type have been obtained for the following complexes: $Mn(CO)_5X$, $(PMe_3)_2Fe(CO)_2X_2$ (X = Cl, Br, or I), and $(PMe_3)_2Ni(CO)I_2$ with AlX_3 (X = Cl or I), $FeCl_3$, and $SbCl_5$;[72] $RuCl_2(CO)_2.(PMe_3)_2$ with $FeCl_3$;[73] $MoCl_2(NO)_2(PMe_3)_2$ with $FeCl_3$;[73] $CpRe(CO)_2Br_2$ with $AlCl_3$;[28] $CpCr(NO)_2Cl$ with $AlCl_3$, $SnCl_4$,[22] and FeCl;[73] $CpFe(CO)_2X$ (X = Cl, Br, or I) with a large set of Lewis acids[73].

According to the shifts of the $\nu(CO)$ frequencies for the adducts compared with the initial complex, in the case of $CpFe(CO)_2$ (X→M′X) the Lewis acids investigated can be arranged in the following sequence in terms of their electron-accepting properties: $SbCl_5 \cong AlCl_3 \cong FeCl_3 > MoCl_5 \cong GaCl_3 \cong AlBr_3 > FeBr_3 \cong AlI_3 > GaI_3 > NbCl_5 > SnCl_4 > InCl_3 \cong TiCl_4 > HgCl_2 \cong Cl_2 > I_2 > Br_2$.[73]

(*d*) *The halides MX_4 of Group IV elements (M = Ti, Ge, or Sn).* Numerous reactions of transition metal complexes with Lewis acids derived from Group IV elements and leading to the formation of oxidative elimination products have been described in the literature[12,13,74–78]. However, in the present review only those reactions are considered in which the initial complex enters wholly into the composition of the adduct. Data for the reversible formation of TMC adducts with Lewis acids $M'X_4$ are presented in Tables 7 and 8.

Table 8. Examples of the interaction of MX_4 with complexes via the transition metal atom.

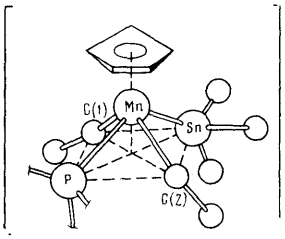
Complex	Lewis acid	Refs.
trans-$IrCl(CO)(PPh_3)_2$	$SnCl_4$	17
$CpM(CO)(NO)(PPh_3)$ (M = Mo, W)	$SnCl_4$	22
$(Et_3C_6)Mn(CO)_3$	$SnCl_4$	23
$CpMn(CO)_2L$ (L = PPh_3, $P(OPh)_3$ etc.)	$SnCl_4$	23, 80
$CpMn(CO)L_2$ (L_2 = diphosphine ligands)	$GeCl_4$, $SnCl_4$, $SnBr_4$, $TiCl_4$	23
$CpRe(CO)_3$	$TiCl_4$	22
$CpRe(CO)_2L$ [L = P(OPh)$_3$, P(OEt)$_3$, PPh_3]	$SnCl_4$, $SnBr_4$, $TiCl_4$	22
(1, 3, 5-$Me_3C_6H_3$) M $(CO)_3$(M = Cr, Mo, W)	$SnCl_4$, $TiCl_4$	22
$(C_6H_6)Cr(CO)_2PPh_3$	$SnCl_4$	22
Cp_2Ru	$SnCl_4$, $SnBr_4$	56
$(Ph_3P^+—C_6H_4^-)M(CO)_3$(M = Cr, Mo, W)	$TiCl_4$	22

In the majority of the cases investigated the interaction of the Lewis acids $M'X_4$ with complexes takes place via the transition metal atom and coordination via the ligand lone electron pair has been observed in only a few instances (Table 7). The adducts $[(PMe_2Ph)_4ReClL]_2.TiCl_4$ or more involved compounds containing solvent molecules, for example, $[ReCl(N_2)(PMe_2Ph)_4]_2.TiCl_4.THF$ (THF = tetrahydrofuran), and $[ReCl(N_2)(PMe_2Ph)_4]_2.TiCl_4.(C_6H_6)_n$ (n = 1–5), have been isolated[79] after the interaction of the compounds *trans*-$(PMe_2Ph)_4ReClL$ (L = CO or N_2) with $TiCl_4$. The decrease of the stretching vibration frequencies of the CO and N_2 groups indicates the coordination of $TiCl_4$ via these groups:

trans-$(PMe_2Ph)_4ReCl(N_2) + TiCl_4 \xrightleftharpoons{C_6H_6}$ *trans*-$[(PMe_2Ph)_4ClRe—N\equiv N—Ti—N\equiv N—ReCl(PMe_2Ph)_4].(C_6H_6)_{1-5}$. The $\nu(N_2)$ frequency of the initial complex (1925 cm^{-1}) shifts to 1814 cm^{-1} in the spectrum of the reaction product. This is the first example of a complex containing two nitrogen bridges.

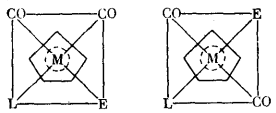
The cyclopentadienyl and arene derivatives of manganese, rhenium, chromium, molybdenum, and tungsten carbonyls [$CpM(CO)_3$, M = Mn or Re; $(Arene)M(CO)_3$, M = Cr, Mo, or W; and their various derivatives] in solutions combine reversibly with Lewis acids derived from Group IV elements

($SnCl_4$, $SnBr_4$, $TiCl_4$, $GeCl_4$) via the transition metal atom[22,23]. The characteristics of the influence of the nature of the metal (see Section II, 2) and the ligands (Section II, 3) on the basicity of the complexes have been examined in relation to these complexes. Solid adducts, having the 1:2 composition, of a series of complexes $CpMn(CO)_2L$ (where $L = PPh_3$, trialkylphosphines, $AsPh_3$, or $SbPh_3$) with $SnCl_4$ have been isolated[23]. X-Ray diffraction studies showed that, for $L = PPh_3$, the adduct has the ionic structure $[(C_5H_5)Mn(CO)_2(PPh_3)SnCl_3]^+SnCl_5^-$ and contains the Sn–Mn bond (with a length of 2.589 Å). The coordination environment of the manganese atom consists of a distorted square pyramid with the C_5H_5 ligand apical. Two CO groups (the OC–Mn–CO angle is 115°), the $SnCl_3$ group, and the PPh_3 ligand are located in the base of the pyramid *trans* to one another[80] (see Figure).



The structure of the cation $[C_5H_5Mn(CO)_2(PPh_3)(SnCl)]^+$.[80] Bond lengths (Å): Mn–P = 2.367, Mn–Sn = 2.589, Mn–C(1) = 1.82, Mn–C(2) = 1.83; valence angles: C(1)–Mn–P = 80.0°, C(2)–Mn–P = 79.6°, C(1)–Mn–C(2) = 115.1°, C(2)–Mn–Sn = 74.4°, C(1)–Mn–Sn = 74.9°, and P–Mn–Sn = 131.1°.

We may note that the addition of the acceptor E to the pseudotetrahedral complexes $(C_5H_5)M(CO)_2L$ can give rise to two isomers with the geometry of a square pyramid, which differ by the *cis*- or *trans*-disposition of the CO groups (or phosphorus nuclei, see below) in the base of the pyramid:



It has been shown by ^1H, ^{13}C, and ^{31}P NMR that, particularly in the protonation (E = H^+) of the complexes $CpM(CO)_2L$ and $CpM(CO)L_2$ (M = Mn or Re; L and L_2 are mono- and bi-dentate phosphines), the products are both *cis*- and *trans*-isomers[81–83]. The infrared spectra of the adducts $[(C_5H_5)Mn(CO)_2(L).SnCl_3]^+SnCl_5^-$ in CH_2Cl_2 as a rule exhibit four and not two ν(CO) bands; the solutions apparently contain a mixture of isomers[23,80].

For $CpRe(CO)_2L$ [$L = PPh_3$, $P(OEt)_3$, or $P(OPh)_3$], the interaction with SnX_4 (X = Cl or Br) leads to the appearance of two new ν(CO) bands in the infrared spectra of the solutions in each case, i.e. only one isomer is formed in this instance. At the same time, a sharp change in the ratio of the ν(CO) band intensity ratios for the adducts is observed compared with initial compounds; this corresponds to an appreciable increase of the angle between the carbonyl groups (from ~100° to ~125°), which is possible only for the *trans*-isomer[22]. On the other hand, the reactions of these complexes with $TiCl_4$ apparently lead to the formation of a mixture of isomers [four ν(CO) infrared bands are observed][22].

There is a further series of examples of the reversible addition of Lewis acids $M'X_4$ to transition metal complexes (Table 8). In particular, the addition of $(Cpylid)M(CO)_3$ ($Cpylid = Ph_3P^+-C_5H_5^-$, M = Cr, Mo, or W) to $TiCl_4$,[22] of *trans*-$(PPh_3)_2Ir(CO)Cl$ to $SnCl_4$,[17] and of $CpM(CO)(NO).PPh_3$ (M = Mo or W) to $SnCl_4$ [22] involves interaction via the metal atom.

The reactions of ferrocene with SnX_4 and TiX_4 (X = Cl or Br) have been investigated. It is suggested that they involve the formation of salt-like products containing the ferrocenium cation and the $Sn_2X_9^-$ and $Ti_3X_{12}^-$ counterions[84]. In contrast to Cp_2M (M = Fe or Ni), ruthenocene is not oxidised under the influence of SnX_4 (X = Cl or Br) but gives rise to yellow products having the composition $2Cp_2Ru.3SnX_4$,[56] for which the structure $[Cp_2Ru–SnX_2–RuCp_2]^{2+}(SnX_5^-)_2$ has been proposed.

Table 9. The interaction of transition metal complexes with metal ions.

Transition metal complex	Reagent	Reaction product*	Refs.
$[Mn(CO)_4L]^-$ (L = CO, PMe_2, Ph, PPh_3, P(OPh)$_3$)	$M^+ = Li^+$, Na^+	$(CO)_3LMn-CO...M^+$	85,86
$[Fe(CO)_3(NO)]^-$	$M^+ = Na^+$, K^+, $(Ph_3P)_2N^+$	$(CO)_3Fe-NO...M^+$	87
$Fe(CO)_5$	$Cd(AsF_6)_2$	$Cd[(Fe(CO)_5)_2]^{2+}(AsF_6^-)_2$	88
$Fe(CO)_5$	$Sn(SbF_6)_2$	$Sn[(Fe(CO)_5)_2]^{2+}(SbFe_6^-)_2$	88
$Fe(CO)_5$	$Fe(SbF_6)_2$	$Fe[(Fe(CO)_5)_2]^{2+}(SbF_6^-)_2$	88
$[Mn(CO)_5)_2]_2$ $[CpMo(CO)_3]_2$ $[CpFe(CO)_2]_2$ $CpFe(CO)_2$ $[Co(CO)_3L]_2$ (L = $PMePh_2$, PPh_3, P$(C_4H_9)_3$	Mg amalgam in the presence of bases; B = THF, tetramethylethylenediamine, or pyridine	$M'C=O...(B_4Mg)...O=CM'$ or $M'C=O...(B_2Mg)...O=CM'$ or $M'-(B_2Mg)-M'$	89,90
$CPW(CO)_3^-$	Al, Al amalgam in THF	$[CpW(CO)_3]_3Al(THF)_3$	91

*The structures of the reaction products have been confirmed[89,91] by X-ray diffraction; $M' = Mn(CO)_4$ in the case of $[Mn(CO)_5]_2$.

2. Reactions with Metal Cations

Metal cations can play the role of electrophiles in relation to TMC (Table 9). The nature of the infrared spectra of the salt-like complexes $M^+[Mn(CO)_4L]^-$ [IV, M = Li or Na; L = CO, PMe_2Ph, PPh_3, or $P(OPh)_3$] [84,85] and $M^+[Fe(CO)_3(NO)]^-$ [V, M = Na, K, or $(Ph_3P)_2N$] in the carbonyl region in THF shows that they exist in two forms in equilibrium—contact ion pairs, where the alkali metal cation interacts with the oxygen atom of the CO ligands of complex (IV) or the NO ligand of complex (V), and ion pairs separated by the solvent. For complexes (IV), the existence of contact ion pairs in solution also follows from conductimetric and kinetic data for their reactions with alkyl halides[86]. When reagents binding alkali metal cations, namely crown-ethers or hexamethylphosphoramide, are added to solutions of the complexes in THF, the ν(CO) bands of the contact ion pairs (M–X≡O.....M', where X = C or N) disappear and only the bands of the free ions remain. Iron pentacarbonyl, which is a weak base, reacts in liquid SO_2

with strong acids—$Cd(AsF_6)_2$, $Sn(SbF_6)_2$, and $Fe(SbF_6)_2$.[88] On the basis of Mössbauer and infrared spectroscopic data, the following structure of the reaction product has been postulated: $[-\underset{/\backslash}{\overset{\backslash/}{Fe}}-M-\underset{/\backslash}{\overset{\backslash/}{Fe}}-]^{2+}.2(EF_6)^-$, where E = As or Sb; thus Lewis acids interact with $Fe(CO)_5$ via the metal atom.

Under the influence of magnesium amalgam, the dimeric complexes $[Mn(CO)_5]_2$, $[CpMo(CO)_2L]_2$, $[CpFe(CO)_2]_2$, and $[Co(CO)_3L]_2$ (L is a phosphine ligand) undergo reductive cleavage in the presence of bases such as pyridine, THF, and tetramethylethylenediamine with formation of the compounds $B_xMg(m)_2$ (B = base, m = group containing a transition metal, and $x = 2$ or 4 depending on the nucleophilic properties of the metal carbonyl group)[89,90]. In tetracoordinate complexes ($x = 2$) the transition metal can be linked to the Mg^{2+} ion both via CO bridging groups (Mg–O≡C–M) and directly (M–Mg). The interaction of groups containing a transition metal with Mg^{2+} in hexacoordinate complexes ($x = 4$) always proceeds via the oxygen atoms of the CO groups[90].

According to X-ray diffraction data[89], the adduct $[CpMo(CO)_3]_2Mg(Py)_4$ has an octahedral structure, the Mg atom being coordinated to four pyridine molecules in the equatorial plane and to the oxygen atoms of two metal carbonyl groups—one from each $CpMo(CO)_3$ residue.

3. Reactions with Halogens, Antimony Pentachloride, and Alkyl Halides

When TMC react with halogens, the X_2 molecules are polarised and the positively charged cation X^+ always adds to the transition metal atom, the coordination number of the central atom increases by unity, and ionic compounds $[L_nMX]^+$ are formed via the mechanism:

$$L_nM + \overset{\delta+}{X}-\overset{\delta-}{X} \rightarrow [L_nMX]^+X^- \text{ or } [L_nMX]^+X_3^- .$$

In a number of cases nucleophilic attack by the X^- anion in the second stage of the reaction leads to the formation from these ionic compounds of oxidative addition or oxidative elimination products, for example[92,93]:

$$Mo(CO)_3(diphos)_2 + I_2 \rightarrow [Mo(CO)_3(diphos)_2I]^+I^- \rightarrow Mo(CO)_2(diphos)_2I_2$$
$$CpRe(CO)_3 + Br_2 \rightarrowtail [CpRe(CO)_3Br]^+Br^- \rightarrow CpRe(CO)_2Br_2 + CO .$$

The reactions with the halogens are known for the octahedral derivatives of chromium, molybdenum, and tungsten hexacarbonyls of the type $M(CO)_{6-n}L_n$ (where L are electron-donating ligands: amines, phosphines, and arsines; $n = 2-4$): $M(CO)_2(L_2)_2$ (L_2 = bidentate phosphine or arsine)[92,94,95]; $(CO)_3M(L_2)_3M(CO)_3$ (L_2 = bridging bidentate phosphine)[95]; $Mo(CO)_4L_2$;[96] $Mo(CO)_3(Amine)_3$ and $Mo(CO)_3Q$ (Q = tridentate amine)[97]; $M(CO)_3Q'$ [M = Mo or W; Q' = polydentate phosphine ligands $PhP(C_6H_4PPh_2\text{-}o)_2$ or $P(C_6H_4.PPh_2\text{-}o)_3$].[98] The addition of halogens has been described for the following π-complexes: (π-Arene)$M(CO)_3$ (M = Mo or W; Arene = $Me_nH_{6-n}C_6$);[99]# $CpMn(CO)_3$;[100] $CpIr(CO)(PPh_3)$;[59] Cp_2Ru.[101]#

When TMC are acted upon by $SbCl_5$, Cl_2 is apparently formed initially as a result of the reaction $SbCl_5 \rightarrow SbCl_3 + Cl_2$ and then Cl^+ adds to the metal atom in the complex and Cl^- adds to a second $SbCl_5$ molecule. For example, the interaction of $CpRe(CO)_3$ with $SbCl_5$ leads to the formation of $[CpRe(CO)_3Cl]^+SbCl_6^-$.[102] The interaction of (π-Arene).$M(CO)_3$ (M = Mo or W),[103] Cp_2Ru,[56] and $[Re(CO)_3]_2$(porphyrin)[104]# with $SbCl_5$ leads to analogous products.

#The structure of the reaction products has been confirmed by X-ray diffraction analysis.

The reaction of $Mo(CO)_3L_3$ with $SbCl_5$ and $FeCl_3$ results in the formation of $[Mo_2(CO)_4L_4(\mu\text{-}Cl)_3]^+X^-$ ($X^- = SbCl^-$ or $FeCl_4^-$).[105]

The positive species adds to the central metal atom when TMC are acted upon by alkyl halides or stronger alkylating agents—trialkyloxonium salts and dialkyl sulphates. These reactions proceed via the mechanism $L_nM + \overset{\delta+}{R}-\overset{\delta-}{X} \rightarrow [L_nM-R]^+X^-$. Depending on the nature of the central atom M, the ligand environment, and X^-, the second reaction stage may involve the migration of R to CO with simultaneous attack by X^-, for example:

$$\underset{L=PPh_3}{CpM(CO)L} + MeI \rightarrow \underset{M=Ir}{[CpM(CO)(L)Me]^+I^-} \rightarrow \underset{M=Co,\ Rh}{CpM(COMe)(L)I} . \quad (3)$$

In relation to this reaction, it is possible to follow the influence of various structural factors[24]. The dicarbonyl complexes $CpM(CO)_2$ do not interact with MeI, since the basicity of the central atom is in this case insufficient. The rate of the bimolecular reaction (3) increases in the sequence Co < Rh ≪ Ir, the rate constants 10^4k amounting to 25.7, 35.0, and 210 litre mol^{-1} s^{-1} respectively. For M = Co and Rh, the reaction does not stop at the first stage and neutral acyl complexes are formed immediately. However, in the case of M = Ir, where the basicity of the central atom is extremely high, the final product is an ionic complex. The rate of reaction depends greatly on R and L: for CpCo(CO)L and MeI, the relative rate increases with enhancement of the electron-donating properties of L in the sequence PPh_3 (25.7) < PPh_2Me (150) < $PPhMe_2$ (330). The dependence of the rate on the solvent in the sequence THF < acetone < CH_2Cl_2 < MeCN shows that there is appreciable charge separation in the transition state.

It is possible to quote a further series of examples of similar reactions of transition metal complexes with alkylating agents: of $W(CO)_2(diphos)_2$ with $[Et_3O]^+BF_4^-$;[106] of $CpM(CO)(PPh_3)$ (M = Co, Rh, or Ir) with MeI and EtI;[24] of $CpIr(CO)(PPh_3)$ with MeCl, MeBr, $C_6H_{13}I$, $C_6H_5CH_2I$, and C_3H_7I;[59] of $CpCoL_2$[107] and FeL_5[108] [L = $P(OMe)_3$] with MeI.

4. Oxidation under the Influence of Electrophiles

When the transition metal atom in the complex is sufficiently basic (in the presence of strong electron-donating ligands), the influence of certain electrophiles can lead to oxidation with electron transfer to the acceptor and the formation of a donor radical-cation: $(L_nM)^0 \overset{-e}{\rightarrow} (L_nM)^{\ddagger}$. There is then a possibility of two cases: (a) the neutral acceptor A accepts an electron and gives rise to the radical-anion A^-, i.e. the reaction product is the radical-ion pair $(L_nM^{\ddagger})(A^-)$; (b) the cationic acceptor A^+ accepts an electron and is converted into a neutral molecule A ("one-electron oxidation"). The formation of radical-ion pairs is characteristic of the most basic complexes in reactions with π-acids (tetracyanoethylene and others). These reactions will be considered in detail below.

In one-electron oxidation reactions the oxidants are usually $NO^+PF_6^-$, diazonium salts, and the silver salts $AgPF_6$ and $AgBF_4$. They accept an electron from the TMC with formation of compounds or species which leave the reaction sphere, displacing thereby the equilibrium in the direction of the formation of the products [$NO^+ \rightarrow NO$; $Ag^+ \rightarrow Ag$ (metallic); diazonium salts → $Ph^{\cdot} + N_2$]. 18-Electron transition metal complexes are converted into 17-electron paramagnetic radical-cations, which give rise to well resolved EPR spectra and possess a magnetic moment corresponding to a single

unpaired electron. We may note that electrochemical as well as chemical oxidation is possible. Measurement of the half-wave potential $E_{1/2}$ permits hypotheses concerning the possibility of the chemical oxidation of the same substrates.

The conversion of the diamagnetic 18-electron complexes into radical-cations is always accompanied by an increase of the ν(CO) infrared frequencies, on average by 100–140 cm^{-1}. There are data[109] showing that the ferrocenium ion can also serve as a one-electron oxidant. It is then converted into ferrocene. We may note in this connection that, among the reactions of metallocenes with various electron acceptors, ferrocene and nickelocene are distinguished by their ability to give up readily one electron with formation of salts of the cations Cp_2Fe^+ and Cp_2Ni^+.

The reactions of Cp_2Fe with metal halides such as MX_4 (M = Ti or Sn; X = Cl or Br), $VOCl_3$, and $SbCl_5$ lead to the formation of the solid salts $Cp_2Fe.3TiX_4$, $Cp_2Fe.2SnX_4$, $Cp_2Fe.VOCl_3$, and $2Cp_2Fe.SbCl_5$, which always contain the Cp_2Fe^+ cation.[84] The compound Cp_2Ni is oxidised under the influence of $TiCl_4$ to $Cp_2Ni^+TiCl_4^-$.[84] On reaction with the sandwich-type acceptor Cb_2Ni, where $Cb = (3)\text{-}1,2\text{-}B_9C_2H_{11}^{2-}$,[84] ferrocene gives rise to a charge-transfer complex (CTC), which is gradually converted into the salt $Cp_2Fe^+.Cb_2Ni^-$. The reaction of Cp_2Ni with Cb_2Ni leads to complete electron transfer and the formation of an ionic compound in which both the cation and anion are sandwich complexes with a central Ni^{3+} ion.

Chemical oxidation reactions have been studied for the following complexes: $(C_6Me_{6-n})Cr(CO)_2(PhC{\equiv}CPh)$ (n = 0, 1);[110] CpFe(diphos)R (R = Me, H, Cl, Br, I, or $SnMe_3$);[111] $CpFe(CO)_nL_{2-n}X$ [n = 0, 1, L = $P(OPh)_3$ or CNPh];[111] $CpMn(CO)L_2$ [L_2 = diphos or $(PPh_3)_2$];[111] $CpV(CO)_2$(diphos) and $CpV(CO)_3L$ (L = PPh_2Me);[112] $Fe(CO)_2L$(diene) [L = CO, PPh_3, or $P(OCH_2)_3CH$)];[113] $Fe(CO)_3L_2$ (L = PPh_3, PPh_2Me, $P(OPh)_3$, or $P(NMe_2)_3$, L_2 = diphos);[114] $CpMn(CO)_2L$ (L = phosphines);[115] $[HCoL_4]^+PF_6^-$;[109] $Cr(CO)_4$(diphos) and $[Cr(NO)(MeCN)_3(diphos)]^+$.[116]

5. Reactions with π-Acids

When transition metal π-complexes react with π-acids, there is a possibility of the formation of charge-transfer complexes with complete electron transfer from the donor to the π-acid in the ground electronic state and the formation of salts of radical-anions.

$$D + A \rightleftarrows D \cdot A\ (CTC) \rightleftarrows D^+ + A^- \rightarrow \text{secondary products}$$

(radical-anion salt)

For weakly bound CTC, the transfer of electron density from the donor to the acceptor in the ground electronic state is slight, while the excited states are structures with complete electron transfer from D to A (i.e. are ionic). When a light quantum $h\nu_{CT}$ is absorbed, the CTC passes from the ground to an excited state and a charge transfer band (CTB) appears in the electronic spectrum. The formation of CTC leads to hardly any changes in the infrared spectra of the donor and acceptor, which is due to the fact that the shift of electron density fron the donor to the acceptor in the ground state is slight. Thus an appreciable displacement of the absorption bands of $(Arene)Cr(CO)_3$ and 1,3,5-trinitrobenzene (TNB) was not observed in the infrared spectra of their CTC.[117] When the electron transfer in the ground electronic state is complete, significant changes in the vibrational and electronic spectra are observed; one may then expect the appearance of an EPR signal.

The spectral changes when the transition metal π-complexes interact with π-acids can be illustrated in relation to the reactions of the manganese complexes $CpMn(CO)_3$, (Et_5C_5).$Mn(CO)_2(PPh_3)$, and CpMn(CO)(diphos) with tetracyanoethylene (TCE) and tetracyanoquinodimethane (TCQD).[118] The interaction of $CpMn(CO)_3$ and $(Et_5C_5)Mn(CO)_2(PPh_3)$ with TCE in CH_2Cl_2 does not lead to changes in the infrared spectra either in the carbonyl region [although the ν(CO) frequencies are extremely sensitive to changes in the distribution of electron density in the molecule] or in the region corresponding to the ν(CN) vibrations of TCE; nor do signals appear in the EPR spectra. New CTB bands, which are absent from the spectra of the initial compounds, appear in the electronic spectra (at 790 and 740 nm respectively).

When a solution of TCQD was added to one of CpMn(CO).(diphos) in CH_2Cl_2, a sharp colour change from yellow to emerald green and the appearance of an EPR signal were observed. At −150 °C the EPR spectrum of the complex CpMn(CO)(diphos).TCQD (VI) in CH_2Cl_2 showed two signals superimposed on one another: one broad signal, apparently due to $[CpMn(CO)(diphos)]^+$, and another, narrow signal due to the presence of TCQD. The electronic spectra of a solution of (VI) also indicate the presence of the TCQD radical-anion. The infrared spectrum of (VI) differs significantly from the spectra of the initial components: the frequencies ν(CO) are displaced by ~100 cm^{-1} towards higher values (as in oxidation by the Ag^+ ion and other oxidants), while the ν(CN) bands of TCQD are displaced towards lower values by ~50 cm^{-1}. These data lead to the conclusion that CpMn(CO)(diphos) undergoes one electron oxidation under the influence of TCQD.

The kinds of products formed in the reactions of transition metal π-complexes with π-acids (CTC or radical-anion salts) depend on the polarity of the solvent and on the relative strength of the donor and the π-acids involved in the interaction. Polar solvents should promote electron transfer and the formation of CTC is more likely in a medium with a low dielectric constant. For example, the CTC $Cp_2Fe.TCE$, which exists in the solid state and in solution in cyclohexane, dissociates in acetonitrile[119,120]:

$$Cp_2Fe \cdot TCE \rightleftarrows Cp_2Fe^+ + TCE^-$$

The complexes $(Arene)Cr(CO)_3$ form CTC with TNB, p-benzoquinone, TCE, and chloranil (CA),[117,121–123] the most stable CTC being formed with TNB.[117,121] The stronger π-acids may promote a more complete electron transfer. In solution the starting materials and the reaction products are involved in an equilibrium whose position depends on the concentration; in dilute solutions the equilibrium is displaced towards the starting materials.

In benzene solutions EPR signals due to mixtures of $(Arene)Cr(CO)_3$ with π-acids (TNB, CA, and TCE) have not been observed, while in nitromethane the signals due to radicals have been noted[121]. Thus the chromium complex is oxidised in a polar solvent.

Solid adducts with π-acids have been obtained for a number of π-complexes. Thus $(C_6H_6)_2Cr$, which is very readily oxidised to $(C_6H_6)_2Cr^+$, like ferrocene, gives rise to solid 1:1 salts with TCE, TNB, CA, and p-quinone, which are stable in air[124]. The oxidation of $(C_6H_6)_2Cr$ by π-acids has been demonstrated convincingly by various methods—EPR, infrared spectroscopy, and electronic spectroscopy. The EPR spectrum of each adduct contains two signals corresponding to $(C_6H_6)_2Cr^+$ and the radical-anions of the π-acids.

Solid adducts of Cp_2Co and Cp_2Ni with CA^- and TNB have been isolated: $Cp_2Co.CA$, $Cp_2Co.2CA$, $Cp_2Ni.2CA$, and $Cp_2Co.TNB$. The 1:1 adducts are CTC, in contrast to the

1:2 adducts, which are salt-like[125]. The above adducts of the complexes Cp_2M are relatively stable in air compared with the initial Cp_2Co or Cp_2Ni, which are unstable as regards oxidation. Ferrocene also forms complexes in solution with *p*-benzoquinone[125], CA,[125] TCQD,[126] TCE,[119,120,123] tetrachlorophthalic anhydride[125], and TNB.[127] The complexes Cp_2M (M = Ru or Os) are oxidised by TCE in acetonitrile with formation of salts of Cp_2M^+.[123]

The solid complex CpMn(CO)(diphos).TCQD, which, as in solutions, has the structure of the salt $[CpMn(CO)(diphos)]^+$. $.TCQD^-$ (EPR and infrared spectra), has been isolated from benzene solution[118].

The problem of the relative orientations of the donor and acceptor molecules in the CTC has been discussed in some studies. According to X-ray diffraction data[122], the TNB molecules in the adduct $(MeC_6H_5)Cr(CO)_3$.TNB are located in planes which are approximately parallel to the planes of the arene rings and the planes passing through the oxygen atoms of the CO groups in the chromium complex. The distance between the planes of the cyclic ligand and the TNB molecule is 3.41 Å, while the plane of the oxygen atoms of the CO groups is separated from the plane of the other acceptor molecule by 2.97 Å. Thus both the arene ring and the CO groups should be involved in the formation of the complex. (2,5-Dimethyldecamethylene-*ansa*-benzene)tricarbonylchromium also forms a complex with TNB.[123] It is postulated in this case that the acceptor molecules form a bond with the CO groups of the chromium complex, since the π-ring is blocked by the bridge with ten CH_2 units. However, this evidence is not convincing, because the decamethylene ring, being fairly long, can bend away and need not block the benzene ring.

The nature of the influence of substituents in the arene ring of the complexes $Arene(CO)_3$ on the frequencies of the charge-transfer bands in the spectra of CTC with TCE has been investigated[128]. The satisfactory correlation between the position of the CTB and the σ^+ constant of the substituent in the aromatic ring led the authors to postulate that, in the formation of the CTC, TCE interacts with the aromatic ring of the arenechromiumtricarbonyl derivatives,

VI. CONCLUSION

It has been shown from extensive experimental data that the TMC possess distinct basic properties and readily interact with a wide range of aprotic acids. The interaction can be both via the central metal atom and via the ligands.

One of the main centres where the acid–base interaction takes place is the transition metal atom. The manifestation of basic properties has been noted for virtually all Group V–VIII transition metals. There are not data for the basic properties of Group III and IV metal (Sc, Y, lanthanides, and titanium and its analogues) complexes as well as complexes in which the metal has the d^{10} configuration and which contain Cu^+, Ag^+, Zn^{2+}, Cd^{2+}, and Hg^{2+}. Thus basic properties are most characteristic of the complexes of metals with partially filled *d*-orbitals containing not less than four *d* electrons.

Allowance for the possibility of the interaction via the metal atom permits a new approach to the problem of the study of the mechanisms of the reactions of TMC, particularly the reactivity of π-complexes containing cyclic π-ligands. Evidently, one cannot regard the reactions of these compounds with electrophiles simply by analogy with the reactions of the free ligands without taking into account the role of the central atom and its ligand environment. Such reactions include the so-called aromatic substitution reactions [characteristic of ferrocene, $(C_5H_5)Mn(CO)_3$ derivatives, and certain other π-complexes]: isotope exchange between hydrogen and acids, acylation, alkylation, mercuration, etc. Throughout the initial period of these studies, it was traditional to compare the rates of these reactions and the properties of the π-complexes and the corresponding benzene derivatives. However, such comparison is apparently not legitimate. Although many reactions of π-complexes and aromatic compounds proceed under similar conditions, their mechanisms can be significantly different.

It was demonstrated above with numerous examples that aprotic acids (aluminium, tin, and iron halides) form adducts with many π-complexes via the central atom or via the ligands. The same halides catalyse Friedel–Crafts alkylation and acylation—reactions characteristic of many π-complexes (ferrocene, cymantrene, etc.). In considering the mechanisms of such reactions, it would therefore be incorrect to ignore the possibility of adduct formation; despite the similarity of conditions, the mechanism of the acylation of organometallic π-complexes can differ significantly from the mechanism of the acylation of benzene and its analogues. It would be no exaggeration to state that, as data on the basicity of TMC accumulate, demonstration is obtained the "ricochet" substitution mechanism, proposed more than 20 years ago by Nesmeyanov and coworkers[129,130], according to which the attack by the reagent is directed initially to the central metal atom, after which there is a change of direction from the metal to the cyclic π-ligand. Many examples of reversible rearrangements of this type with migration of a proton[131–133] as well as alkyl and other groups[134,135] have been found recently. The ricochet substitution mechanism has been used to account for the mechanism of the acid exchange of hydrogen in cyclic π-ligands (cyclopentadienyl, benzene) in iron, manganese, chromium, and rhenium complexes[136]. The ideas concerning the basicity of the complexes and the important role of the central metal atom can be used to explain the specificity, kinetics, and nature of the products of many other reactions of π-complexes with electrophiles, for example, the cleavage of the M–C σ-bonds and metal–metal bonds under the influence of hydrogen halides, halogens, and mercury salts HgX_2.

In conclusion, at present the extensive data concerning the basicity of the TMC contain virtually no quantitative data based on the study of the kinetics and thermodynamics of the interaction of the TMC with various electrophiles and that the entire data available are so far purely qualitative.

REFERENCES

1. G.Wilkinson and J.M.Birmingham, J.Amer.Chem.Soc., **77**, 3421 (1953).
2. A.Davison, W.McFarlane, L.Pratt, and G.Wilkinson, J.Chem.Soc., 3653 (1962).
3. B.V.Lokshin, V.I.Zdanovich, N.K.Baranetskaya, V.N.Setkina, and D.N.Kursanov, J.Organometal. Chem., **37**, 331 (1972).
4. D.N.Kursanov, V.N.Setkina, P.V.Petrovsky, V.I.Zdanovich, N.K.Baranetskaya, and I.D.Rubin, J.Organometal.Chem., **37**, 339 (1972).
5. B.V.Lokshin, A.G.Ginzburg, V.N.Setkina, D.N.Kursanov, and I.B.Nemirovskaya, J.Organometal. Chem., **37**, 347 (1972).
6. J.C.Kotz and D.G.Pedrotty, Organometal.Chem. Rev.(A) **4**, 479 (1969).
7. D.F.Shriver and A.Alich, Coordinat.Chem.Rev., **8**, 15 (1972).
8. D.F.Shriver, J.Organometal.Chem., **94**, 259 (1975).

9. B.Demerseman, G.Bouquet, and M.Bigorgne, J.Organometal.Chem., **35**, 341 (1972).
10. J.P.Collman and W.R.Rooper, Adv.Organometal. Chem., **7**, 53 (1968).
11. Z.Vaska, Acc.Chem.Res., 1, 335 (1968).
12. K.Edgar, B.F.G.Johnson, J.Lewis, and S.B.Wild, J.Chem.Soc.(A), 2851 (1968).
13. R.Kummer and W.A.G.Graham, Inorg.Chem., **7**, 315 (1968).
14. D.F.Shriver, Acc.Chem.Res., **3**, 231 (1970).
15. R.S.Nyholm and K.Vriese, J.Chem.Soc., 5337 (1965).
16. R.N.Scott, D.F.Shriver, and L.Vaska, J.Amer. Chem.Soc., **90**, 1079 (1968).
17. C.B.Dammann, L.J.Hughey, D.C.Jocha, T.J.Meyer, P.E.Rahita, and T.R.Weaver, Inorg.Chem., 12, 2206 (1973).
18. B.V.Lokschin, A.A.Pasinsky, N.E.Kolobova, K.N.Anisimov, and Yu.V.Makarov, J.Organometal. Chem., **55**, 315 (1973).
19. J.C.Kotz and D.G.Pedrotty, J.Organometal.Chem., **22**, 425 (1970).
20. B.V.Lokshin, E.B.Rusach, V.S.Kaganovich, V.V.Krivykh, A.N.Artemov, and N.I.Sirotkin, Zhur.Strukt.Khim., **16**, 592 (1975).
21. D.C.Harris and H.B.Gray, Inorg.Chem., **14**, 1215 (1975).
22. B.V.Lokshin, E.B.Rusach, N.E.Kolobova, Yu.V.Makarov, N.A.Ustynyk, V.I.Zdanovich, A.Zh.Zhakaeva, and V.N.Setkina, J.Organometal. Chem., **108**, 353 (1976).
23. A.G.Ginzburg, B.V.Lokshin, V.N.Setkina, and D.N.Kursanov, J.Organometal.Chem., **55**, 357 (1973).
24. A.J.Hart-Davis and E.A.G.Gracham, Inorg.Chem., **9**, 2658 (1970).
25. D.F.Shriver, M.P.Jonson, R.N.Scott, and J.F.Yackovitz, "Proceedings of the International Conference on Coordination Chemistry, Zakopane, 1966", p.248.
26. P.Powell and H.Nöth, Chem.Comm., 637 (1967).
27. T.D.Coyle and F.G.A.Stone, in "Progress in Boron Chemistry" (Edited by H.Steinberg and A.L.McCloskey), The Macmillan Co., New York, 1964, Vol.65.
28. B.V.Lokshin, E.B.Rusach, Z.P.Valueva, A.G.Ginzburg, and N.E.Kolobova, J.Organometal. Chem., **102**, 535 (1975).
29. Yu.A.Kharitonov, Kh.U.Ikramov, and A.V.Babaeva, Zhur.Neorg.Khim., 10, 2424 (1965)[Russ.J.Inorg. Chem., No.11 (1965)].
30. Yu.A.Kharitonov, Kh.U.Ikramov, and A.V.Babaeva, Dokl.Akad.Nauk SSSR, **158**, 1412 (1964).
31. B.Swanson and D.F.Shriver, Inorg.Chem., **9**, 1406 (1970).
32. J.S.Kristoff and D.F.Shriver, Inorg.Chem., 12, 1788 (1973).
33. N.E.Kim and D.F.Shriver, J.Amer.Chem.Soc., **91**, 5173 (1969).
34. N.E.Kim, N.J.Nelson, and D.F.Shriver, Chem. Chim.Acta, **7**, 393 (1973).
35. J.S.Kristoff and D.F.Shriver, Inorg.Chem., **13**, 499 (1974).
36. A.Alich, N.J.Nelson, and D.F.Shriver, Chem. Comm., 254 (1971).
37. Y.C.Kotz and C.D.Turnipsed, Chem.Comm., 41 (1970).
38. A.Crease and P.Legzdins, J.Chem.Soc., Dalton Trans., 1501 (1973).
39. B.V.Lokshin and E.B.Nazarova, Koord.Khim., **3**, 857 (1977).
40. B.D.Dombek and R.J.Angelici, J.Amer.Chem.Soc., **96**, 7568 (1974).
41. K.Dey and H.Werner, J.Organometal.Chem., **137**, C28 (1977).
42. A.I.Gusev and Yu.T.Struchkov, Zhur.Strukt.Khim., 12, 1121 (1971).
43. D.J.Cook, J.L.Dawes, and R.D.W.Kemmitt, J.Chem. Soc.(A), 1547 (1967).
44. J.N.Nowell and D.R.Russell, Chem.Comm., 817 (1967).
45. W.H.Morrison and D.N.Hendrickson, Inorg.Chem., 11, 2913 (1972).
46. J.N.Nowell and D.R.Russell, J.Chem.Soc., Dalton Trans., 2393 (1972).
47. J.N.Nowell and D.R.Russell, J.Chem.Soc., Dalton Trans., 2393 (1972).
48. A.N.Nesmeyanov, E.G.Perevalova, R.V.Golovnya, and O.A.Nesmeyanova, Dokl.Akad.Nauk SSSR, **97**, 459 (1954).
49. A.N.Nesmeyanov, K.N.Anisimov, and Z.P.Valueva, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 1683 (1962).
50. A.N.Nesmeyanov, K.N.Anisimov, N.E.Kolobova, and L.I.Baryshnikov, Izv.Akad.Nauk SSSR, Otd. Khim.Nauk, 1135 (1964).
51. G.K.-I.Magomedov, V.G.Syrkin, A.S.Frenkel', and O.A.Zakharchenko, Zhur.Obshch.Khim., **45**, 2530 (1975).
52. G.K.-I.Magomedov, A.I.Gusev, A.S.Frenkel', V.G.Syrkin, L.I.Chaplina, and S.N.Gurkova, Koord.Khim., 2, 257 (1976).
53. A.G.Ginsberg, G.K.-I.Magomedov, A.S.Frenkel', V.N. Setkina, and D.N.Kursanov, Izv.Akad.Nauk SSSR, Ser.Khim., 2405 (1978).
54. D.M.Adams, D.J.Cook, and R.D.W.Kemmitt, Nature, **205**, 589 (1965).
55. D.M.Adams, D.J.Cook, and R.D.W.Kemmitt, J.Chem. Soc.(A), 1067 (1968).
56. K.R.Mann, W.H.Morrison, and D.N.Hendrickson, Inorg.Chem., 13, 1181 (1974).
57. J.P.Collman and W.R.Roper, Chem.Comm., 244 (1966).
58. L.I.Denisovich, N.V.Sakurin, A.A.Bezrukova, and S.P.Gubin, J.Organometal.Chem., **81**, 207 (1974).
59. A.J.Oliver and W.A.G.Graham, Inorg.Chem., **9**, 2653 (1970).
60. J.S.Kristoff, N.J.Nelson, and D.F.Shriver, J.Organometal.Chem., 49, C82 (1973).
61. J.Chatt, R.H.Crabtree, E.A.Jeffery, and R.L.Richards, J.Chem.Soc., Dalton Trans., 1167 (1973).
62. D.F.Shriver and A.Alich, Inorg.Chem., 11, 2985 (1972).
63. M.Aresta, Gazzetta, **102**, 781 (1972).
64. J.M.Burlitch and R.B.Petersen, J.Organometal. Chem., **24**, C65 (1970).
65. J.Z.Bilhou and J.M.Basset, J.Organometal.Chem., 132, 395 (1977).
66. M.P.Johnson and D.F.Shriver, J.Amer.Chem.Soc., **88**, 301 (1966).
67. H.Brunner, P.C.Wailes, and H.D.Kaesz, Inorg. Nuclear Chem.Letters, 1, 125 (1965).
68. A.Storr and B.S.Thomas, Canad.J.Chem., 49, 2504 (1971).
69. P.C.Wailes and H.Weigold, J.Organometal.Chem., **24**, 713 (1970).
70. D.F.Shriver, J.Amer.Chem.Soc., **85**, 1403 (1963).
71. D.Hall, J.H.Slater, B.W.Fritzsimmons, and K.Wade, J.Chem.Soc.(A), 800 (1971).

72. M.Pankowski, D.Demerseman, G.Bouquet, and M.Bigorgne, J.Organometal.Chem., **35**, 155 (1972).
73. M.Pankowski and M.Bigorgne, J.Organometal. Chem., **110**, 331 (1976).
74. R.Kummer and W.A.G.Graham, Inorg.Chem., 7, 1208 (1968).
75. T.Takano, Bull.Chem.Soc.Japan, **46**, 552 (1973).
76. D.J.Patmore and W.A.G.Graham, Inorg.Chem., 7, 771 (1968).
77. A.J.Oliver and W.A.G.Graham, Inorg.Chem., 10. 1 (1971).
78. J.K.Still and K.S.Y.Lau, Acc.Chem.Res., **10**, 434 (1977).
79. R.Robson, Inorg.Chem., **13**, 475 (1974).
80. A.G.Ginzburg, N.G.Bokyi, A.I.Yanovsky, Yu.T.Struchkov, V.N.Setkina, and D.N.Kursanov, J.Organometal.Chem., **136**, 45 (1977).
81. A.G.Ginzburg, L.A.Fedorov, P.V.Petrovsky, E.I.Fedin, V.N.Setkina, and D.N.Kursanov, J.Organometal.Chem., **73**, 77 (1974).
82. A.G.Ginzburg, P.O.Okulevich, V.N.Setkina, G.A.Panosyan, and D.N.Kursanov, J.Organometal. Chem., **81**, 201 (1974).
83. N.I.Pyshnograeva, V.N.Setkina, G.A.Panosyan, P.V.Petrovsky, Yu.V.Makarov, N.E.Kolobova, and D.N.Kursanov, J.Organometal.Chem., **108**, 85, 209 (1976).
84. I.Klikorka, J.Pavlik, E.Večernikova, and M.Fojtkova, "Proceedings of the IInd Conference on Coordination Chemistry, Bratislava, 1972", p.171.
85. C.D.Pribula and T.Z.Brown, J.Organometal.Chem., 71, 415 (1974).
86. M.Y.Darensbourg, D.I.Darensbourg, D.Burns, and D.A.Drew, J.Amer.Chem.Soc., **98**, 3127 (1976).
87. K.H.Pannell, Yu-Shen Chen, and K.L.Belknar, Chem.Comm., 362 (1977).
88. P.A.W.Dean, D.G.Ibbott, and G.M.Rancroft, Chem. Comm., 901 (1976).
89. S.W.Ulter, P.M.Scarstad, J.M.Burlitch, and G.M.Hughes, J.Amer.Chem.Soc., **95**, 4469 (1973).
90. G.B.McVicker, Inorg.Chem., **14**, 2087 (1975).
91. R.B.Petersen, J.J.Stezowski, C.Wan, J.M.Burlitch, and R.E.Hughes, J.Amer.Chem.Soc., **93**, 3532 (1971).
92. M.R.Snow and F.L.Wimmer, Austral.J.Chem., **29**, 2349 (1976).
93. A.N.Nesmeyanov, N.E.Kolobova, Yu.V.Makarov, and K.N.Anisimov, Izv.Akad.Nauk SSSR, Ser.Khim., 1826 (1969).
94. A.M.Bond, R.Colton, and J.J.Jackowski, Inorg. Chem., **14**, 2526 (1975).
95. J.A.Connor, G.K.McEwen, and J.Rix, J.Chem.Soc., Dalton Trans., 589 (1974).
96. S.C.Tripathi, S.C.Srivastava, and A.K.Shrimal, Inorg.Chim.Acta, **18**, 231 (1976).
97. J.G.Dunn and D.A.Edwards, J.Organometal.Chem., **36**, 153 (1972).
98. I.V.Howell and L.M.Venanzi, Inorg.Chim.Acta, **3**, 121 (1969).
99. M.R.Snow, P.Pauling, and M.H.B.Stiddard, Austral.J.Chem., **22**, 709 (1969).
100. V.V.Korol'kov, L.M.Epshtein, E.V.Shumilina, and T.P.Tolstaya, Vestnik Moskov.Gos.Univ., **18**, 98 (1977).
101. Y.S.Sohn, A.W.Schlueter, D.N.Hendrickson, and H.B.Gray, Inorg.Chem., **13**, 301 (1974).
102. R.B.King, J.Inorg.Nuclear Chem., 25, 179 (1967).
103. M.H.B.Stiddard and R.E.Townsend, J.Chem.Soc.(A), 2355 (1969).
104. S.Kato, M.Tsutsui, D.L.Cullen, and E.F.Meyer, J.Amer.Chem.Soc., **99**, 620 (1977).
105. G.Bouquet, B.Demerseman, and M.Bigorgne, J.Organometal.Chem., **127**, 175 (1977).
106. B.D.Dombek and R.J.Angelichi, J.Amer.Chem.Soc., **97**, 1261 (1975).
107. H.Werner, H.Neukomm, and W.Klani, Helv.Chim. Acta, **60**, 326 (1977).
108. E.L.Muetterties and J.W.Rathke, Chem.Comm., 850 (1974).
109. I.R.Sanders, J.Chem.Soc., Dalton Trans., 2340 (1975).
110. N.G.Connelly and G.A.Johnson, J.Organometal. Chem., 77, 341 (1974).
111. P.M.Treichel, K.P.Wagner, and H.J.Much, J.Organometal.Chem., **86**, C13 (1975).
112. N.G.Connelly and M.D.Kitchen, J.Chem.Soc., Dalton Trans., 2165 (1976).
113. N.G.Connelly and R.L.Kelly, J.Organometal.Chem., **120**, C16 (1976).
114. N.G.Connelly and K.R.Somers, J.Organometal.Chem., **113**, C39 (1976).
115. N.G.Connelly and M.D.Kitchen, J.Chem.Soc., Dalton Trans., 931 (1977).
116. J.A.Connor, P.I.Riley, and C.I.Rix, J.Chem.Soc., Dalton Trans., 1317 (1977).
117. G.Huttner and E.O.Fischer, J.Organometal.Chem., **6**, 288 (1966).
118. B.V.Lokshin, E.B.Nazarova, and A.G.Ginzburg, J.Organometal.Chem., 129, 379 (1977).
119. M.Rosenblum, R.W.Fish, and C.Bennett, J.Amer. Chem.Soc., **86**, 5166 (1964).
120. O.W.Webster, W.Mahler, and R.E.Benson, J.Amer. Chem.Soc., **84**, 3678 (1962).
121. J.W.Fitch and J.J.Lagowski, J.Organometal.Chem., 5, 480 (1966).
122. O.L.Carter, A.T.McPhail, and G.A.Sim, J.Chem. Soc.(A), 822 (1966).
123. G.Huttner and E.O.Fischer, J.Organometal.Chem., **8**, 299 (1967).
124. J.W.Fitch and J.J.Lagowski, Inorg.Chem., 4, 864 (1965).
125. J.C.Goan, E.Berg, and H.E.Podall, J.Org.Chem., **29**, 975 (1964).
126. L.R.Melby, R.J.Harder, W.R.Hertler, W.Mahler, R.E.Benson, and W.E.Mochel, J.Amer.Chem.Soc., **84**, 3374 (1962).
127. B.Hetnarski, Bull.Acad.Polon.Sci., **13**, 563 (1965).
128. A.N.Egorochkin, V.A.Kuznetsov, A.N.Artemov, N.I.Sirotkin, V.G.Kirilicheva, and G.A.Razuvaev, Dokl.Akad.Nauk SSSR, **227**, 878 (1976).
129. A.N.Nesmeyanov, Bull.Soc.chim.France, 1229 (1965).
130. A.N.Sorokin and G.A.Domrachev, "Trudy po Khimii i Khimicheskoi Tekhnologii" (Reports on Chemistry and Chemical Engineering), Izd. Gor'kovsk.Gos.Univ., 1965, p.665.
131. B.F.G.Johnson, J.Lewis, and D.J.Yarrow, J.Chem. Soc., Dalton Trans., 2084 (1972).
132. H.Werner, G.Matmann, A.Salzer, and E.Winkler, J.Organometal.Chem., **25**, 461 (1970).
133. J.W.Byrne, H.V.Blaser, and I.A.Osborn, J.Amer. Chem.Soc., **97**, 3871 (1975).
134. F.W.S.Bernfield and M.L.H.Green, J.Chem.Soc., Dalton Trans., 1324 (1974).
135. W.K.Dean and W.A.G.Graham, Inorg.Chem., **16**, 1061 (1977).

136. V.N.Setkina, N.K.Baranetskaya, A.G.Ginzburg, V.I.Zdanovich, M.N.Nefedova, and D.N.Kursanov, J.Organometal.Chem., **61**, 287 (1973).

Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow

Translated from *Uspekhi Khimii*, **49**, 252-282 (1980) U.D.C. 541.515

Photochemical Reactions of Free Radicals in the Solid Phase

M.Ya.Mel'nikov and N.V.Fok

The photochemical reactions of free radicals of different classes in the solid phase (solids, low-molecular-weight organic compounds, and polymers) are examined and data characterising the absorption spectra of the radicals are presented. The role of free radicals in processes involving the breakdown of substances under the action of light is discussed. The bibliography includes 299 references.

CONTENTS

I.	Introduction	131
II.	Photochemical reactions of alkyl radicals	131
III.	Photochemical reactions of alkoxy- and peroxy-radicals	135
IV.	Photochemical reactions of acyl radicals	136
V.	Photochemical reactions of radicals derived from alcohols and ethers	137
VI.	Photochemical reactions of radicals derived from esters, aldehydes, ketones, acids, and acid anhydrides	139
VII.	Conclusion	142

I. INTRODUCTION

The photochemical reactions of free radicals are varied and numerous published reports have presented experimental evidence confirming their occurrence. However, their mechanism is in many instances still unestablished.

The study of the general features of the photochemical reactions of free radicals is important for the determination of the relation between the nature of the excited state and the mode of chemical reactions, and also in connection with the role which these processes play in the breakdown of substances under the action of light.

The absorption spectra of free radicals formed in solid-phase photolysis and radiolysis at relatively high concentrations are characterised by a bathochromic shift relative to the spectra of the initial compounds and fairly high extinction coefficients. On irradiation, more active species are formed from the radicals, unstable under these conditions and regenerating the initial radicals in reactions with water molecules. As a result, radical photochemical chain processes arise in the system and lead to an appreciable decomposition of the medium:

$$\dot{\text{C}}\!-\!\Phi \xrightarrow{h\nu} \text{M}_1 + \dot{\text{R}}$$

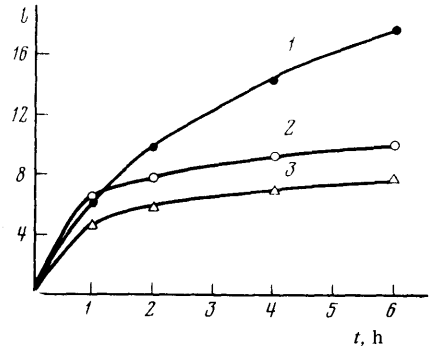
$$\dot{\text{R}} + \text{M}_0 \rightarrow \text{M}_2 + \dot{\text{C}}\!-\!\Phi,$$

where Φ is a functional group, M_0 a molecule of the medium and M_1 and M_2 are reaction products. The Figure presents experimental relations characterising the development of photochemical radical chains in methylamine, ethanol, and acetic anhydride. The average photochemical radical chain length $l = [M_1]/[\dot{C}\!-\!\Phi]_0 = [M_2]/[\dot{C}\!-\!\Phi]_0$ in the test systems did not exceed 20 and the main factor limiting it is radical recombination processes.

In order to determine the mechanisms of photochemical reactions, studies were made on the nature and kinetics of the formation of free radicals in the solid phase by ultraviolet and infrared spectroscopy, etc., and also on the nature of the stable reaction products—by gas–liquid chromatography, mass spectrometry, etc.

Reviews have been published recently in which the optical properties of free radicals are discussed[2], the available information about the photochemical reactions involving them is compiled[3-5], and attempts are made at a general survey and the determination of several general characteristics of these processes[6,7].

In the present review we confined ourselves to an examination of the photochemical reactions of certain free radicals and their role in solid-phase photolytic processes.



Variation of the photoradical chain length l in the photolysis of radicals by light at a wavelength $\lambda \geq 300$ nm at 77 K in different solvents: 1) methylamine; 2) ethanol; 3) acetic anhydride[1].

II. PHOTOCHEMICAL REACTIONS OF ALKYL RADICALS

ESR data have shown that the unpaired electron in alkyl radicals is in the p_z orbital of the carbon atom. Alkyl radicals are formed in a chemically excited state as a result of the transfer of the unpaired electron from the p_z orbital to an antibonding σ-orbital and from a bonding σ-orbital to a non-bonding orbital (σ–π^* transition). These transitions are symmetry-forbidden, but analysis of literature data nevertheless shows that alkyl radicals absorb light at wavelengths $\lambda \leq 300$ nm and have fairly high extinction coefficients. A short-wavelength absorption corresponds to π–σ^*

transition. The absorption associated with the $\sigma-\pi^*$ transition could not be observed experimentally. It follows from the analysis of the vibrational structure of the absorption spectra of methyl radicals in the gas phase that, on transition to an electronically excited state[8], the geometry of the methyl radical does not change significantly.

Table 1 presents the available literature data for the absorption spectra of alkyl radicals.

Table 1. Absorption spectra of alkyl radicals.

Radical	λ_{max}	$10^{-3}\varepsilon_{\lambda max}$, litre mol^{-1} cm^{-1}	Conditions of generation*	Refs.
$\dot{C}H_3$	216	—	f.p. of $Hg(CH_3)_2$ and $(CH_3)_2O$	9,10
$\dot{C}H_3$	216	—	p. of $(CH_3)_2O$, 1180 K	11
$\dot{C}H_3$	215.8	—	py of $(CH_3)_2N_2$	12
$\dot{C}H_3$	216.4	—	py of CH_4	13
$\dot{C}H_3$	—	$\varepsilon_{210}=0.85$	p.r. of CH_4 in H_2O	14
$\dot{C}H_3$	217	$\varepsilon G^{**}=14$	proton p.r. of CH_4	15
$\dot{C}H_3$	216	—	f.p. of but-1-ene and hexa-1,5-diene, 298 K	16
$\dot{C}H_3$	215.8; 216.4	—	f.p. of acetaldazine	17
$\dot{C}H_3$	216	1.01 ± 0.07	f.p. of acetone, 298 K	18
$\dot{C}H_3$	213 ± 2	1.6	p.r. of CH_4 in H_2O, 298 K	19
$\dot{C}H_3$	216.5	—	p. of azomethane	20
$\dot{C}H_3$	216	—	f.p. of CH_3Hal and alkyl nitrates	21
$\dot{C}H_3$	216	1.6	f.p. of azomethane in H_2O	22
$\dot{C}H_3$	216.4	—	f.p. of azomethane	23
$\dot{C}D_3$	214	—	f.p. of CD_3I	24
$\dot{C}D_3$	214—215	—	p. of $(CD_3)_2N_2$	25
$\dot{C}_2H_5$	227	$\varepsilon G=22$	proton p.r. of C_2H_6	15
$\dot{C}_2H_5$	200	$\varepsilon_{210}=0.74$	p.r. of C_2H_6 in H_2O	19
$\dot{C}_2H_5$	248	0.75 ± 0.18	p. of azoethane	20
$\dot{C}_2H_5$	222—224.2	—	py of $(C_2H_5)_2O$ and C_2H_6	26
$\dot{C}_2H_5$	206 ± 1	—	p. of $H_2+C_2H_4$ and $H_2+C_2H_6$	27
n-$\dot{C}_3H_7$	225	$\varepsilon G=23$	proton p.r. of C_3H_8	15
iso-$\dot{C}_3H_7$	260	—	r- of $(CH_3)_2CHBr$ in 3-MP, 77 K	28
iso-$\dot{C}_3H_7$	233	2.34 ± 0.6	p. of azoisopropane	20
n-$\dot{C}_4H_9$	232	$\varepsilon G=19$	proton p.r. of C_4H_{10}	15
t-$\dot{C}_4H_9$	229	3.1	p. of 2,2-azoisobutane	29
t-$\dot{C}_4H_9$	229	4.8	p. of 2,2-azoisobutane	20
t-$\dot{C}_4H_9$	230	$\varepsilon_{254}=0.8\pm0.3$	r. of $(CH_3)_3CCl$ in 3-MP, 77 K	30
n-$\dot{C}_5H_{11}$	234	1.7	p.r. of C_5H_{12}, 297 K	31
n $\dot{C}_5H_{11}$	234	1.1	p.r. of C_5H_{12} in H_2O, 297 K	31
n-$\dot{C}_5H_{11}$	245	$\varepsilon G=22$	proton p.r. of C_5H_{12}	15
n-$\dot{C}_6H_{13}$	240	2.1 ± 0.4	p.r. of C_6H_{14}, 293 K	32
$\dot{C}_6H_{13}$	230	1.0 ± 0.3	r. of 2,3-dimethylbutane, 77 K	30
$\dot{C}_6H_{13}$	218	—	r. of 2-methylpentane in adamantane, 298 K	33
$\dot{C}_6H_{13}$	250	—	r. of 3-MP, 77K	34
$\dot{C}_6H_{13}$	240	1.8 ± 0.6	r. of 3-MP, 77 K	35,36
$\dot{C}_7H_{15}$	240	1.6 ± 0.6	r. of 3-ethylpentane, 77 K	36
$\dot{C}_8H_{17}$	245	1.4 ± 0.5	r. of 3-methylheptane, 77 K	36
C_8H_{17}	245	1.4 ± 0.5	r. of 4-methylheptane, 77 K	36
cyclo-$\dot{C}_5H_9$	—	$\varepsilon_{280}=0.43$	p.r. of cyclopentane in H_2O, 293 K	37
cyclo-$\dot{C}_5H_9$	—	$\varepsilon_{215}=1$	p.r. of cyclopentane in H_2O, 293 K	38
cyclo-$\dot{C}_5H_9$	235	$\varepsilon_{248}=0.48$	p.r. of cyclopentane, 77 K	39
cyclo-$\dot{C}_6H_{11}$	235	1.4 ± 0.3	p.r. of cyclohexane, 293 K	32
cyclo-$\dot{C}_6H_{11}$	255	0.34	p.r. of cyclohexane, 293 K	40
cyclo-$\dot{C}_6H_{11}$	240	1.5	p.r. of cyclohexane, 293 K	41
cyclo-$\dot{C}_6H_{11}$	240	$\varepsilon_{250}=0.92$	p.r. of cyclohexane in H_2O	38
cyclo-$\dot{C}_6H_{11}$	210, 245	—	proton p.r. of cyclohexane	15
 $-CH_3$	245	1.4 ± 0.2	p.r. of methylcyclohexane, 293 K	42
$\sim CH_2\dot{C}HCH_2\sim$	250	1.5	r. of polyethylene, 103 K	43
$\sim CH_2\dot{C}HCH_2\sim$	215	1.8 ± 0.3	r. of polyethylene, 77 K	44
$\sim CH_2\dot{C}HCH_2\sim$	216	—	r. of polyethylene, 77K	45
$\sim CD_2\dot{C}DCD_2\sim$	216	—	r. of deuteropolyethylene, 77 K	46
$\dot{C}Cl_3$	230	2.3 ± 0.45	f.p. of CCl_4 in H_2O, 293 K	47
$\dot{C}_2Cl_5$	250	—	f.p. of $C_2Cl_4+Cl_2$, 300 K	48
$\sim CF_2\dot{C}(CF_3)CF_2\sim$	265	—	r. of TFE-hexafluoropropene copolymer, 77 K	49

*Notation: f.p. = flash photolysis; p.r. = pulse radiolysis; p. = photolysis; r = radiolysis; py = pyrolysis (flame).
**G = radiation-chemical yield.

Excited alkyl radicals can be involved in reactions of various types: isomerisation, substitution, and dissociation. We shall examine a number of specific examples of such reactions. Following irradiation at $\lambda = 260$ nm of t-butyl radicals, obtained in isobutyl bromide γ-irradiated at 77 K, the 10-line ESR spectrum of the t-butyl radical with a binomial distribution of intensities and a splitting of 23 G is transformed into a 5-line spectrum with intensity ratios 1:2:2:2:1 and a splitting of 21 G, which is due to the isobutyl radical[50]. The reaction is reversible and the reverse process occurs in various systems after the latter have been kept for a long time at 77 K:[51-54]

$$CH_3-\dot{C}(CH_3)_2 \overset{h\nu}{\rightleftarrows} \dot{C}H_2-CH(CH_3)_2.$$

The action of the total radiation of a high-pressure mercury lamp on t-butyl radicals obtained in isobutene γ-irradiated at 77 K leads to the formation of isobutyl and methylallyl radicals[54]. The authors attribute the appearance of isobutyl radicals to the possibility of isomerisation reactions, the dissociation of t-butyl radicals, or their reactions with the molecules of the medium.

Analogous photochemical processes take place under the influence of ultraviolet radiation in γ-irradiated n-, s-, iso-, and t-butyl chlorides, where the conversion of s-butyl radicals into n-butyl radicals and of t-butyl radicals into isobutyl radicals was observed by ESR.[55] When isotactic polypropylene (PP) γ-irradiated at 77 K is acted upon by radiation with $\lambda = 253.7$ nm, the resolution of the ESR spectrum is improved and a 4-line spectrum with the intensity ratios 1:3:3:1 and a splitting of 25.5 G appears. It has been attributed[56,57] to the isomerisation reaction

$$\sim CH_2-\dot{C}CH_3-CH_2\sim \overset{h\nu}{\rightleftarrows} \sim CH_2-CH(\dot{C}H_2)-CH_2\sim.$$

At the same time, a singlet line with $\Delta H \cong 17$ G was noted in the ESR spectra when deuteropolypropylene (DPP) was γ-irradiated at 77 K. The absence of hyperfine structure (HFS) components from the ESR spectrum of DPP suggested that the singlet spectrum is due to allyl radicals. Subsequent exposure to ultraviolet radiation leads to the disappearance of the singlet line and the appearance of an ESR spectrum consisting of 15 HFS lines with a splitting of 3.7 G, corresponding to the radical $\sim CD_2-\dot{C}(CD_3)-CD_2\sim$. These radicals are stable with respect to irradiation and do not undergo further photochemical reactions. The data obtained by Klinshpont et al.[58] suggest that the changes observed by Iwasaki et al.[56] are associated with the reactions of allyl and not alkyl radicals.

The action of ultraviolet radiation on the radical $\sim CF_2-\dot{C}(CF_3)-CF_2\sim$, obtained in the tetrafluoroethylene (TFE)–hexafluoropropylene copolymer γ-irradiated at 77 K, leads to the formation of the radicals $\sim CF_2-\underset{\dot{C}F_2}{CF}-CF_2\sim$, detected by their characteristic ESR spectrum[49].

Following γ-irradiation of polyisobutylene (PIB) at 77 K, a doublet with a splitting of 22 G was recorded in the ESR spectrum and was assigned to the radical $\sim C(CH_3)_2-\dot{C}H-C(CH_3)_2\sim$. When the specimens are heated to 213 K for 5 min, cooled to 77 K, and exposed to light with $\lambda \leqslant 303$ nm, the initial doublet is rapidly converted into a spectrum consisting of 15 lines[59]. These changes can be explained by the isomerisation

$$\sim \dot{C}H-CH(CH_3)_2 \overset{h\nu}{\rightleftarrows} \sim CH_2-\dot{C}(CH_3)_2.$$

On the basis of the change in the ESR spectra, it has been suggested that, after exposure to radiation with $\lambda = 253.7$ nm, the alkyl (n-propyl and t-butyl) radicals, formed on γ-irradiation of propene and isobutene at 77 K in an argon matrix,

may be converted into the corresponding allyl radicals[60,61]:

$$CH_3-CH_2-\dot{C}H_2 \xrightarrow{h\nu} CH_2 \cdots CH \cdots CH_2 + 2H(H_2) \ .$$

However, the absence of an analysis of the stable reaction products makes this hypothesis questionable. We believe that the mechanism proposed by Shamonina and Krotov[54] and involving the reaction of the excited alkyl radical with a molecule of the unsaturated compounds, for example

$$CH_3CH_2\dot{C}H_2 + CH_3CH=CH_2 \xrightarrow{h\nu} C_3H_8 + CH_2 \cdots CH \cdots CH_2 \ ,$$

is more probable.

It is important to note that the yields of the majority of the radicals quoted above are based solely on the analysis of the changes in the ESR spectra, which involves serious difficulties under the conditions of the solid-phase photolysis and radiolysis, particularly in polymeric matrices. Furthermore, in radiolysis there is a possibility of the formation of allyl radicals, whose photochemical reactions, which have been examined in detail in a number of reviews[3,6,7], can mask the reactions of alkyl radicals, as shown for DPP.[58]

When 0.01 M solutions of t-butyl chloride in 3-methylpentane (3-MP), γ-irradiated at 77 K, were irradiated in the wavelength range $240 \leq \lambda \leq 270$ nm, t-butyl radicals disappeared and 3-methylpentyl radicals appeared. The total number of free valences does not change under these conditions. The quantum yield Φ of the reaction in 3-MP was determined as 0.5 ± 0.15 from the initial sections of the kinetic curves for the disappearance of t-butyl radicals[30]. In this case there is apparently a reaction between the excited t-butyl radicals and the matrix molecules. The isomerisation of alkyl radicals in γ-irradiated frozen alkyl halides and other systems, observed previously[49,50,55,60,61], can also be explained by the reactions of excited alkyl radicals with matrix molecules:

$$\dot{R}^* + R_1-X \rightarrow R-X + \dot{R}_1 .$$

The formation of 3-methylpentyl radicals when alkyl radicals, obtained on γ-irradiation of 1 M solutions of alkyl chlorides in 3-MP, are exposed to radiation with $\lambda = 253.7$ nm at 77 K, was observed also in another study[62]. The fact that t-butyl radicals are partly converted into isobutyl radicals in solutions of t-butyl chloride in 3-MP is apparently associated with the high concentration of the solutions and the possibility of reactions involving associated species. According to Burbo's results[63], the formation of associated species from alkyl halide molecules in hydrocarbon matrices is observed at concentrations above 0.01 M.

By analysing the reaction products and the changes in the ESR spectra, it has been shown in a number of studies that alkyl radicals can dissociate on excitation. Thus, after photolysis of a solid solution of n-butyl iodide in argon at 4 K by radiation with $\lambda = 246$ nm, methyl radicals and hydrogen atoms appear, which the authors attribute to the dissociation of n-butyl radicals[64]. The rate constant for the abstraction of a hydrogen atom from the electronically excited radicals can reach approximately 10^9 s^{-1}:[65]

$$CH_3CH_2CH_2CH_2 \xrightarrow{h\nu} \begin{cases} \rightarrow CH_3CH_2CH=CH_2 + H \\ \rightarrow \underline{-CH_2CH_2CH_2-} + \dot{C}H_3 \end{cases} .$$

The formation of methyl radicals when isobutyl vinyl ether γ-irradiated at 77 K was exposed to ultraviolet light was recorded by ESR:[66]

$$\dot{C}H_2CH(CH_3)CH_2OCH=CH_2 \xrightarrow{h\nu} \dot{C}H_3 + CH_2=CHCH_2OCH=CH_2 \ .$$

The study of the kinetics of the accumulation of gaseous products in the photolysis of isotactic PP by the total radiation of the high-pressure mercury lamp showed[67] that the observed rates of gas evolution in photolysis are greater by 3–5 orders of magnitude than the rates which would be expected if the macroradicals underwent thermal decomposition. According to the authors[67], this implies that the macroradicals are to a large extent decomposed on electronic excitation. The study of the kinetics of the accumulation of gaseous products of the photolysis of PP in the presence of 2,2′,6,6′-tetramethylpiperidine 1-oxide showed that the yield of methane then increases almost by a factor of 250, while the yield of the remaining photolysis products hardly changes. Since methyl radicals and hence methane could not be formed from nitroxy-radicals, it was suggested[68] that the vigorous formation of methane is a consequence of the photochemical decomposition of the central PP macroradicals, arising in the reaction of excited nitroxy-radicals with the macromolecules:

$$\dot{R}^* + \sim CH_2-CH(CH_3)-CH_2\sim \rightarrow RH + \sim CH_2-\dot{C}(CH_3)-CH_2\sim \ ,$$
$$\sim CH_2-\dot{C}(CH_3)-CH_2\sim \xrightarrow{h\nu} \dot{C}H_3 + \sim CH_2\sim\ddot{C}-CH_2\sim \ .$$

The biradicals arising in the photolysis react with the polymer, which leads to the regeneration of the central PP macroradicals.

Irradiation of PP in the presence of an added aromatic sensitiser (hexahydropyrene) at 77 K by light at wavelengths in the range $260 \leq \lambda \leq 380$ nm, corresponding to the sensitiser absorption band, leads to the appearance of a 4-line ESR spectrum with nearly binomial intensity ratios, which was assigned to the radical $\sim CH(CH_3)\dot{C}HCH(CH_3)\sim$. On subsequent irradiation of the same specimens with radiation at wavelengths in the range $240 \leq \lambda \leq 270$ nm, which is hardly absorbed by the sensitiser so that there is virtually no sensitised radical formation, components due to the methyl radical are clearly manifested in the ESR spectrum. The action of light at wavelengths of $240 \leq \lambda \leq 270$ nm on the radicals $\sim CMe_2-\dot{C}H-CMe_2\sim$, formed in PIB on photolysis and radiolysis sensitised by aromatic compounds at 77 K, also leads to the formation of methyl radicals. These processes in PP and PIB take place without a change of the total number of free valences. The formation of methyl radicals under the influence of ultraviolet radiation on the macroradicals in PP and PIB apparently proceeds via the reactions[69,70]

$$\sim CH(CH_3)\dot{C}HCH(CH_3)\sim \xrightarrow{h\nu} \sim CH(CH_3)CH=CHCH_2\sim + \dot{C}H_3 \ ,$$
$$\sim C(CH_3)_2\dot{C}HC(CH_3)_2\sim \xrightarrow{h\nu} \sim C(CH_3)_2CH=C(CH_3)\sim + \dot{C}H_3 \ .$$

The numerous instances of the formation of methyl radicals when PP is exposed to radiation with $\lambda \leq 300$ nm can in fact be accounted for by the photolysis of alkyl macroradicals[71–77]. It has been shown that the additional action of radiation at wavelengths in the range $240 \leq \lambda \leq 270$ nm does not entail significant changes in the molecular weight of PP and PIB. Evidently the reactions

$$\sim CH(CH_3)\dot{C}HCH(CH_3)\sim \rightarrow \sim CHCH_3-CH=CHCH_3 + \dot{C}H_2CH(CH_3)CH_2\sim \ ,$$
$$\sim C(CH_3)_2\dot{C}HC(CH_3)_2\sim \rightarrow \sim (CH_3)_2CH=C(CH_3)_2 + \dot{C}H_2C(CH_3)_2CH_2\sim$$

which lead to the dissociation of the polymer chain, take place with low quantum yields if at all and do not cause an appreciable change in molecular weight[69,70].

At the same time, analysis of the composition of the products (methane, ethane, and ethylene), resulting from the exposure to light of alkyl radicals in γ-irradiated polyethylene (PE) at 77 K, led to the following reaction mechanism[78]:

$$\sim CH_2-\dot{C}H-CH_2\sim \xrightarrow{h\nu} \sim CH_2-\dot{C}H-CH_3 + CH_2=CH\sim \ ,$$
$$\sim CH_2-\dot{C}H-CH_3 \xrightarrow{h\nu} \begin{cases} \rightarrow \sim CH=CH_2 + \dot{C}H_3 \\ \rightarrow \sim CH_2-\dot{C}H-CH_3 + C_2H_4 \end{cases} ,$$

incorporating processes leading to the decomposition of the main polymer chain.

Significant changes occur in the ESR spectra of γ-irradiated branched aliphatic hydrocarbons at 77 K, following exposure to short-wavelength ultraviolet radiation. Thus the action of ultraviolet radiation on 3-MP γ-irradiated at 77 K leads, according to the authors[79,80], to the formation of methyl radicals:

$$C_2H_5\dot{C}(CH_3)C_2H_5 \xrightarrow{h\nu} C_2H_5C(CH_3)=CH_2 + \dot{C}H_3 \ .$$

However, one should note that the study of the structure of the radicals in branched aliphatic hydrocarbons γ-irradiated at 77 K established[81-84] that in this case the radicals $CH_3\dot{C}HR$, arising on dissociation of a secondary C–H bond, are formed preferentially. The mechanism of the formation of methyl radicals, proposed in the studies mentioned above[79,80], therefore requires revision. Analogous changes in the ESR spectra of 3-MP and deuterated 3-MP γ-irradiated at 77 K, have been observed after irradiation in another investigation[85].

Analysis of the changes in the ESR spectra occurring under the influence of radiation at wavelengths in the range $240 \leq \lambda \leq 270$ nm on 3-MP and 3-ethylpentane γ-irradiated at 77 K suggested that the photolysis of the corresponding hydrocarbon radicals proceeds with formation of ethyl radicals[35,36]. Ethane was detected among the gaseous reaction products, which constitutes additional confirmation of this conclusion:

$$CH_3\dot{C}HCH(CH_3)C_2H_5 \xrightarrow{h\nu} \dot{C}_2H_5 + CH_3CH=CHCH_3 \ .$$

When hydrogen sulphide and alkanethiols are photolysed in a 2-MP matrix at 77 K by radiation with $\lambda = 253.7$ nm, the changes in the ESR spectrum of 3-methylpentyl radicals are evidently associated with the appearance of small amounts of ethyl radicals as a result of the photolysis of the 3-methylpentyl radicals[86].

Table 2. Absorption spectra of alkoxy-radicals.

Radical	λ_{max}	$10^{-3}\varepsilon_{\lambda max}$, litre mol^{-1} cm^{-1}	Conditions of generation*	Refs
ȮH	280	—	r. of ice, 77 K	98,99
ȮH	280±10	0.45±0.14	r. of ice, 77 K	100
ȮH	280±5	0.56±0.05	p.r. of ice, 143-217 K	101
ȮH	230	—	f.p. of H_2O, 297 K	102
ȮH	<200	$\varepsilon_{200}=0.509$, $\varepsilon_{220}=0.523$, $\varepsilon_{230}=0.543$, $\varepsilon_{250}=0.463$	p.r. of $HClO_4$ in H_2O, 296-298 K	103
ȮH	—	$\varepsilon_{260}=0.37$	p.r. of $HClO_4$ in H_2O	104
ȮH	250—260	0.2	p.r. of H_2O	105
ȮH	260	—	p.r. of H_2O_2 in H_2O	106
ȮH	—	0.41±0.05	p.r. of H_2O_2 in H_2O	107
ȮH	230	0.543	p.r. of HCN in H_2O	108
ȮH	230	0.6	p.r. of NaCl in H_2O	109
ȮD	235	0.55	p.r. of $DClO_4$ in H_2O	110
$CH_3\dot{O}$	199.9; 203.6, 206.4	—	f.p. of methyl nitrite	111,112

*The notation is the same as in Table 1.

The exposure to radiation with $\lambda = 254$ nm of γ-irradiated polycrystalline n-hexane[87], 3-methylheptane, and 4-methylheptane[36] at 77 K led to the observation of changes in the ESR spectra, which could be attributed to the isomerisation of alkyl radicals:

$$\sim CH_2\dot{C}HCH_2\sim \xrightarrow{h\nu} \sim CH_2\dot{C}HCH_3 \ .$$

At the same time the observed reactions can be accounted for fully by the reaction of the excited alkyl radicals with matrix molecules.

Table 3. Absorption spectra of peroxy-radicals.

Radical	λ_{max}	$10^{-3}\varepsilon_{\lambda max}$, litre mol^{-1} cm^{-1}	Conditions of generation*	Refs.
$H\dot{O}_2$	230	$\varepsilon_{254}=0.83\pm0.125$	p.r. of $HClO_4$ in H_2O	115
$H\dot{O}_2$	230	—	p.r. of H_2SO_4 in H_2O, 298 K	116
$H\dot{O}_2$	243	$\varepsilon_{260}=0.34$	p.r. of H_2SO_4 in H_2O	117
$H\dot{O}_2$	240	1.15	r. of ice, 77 K	101
$H\dot{O}_2$	210	1.20	p. of H_2O_2, 298 K	118
$H\dot{O}_2$	230	1.07	p.r. of $HClO_4$ in H_2O	119
$H\dot{O}_2$	240	1.15	p.r. of H_2O_2 in H_2O	120
$H\dot{O}_2$	<220	$\varepsilon_{230}=0.66$	decomp. of H_2O_2, 1000 K	121
$H\dot{O}_2$	240	1.00	f.p. of H_2O_2 in $HClO_4$	122
$H\dot{O}_2$	200—210	—	decomp. of H_2O_2 in shock wave, 900-1500 K	123
$H\dot{O}_2$	205	1.77±0.15	f.p. of H_2O	124
$H\dot{O}_2$	205	0.82	decomp. of H_2O_2, 1100 K	125
$CH_3\dot{O}_2$	235	2.64	p. of azomethane	11
$CH_3\dot{O}_2$	250	1.2	p.r. of CH_4 in H_2O, 298 K	19
$CH_3\dot{O}_2$	235	0.81	f.p. of azomethane	22
$C_2H_5\dot{O}_2$	240	2.64	p. of azoethane	11
$C_2H_5\dot{O}_2$	250	1.25	p.r. of ethane in H_2O 298 K	19
$C_5H_{11}\dot{O}_2$	270	3.2±0.9	p.r. of isopentane in soln.	126
$C_5H_{11}\dot{O}_2$	260	3.2±0.6	r. of isopentane, 77 K	127
$C_5H_{11}\dot{O}_2$	250	$\varepsilon_{280}=0.91\pm0.05$	p.r. of pentane, 298 K	31
$C_6H_{13}\dot{O}_2$	255	1.9	p.r. of hexane, 295 K	41
$C_7H_{15}\dot{O}_2$	270	3.2±0.9	p.r. of heptane, 300 K	126
$C_8H_{17}\dot{O}_2$	270	3.2±0.9	p.r. of isooctane, 300 K	126
$C_9H_{19}\dot{O}_2$	260	3.4±0.7	r. of 2,3,5-trimethylhexane, 77 K	127
$C_5H_9\dot{O}_2$	270	1.45±0.15	p.r. of cyclopentane in H_2O, 293 K	39
$C_6H_{11}\dot{O}_2$	275	2.0±0.4	p.r. of cyclohexane	128—130
$C_6H_{11}\dot{O}_2$	260	2.9±0.9	r. of 3-methylpent-1-ene, 77 K	126
$C_6H_{11}\dot{O}_2$	260	2.7±0.6	r. of 3-methylpent-1-ene, 77 K	127
$C_6H_{11}\dot{O}_2$	260	3.0±0.9	r. of 3-methylpent-2-ene, 77 K	126
$C_6H_{11}\dot{O}_2$	260	2.7±0.6	r. of 3-methylpent-2-ene, 77 K	127
$C_6H_{11}\dot{O}_2$	260	2.9±0.9	r. of 2-methylpent-2-ene, 77 K	126
$C_7H_{13}\dot{O}_2$	260	2.9±0.9	r. of hept-1-ene, 77 K	126
$C_7H_{13}\dot{O}_2$	260	2.8±0.6	r. of hept-1-ene, 77 K	131
$C_7H_{13}\dot{O}_2$	270	2.9±0.9	p.r. of hept-1-ene, 300 K	131
$C_7H_{13}\dot{O}_2$	260	2.8±0.6	r. of hept-1-ene, 77 K	127
$C_6H_9\dot{O}_2$	260	—	p.r. of cyclohexene in H_2O, 298 K	132
$HOCH_2\dot{O}_2$	255	0.7	p.r. of methanol in H_2O, 298 K	132
$HOCH_2\dot{O}_2$	≤230	$\varepsilon_{248}=1.07$	p.r. of methanol in H_2O, 298 K	133
$HOCH(\dot{O}_2)CH_3$	255	1	p.r. of ethanol in H_2O, 298 K	132
$HOC(CH_3)_2\dot{O}_2$	250	1.3	p.r. of isopropyl alcohol in H_2O, 198 K	134
$HOC(CH_3)_2\dot{O}_2$	248	1.1±0.1	p.r. of isopropyl alcohol in H_2O	135
$C_6H_{10}OH\dot{O}_2$	280	2.5±0.5	p.r. of benzene in H_2O	136
$C_6H_{11}OH\dot{O}_2$	302	2.3±0.5	p.r. of cyclohexanol	129, 130
$C_2H_5OCH\dot{O}_2CH_3$	245	9	p.r. of $C_2H_5OC_2H_5$ in H_2O, 298 K	132
$R_1R_2C(\dot{O}_2)OH$	240—250	—	p.r. of aqueous solns of acids	137
$\dot{O}_2CH_2COOH$	290	0.9	p.r. of CH_3COOH in H_2O	138
$C_2Cl_5\dot{O}_2$	250	—	f.p. of C_2Cl_4 + Cl_2, 300 K	48
$C_2Cl_5\dot{O}_2$	250	$\varepsilon_{268}=0.39\pm0.17$	f.p. of C_2Cl_4 + Cl_2, 297 K	139

*The notation is the same as in Table 1.

The reactions of radicals in 3-MP, 3-ethylpentane, and 3-methylheptane γ-irradiated at 77 K, observed after exposure to ultraviolet radiation, were explained by the conformational transitions in the radicals, which take place on local heating of the matrix in consequence of the dissipation

of the energy of the light quantum absorbed by the radical[88]. Estimates based on the data of Vasil'ev and Tal'roze[89] have shown that the temperature rise can reach several tens of degrees.

The study of the photochemical reactions of the radicals $(CH_3)_2\dot{C}CH(CH_3)_2$, formed on γ-irradiation and hexahydropyrene-sensitised photolysis of 2,3-dimethylbutane at 77 K, not only established that the reaction product is methyl radicals but also led to the determination of the quantum yield in the accumulation of methane under the influence of radiation having a wavelength in the range $240 \leq \lambda \leq 270$ nm, which proved to be 0.01.[30]

Thus it can now be regarded as established that alkyl radicals can undergo photochemical substitution and dissociation reactions. The question of the possible isomerisation and the explanation of the observed changes in the ESR spectra by conformational transitions occurring on local heating of the matrix require further confirmation.

III. PHOTOCHEMICAL REACTIONS OF ALKOXY- AND PEROXY-RADICALS

The alkoxy-radicals RȮ are formed as intermediates when many organic compounds are irradiated, but their high reactivity makes their direct experimental detection extremely difficult. The rate constants for the reactions of RȮ with alcohol, ester, and aldehyde molecules at 20 °C are in the range 10^5–10^6 litre mol^{-1} s^{-1}.[90,91] The RȮ radicals are usually detected by the spin-trapping method, which makes it possible to reach a conclusion, by analysing the ESR spectrum of the resulting radical adduct, concerning the presence or absence of alkoxy-radicals among the reaction products[92].

The ESR spectra of alkoxy-radicals consist of singlet lines with a *g*-factor in the range 2.0065–2.008 [93,94] or 2.015 ± 0.02 [95] and a half-width in the range 3–6 G.[95,96] The ESR spectra of the radicals ȮH and ȮD are well known in the literature[97]. Table 2 shows that the optical absorption spectra of alkoxy-radicals have been studied inadequately.

The observed photochemical reactions have been attributed to alkoxy-radicals in a number of investigations. However, this is a consequence of an inaccurate identification of the singlet ESR spectra (see for example, Lenci and Neubacher[113] and Moan[114]), observed in the course of the low-temperature photolysis and radiolysis, and is as a rule associated with the photochemical reactions of acyl radicals.

On irradiation in the presence of oxygen or on interaction of irradiated substances with oxygen, a characteristic signal, consisting of a single asymmetric line due to peroxy-radicals, appears in the ESR spectra.

Electronically excited states of peroxy-radicals arise as a result of electron transfer from the n-orbital of the oxygen atom to the antibonding π-orbital. Table 3 presents data characterising the absorption regions and the extinction coefficients of peroxy-radicals.

In γ-irradiated PP the peroxy-radicals obtained as a result of the oxidation of alkyl radicals (heating to 173–193 K after γ-irradiation at 77 K) and allyl radicals (irradiation at room temperature) are converted into the corresponding alkyl radicals under the influence of ultraviolet radiation with $\lambda \geq 280$ nm.[140] Analogous reactions under the influence of light with $\lambda \leq 370$ nm are undergone by the peroxy-radicals obtained as a result of the oxidation of polyene radicals in PP.[141] The action of radiation with $\lambda \geq 280$ nm on peroxy-radicals in PP is not accompanied by a change in the total number of free valences. It has been suggested that the excited peroxy-radicals formed under the influence of light react with matrix molecules to form hydroperoxides:

$$R\dot{O}_2^* + RH \rightarrow \dot{R} + ROOH .$$

The decomposition of the hydroperoxide under the influence of radiation with $\lambda \leq 280$ nm can lead to the development of a chain process with photochemical chain branching[142]:

$$ROOH \xrightarrow{h\nu} R\dot{O} + \dot{O}H ,$$
$$\dot{O}H + RH \rightarrow \dot{R} + H_2O ,$$
$$R\dot{O} + RH \rightarrow \dot{R} + ROH .$$

A three-fold increase of the number of free valences is then observed.

The time variation of the overall radical concentration under the influence of light on peroxy-radicals, obtained by the oxidation of allyl radicals in PP, is described by the equation

$$[\dot{R}] = \left[1 + 2\left(1 + \frac{I}{\alpha - I}e^{-\alpha\tau} - \frac{\alpha}{\alpha - I}e^{-\tau}\right)\right],$$

where $\alpha = k_2/k_1$, k_1 is the rate constant for the conversion of peroxy-radicals into alkyl radicals, k_2 the rate constant for the decomposition of hydroperoxides, $\tau = k_1 It$, I is the light intensity, and t the irradiation time. The experimental values agree satisfactorily with the curve calculated for $\alpha = 2.1$, determined from linear logarithmic modifications of the curves describing the disappearance of peroxy-radicals on irradiation at wavelength $\lambda \geq 280$ nm and the accumulation of radicals on subsequent ultraviolet irradiation light at wavelength $\lambda \leq 280$ nm.[141]

However, it was established that the rate of accumulation of radicals in the photolysis of oxidised PP exceeds approximately by a factor of 7 the rate of decomposition of hydroperoxy-groups[143]. The study of the rate of accumulation of 3-methylpentyl radicals under the influence of light at a wavelength in the range $240 \leq \lambda \leq 270$ nm at 77 K on peroxy-radicals in 3-MP (at a concentration of approximately 0.001 M) and in solutions of t-butyl hydroperoxide in 3-MP at the same concentration showed that in the latter case the rate of accumulation is smaller almost by an order of magnitude[144]. Together with data for the extinction coefficients of the hydroperoxides (for example, $\varepsilon_{260} = 6$, $\varepsilon_{240} = 16$, and $\varepsilon_{200} = 70$ litre mol^{-1} cm^{-1} for t-butyl hydroperoxide[145]), these results show that, under the conditions of simultaneous absorption of radiation by alkyl radicals ($\lambda_{max} = 220$–240 nm, $\varepsilon \approx 10^3$ litre mol^{-1} cm^{-1}) and peroxy radicals [$\lambda_{max} = 250$–260 nm, $\varepsilon \cong (2$–$3) \times 10^3$ litre mol^{-1} cm^{-1}], present at comparable concentrations, the decomposition of hydroperoxide molecules is greatly hindered. Furthermore, one should note that the threefold increase of the number of free valences observed by Klinshpont et al.[141] is difficult to explain by the decomposition of the hydroperoxide formed in the reaction of the electronically excited peroxy-radical with matrix molecules, because "quasi-cage" radical recombination processes and radical recombination processes within the cage should then play a major role. The quantum yield of free radicals in the photolysis of hydrogen peroxide solutions in reactive and inert matrices at 77 K is known to be in the range from 10^{-4} to 0.3,[146,147] i.e. is less than unity.

At the same time, when peroxy-radicals derived from PP are irradiated at a wavelength $\lambda \leq 300$ nm in methyl methacrylate (MMA) vapour, the concentration of peroxy-radicals diminishes and the number of radicals of the growing polymeric PMMA chain increases, the overall radical concentration increasing under these conditions by a factor of 2–3.[148,149]

Under the influence of irradiation in the wavelength range $240 \leq \lambda \leq 270$ nm, the dissociation of peroxy-radicals plays an important role in processes involving them[69,144]. Thus the photolysis of peroxy-radicals (77 K), obtained by the γ-irradiation of solutions of butyl chlorides in 3-MP, leads to the formation of 3-methylpentyl radicals from n-, s-, and t-butyl chlorides, while isobutyl chloride gives rise to isobutyl radicals. It is believed that both substitution reactions and peroxy-radical dissociation reactions can occur:

$$R\dot{O}_2 \xrightarrow{h\nu} \dot{R} + O_2 \ .$$

The quantum yields in the consumption of peroxy-radicals, measured in PE, DPE, PP, and DPP, are presented in Table 4. Evidently, with increase of temperature from 77 to 300 K, the quantum yield increases significantly, the increase occurring over a narrow temperature range above 170 K, because, for example, in PP, the rate of the photochemical reaction of peroxy-radicals does not change in the temperature range from 77 to 170 K.[141]

Table 4. The quantum yields of photochemical reactions of peroxy-radicals[150-151] (ROȮ → Ṙ).

Polymer	Quantum yield		Polymer	Quantum yield	
	77 K	300 K		77 K	300 K
PE	0.3±0.1	—	PP	0.1±0.03	—
DPE	0.2±0.07	0.7±0.3	DPP	0.04±0.01	0.7±0.3

The ESR spectra of peroxy-radicals in γ-irradiated PTFE, obtained by the reaction with oxygen of the terminal and central macroradicals, are identical and consist of an asymmetric signal with $g_\perp = 2.007$ and $g_\parallel = 2.038$.[152] The action of radiation at a wavelength $\lambda \leq 280$ nm on the central radicals ~$CF_2C(O\dot{O})FCF_2$~ induces their conversion into terminal fluoroalkyl radicals[152-156]. CF_2O and CO were detected among the reaction products by mass spectrometric and infrared spectroscopic methods[152]. It has been suggested that the photolysis proceeds as follows:

$$\sim CF_2\underset{\underset{O\dot{O}}{|}}{CF}CF_2 \sim \xrightarrow{h\nu} \sim CF_2\dot{C}F_2 + CF_2O + CO + CF_3{-}CF_2\sim .$$

The action of light on the terminal peroxy-radicals in PTFE at temperatures below 170 K leads to the formation of terminal fluoroalkyl radicals and oxygen[152]:

$$\sim CF_2CF_2O\dot{O} \xrightarrow{h\nu} \sim CF_2\dot{C}F_2 + O_2 \ .$$

The results presented agree satisfactorily with data obtained in the study of the thermal decomposition of peroxy-radicals in PTFE *in vacuo* at 473 K.[157,158] It was observed that the decomposition of the peroxy-radicals obtained from the central and terminal macroradicals leads to the appearance in the ESR spectra of signals due to the central and terminal macroradicals. At the same time, the formation of considerable amounts of CO, CO_2, and CF_2O among the gaseous reaction products has been observed, which indicates the dissociation of the C–C bonds in the polymer chain. It is important to note that the decomposition of the peroxy-radicals obtained from the central macroradicals leads to a significant decrease of the molecular weight, while the decomposition of the peroxy-radicals obtained from the terminal macroradicals hardly changes this quantity.

The photolysis of the peroxy-radical ~$CF_2\underset{\underset{{}^{18}O{}^{18}\dot{O}}{|}}{CF}CF_2$~, labelled with the ^{18}O isotope, leads to the formation of considerable amounts of $C^{18}OO$ and $C^{18}O$, which the authors[158] attribute to the occurrence of the following reactions:

$$\sim CF_2C(^{18}O{}^{18}\dot{O})FCF_2 \sim \xrightarrow{h\nu} [\sim CF_2CF^{18}O{}^{18}OCF_2\sim] \rightarrow \sim CF_2\underset{\underset{{}^{18}O}{\|}}{CF} + {}^{18}\dot{O}CF_2\sim \ ,$$

$$^{18}\dot{O}CF_2\sim \rightarrow CF_2{}^{18}O + \dot{C}F_2\sim \ ,$$

$$CF_2{}^{18}O + H_2O \rightarrow HF + C^{18}OO \ .$$

At temperatures above 170 K, the photodissociation of the peroxy-radicals obtained from the terminal macroradical proceeds via the reaction

$$\sim CF_2CF_2O\dot{O} \xrightarrow{h\nu} \sim CF_2\dot{C}F_2 + 2CF_2O \ .$$

In each decomposition step the free valence migrates via the polymer chain over a distance equal to two C–C bond lengths, which leads to the photorecombination of the radicals in the system[149,159]. Analysis of the amounts of fluoride ions obtained by the hydrolysis of the gaseous products evolved on photolysis shows that between 50 and 90 fluoride ions are produced for each disappearing peroxy-radical, which confirms the chain mechanism of the photochemical reactions of peroxy-radicals in PTFE. The quantum yields in the consumption of peroxy-radicals in PTFE are 0.015 ± 0.005 at 77 K and 0.1 ± 0.03 at 300 K.[150]

Thus the mode of photodissociation of peroxy-radicals in PTFE depends on their nature and is accompanied by the dissociation of C–C or C–O bonds. The peroxy-radicals obtained in hydrocarbon matrices can apparently undergo dissociation and substitution reactions.

IV. PHOTOCHEMICAL REACTIONS OF ACYL RADICALS

The study of the mechanisms of the low-temperature photolysis and radiolysis of various classes of oxygen-containing compounds by ESR led to the observation of radicals giving rise to spectral lines with a *g*-factor smaller than for the free electron. The absence of HFS in the ESR spectra made it difficult to explain the nature of the radical species and initially many investigators attributed the singlet line either to alkoxy-radicals RȮ[160-165] or to the radicals RCOȮ.[166]

Analysis of the literature data shows that the singlet lines in the EPR spectra with $\Delta H \cong 10$–16 G and $g \cong 2.0010$ are due to the acyl radicals RĊO. In certain cases HFS is observed with a splitting of approximately 5 G,[167-171] which is confirmed by the theoretical calculation for the acetyl radical[172]. Acyl radicals can be formed in photochemical processes either as a result of the photolysis of molecules[173-179] or as a result of secondary photochemical reactions of radicals.[180-182]

Data for the absorption spectra of acyl radicals are presented in Table 5. The unpaired electron is located in acyl radicals in the sp^2-orbital. The absorption in the range 500 to 550 nm is associated with the transfer of the unpaired electron to the π*-orbital (the C–CO angle then changes from 120° to 180°, i.e. the radical acquires a linear structure). The absorption in the range 450–500 nm is associated with the transfer of the lone electron pair in the *p*-orbital of the oxygen atom to the π*-orbital[7].

The excitation of acyl radicals leads to their dissociation (the dissociation energies of these radicals are low and are in the range 5.4–11 kcal mol^{-1} [195-197]). The dissociation of acyl radicals with the formation of the corresponding alkyl radicals and carbon monoxide under the influence of radiation at the wavelength corresponding to the absorption band has been observed in many systems (see, for example, Refs.198

to 201). The reverse process, involving the addition of CO to radicals, takes place effectively in the dark.

At the same time it has been noted[178] that the action of ultraviolet radiation on acyl radicals at 77 K in di-n-heptadecyl ketone results in the disappearance of the singlet line with $\Delta H \cong 15$ G from the ESR spectrum and the appearance of a multiplet spectrum with an overall width of approximately 170 G, which the authors assigned to the radical $\sim CH_2\dot{C}HCHO$. These changes were explained by the isomerisation of the acyl radicals:

$$\sim CH_2CH_2\dot{C}O \overset{h\nu}{\rightleftarrows} \sim CH_2\dot{C}HCHO \ .$$

The hypothesis of the isomerisation reactions also served as the basis of an explanation of the results obtained in the photolysis of PE and PP.[176,177]

Table 5. Absorption spectra of acyl radicals.

Radical	λ_{max}	Conditions of generation*	Refs.
$H\dot{C}O$	510; 533; 555; 579; 605; 635; 670	p. of HI in CO, 20 K	183
$H\dot{C}O$	613,8—617,2; 562,4—565,5	f.p. of glyoxal, HCHO, and CH_3CHO	184
$H\dot{C}O$	520	f.p. of acetaldazine	185
$H\dot{C}O$	210—260; 460—860	p. of HCl, H_2O, and CH_4 in argon, 14 K	186
$F\dot{C}O$	220—340, 539	p. of F_2O and F_2CO in CO, 4.2 K	187
$F\dot{C}O$	220—340	f.p. of N_2F_4 and CO	188
$Cl\dot{C}O$	532—534	p. of HCl and Cl_2 in CO, 14 K	189
$CH_3\dot{C}O$	340, 500, 540	r. of CH_3COCl in methyltetrahydrofuran (MTHF), 77 K	190
$CH_3\dot{C}O$**	—	p.r. of acetic acid	191
$CH_3\dot{C}O$***	540	r. of C_2H_5OH and $C_2H_5OC_2H_5$, 80 K	180, 192
$CH_3\dot{C}O$	505	r. of acetic anhydride, 80 K	192
$C_2H_5\dot{C}O$	330; 480; 540	r. of C_2H_5COCl in MTHF, 77 K	190
$C_2H_5\dot{C}O$	530	r. of 1-propanol, 77 K	193
$C_2H_5\dot{C}O$	530	r. of C_2H_5OH and $C_2H_5OC_2H_5$	192
$\sim(CH{=}CH)_n{-}\dot{C}O$	375; 400; 500	r. of poly(vinyl alcohol)	194

*The notation is the same as in Table 1.
**$\varepsilon_{260} = 940$ litre mol^{-1} cm^{-1}.
***$\varepsilon_{540} = 40 \pm 15$ litre mol^{-1} cm^{-1}.

Analogous changes in the ESR spectra were observed in the photolysis of acyl radicals in isobutyraldehyde at 77 K. However, mass spectrometric analysis of the gaseous products showed that this entails vigorous formation of CO and the consequent establishment of a rapid sequence of the following reactions[173]:

$$(CH_3)_2CH\dot{C}O \overset{h\nu}{\rightleftarrows} (CH_3)_2\dot{C}H + CO \ ,$$

$$(CH_3)_2\dot{C}H + (CH_3)_2CHCHO \rightarrow \begin{cases} (CH_3)_2CH\dot{C}O \\ (CH_3)_2\dot{C}CHO \end{cases} + (CH_3)_2CH_2 \ .$$

Thus data [176–178] obtained solely on the basis of the analysis of poorly resolved ESR spectra are open to objection and at the present time it can be regarded as established that the principal photochemical process involving acyl radicals is their dissociation.

The formation of acyl radicals in the course of photolysis and radiolysis greatly increases the region of the spectral sensitivity of the materials and promotes their effective decomposition under the influence of light. For example, a study of the mechanism of the photolysis of acetaldehyde at 77 K showed that the rate of accumulation of CO and methane exceeds almost by an order of magnitude the rate of accumulation of the radicals[200]. Since, according to the results of Pariiskii et al.[201], the contribution of the molecular decomposition of acetaldehyde in photolysis by the total radiation of a high-pressure mercury lamp at 77 K is 30%, the high rate of accumulation of gaseous products is associated with the effective dissociation of the acetyl radical:

$$CH_3\dot{C}O \overset{h\nu}{\rightleftarrows} \dot{C}H_3 + CO \ .$$

V. PHOTOCHEMICAL REACTIONS OF RADICALS DERIVED FROM ALCOHOLS AND ETHERS

The radiolysis of alcohols and ethers and their photolysis sensitised or initiated by various additives in the solid phase involve the preferential formation of the radicals $R_1R_2\dot{C}OR_3$ most stable under these conditions, where R_1, R_2, and R_3 are hydrogen atoms or alkyl groups.

The conjugation of the unpaired electron with the electrons of the lone pair of the oxygen atom leads to a bathochromic shift in the absorption spectra of the radicals relative to the spectra of the initial compounds. Table 6 presents the available literature data for the absorption spectra of radicals derived from alcohols and ethers. The excited state of alcohol and ether radicals arises when a π-electron of the carbon atom is transferred to the σ^*-orbital (the transition is forbidden by symmetry rules)[6]. The action of radiation at the wavelengths corresponding to the absorption bands of the alcohol and ether radicals induces photochemical reactions, which have been investigated in a large number of studies[113, 114,160–164,167,168,180,192,193,210–212,218,229,230,233–262].

The photochemical reactions of alcohol and ether radicals were first observed in a study[211] where the changes occurring under the influence of radiation on a series of alcohols and ethers subjected to preliminary γ-irradiation at 77 K were recorded by ESR. For methanol and CH_3OD, a doublet ESR spectrum was observed under these conditions with a splitting of 129 G, but for deuteromethanol (CD_3OD) a doublet spectrum was not noted. The lack of a correct interpretation of the ESR spectra precluded the explanation of the experimental results.

When dilute frozen solutions of acetaldehyde in ethanol were photolysed at 77 K directly in the resonator of the ESR spectrometer, it was observed[233,234] that the alcohol radicals $CH_3\dot{C}HOH$ formed in this system in the course of the photolysis are effectively decomposed by ultraviolet radiation with formation of methyl radicals.

A sharp increase of the yield of gaseous and liquid products was observed[235,236] after the ultraviolet irradiation of alcohols subjected to preliminary γ-radiolysis at 77 K. The increase of the amounts of hydrogen and CO was attributed in the case of methanol to the photolysis of the radicals $\dot{C}H_2OH$:

$$\dot{C}H_2OH \overset{h\nu}{\rightarrow} H\dot{C}O + H_2 \ ,$$

$$H\dot{C}O \overset{h\nu}{\rightarrow} H + CO \ .$$

However, the proposed mechanism did not explain the increase of the yield of the remaining gaseous and liquid products. The authors[235,236] suggested that complexes of the radicals with alcohol molecules are formed, in which the alcohol molecule can be decomposed as a result of the absorption of radiation by the radical.

Table 6. Absorption spectra of radicals derived from alcohols and ethers.

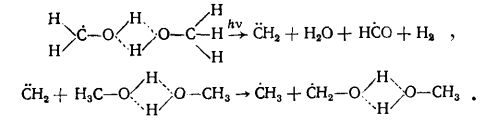
Radical	λ_{max}	$10^{-3}\varepsilon_{\lambda max}$, litre mol^{-1} cm^{-1}	Conditions of generation*	Refs.
$\dot{C}H_2OH$	<230	—	p.r. of methanol	204
$\dot{C}H_2OH$	<210	—	p.r. of methanol in water	204
$\dot{C}H_2OH$	<250	$\varepsilon_{300}G=2.6\pm0.3$	p.r. of methanol	165
$\dot{C}H_2OH$	<260	$\varepsilon_{311}=0.025$	p.r. of methanol in water	205
$\dot{C}H_2OH$	<213	$\varepsilon G=5.89$	r. of methanol, 80 K	206
$\dot{C}H_2OH$	<210	$\varepsilon_{277}=0.978$	r. of methanol, 80 K	207
$\dot{C}H_2OH$	~260	—	p.r. of methanol in water	208
$\dot{C}H_2OH$	~265	—	r. of methanol, 77 K	165
$\dot{C}H_2OH$	290	$\varepsilon G=7.2$	p.r. of methanol	209
$\dot{C}H_2OH$	<204	$\varepsilon G=12.4$	r. of methanol, 77 K	209, 210
$\dot{C}H_2OH$	<220	—	r. of methanol, 77 K	211
$\dot{C}H_2OH$	280	0.6±0.1	p.r. of methanol in water	212
$\dot{C}H_2OH$	270	—	r. of methanol, 77 K	213
$CH_3\dot{C}HOH$	<210	—	p.r. of ethanol	204
$CH_3\dot{C}HOH$	240	0.5±0.05	p.r. of ethanol in water	213
$CH_3\dot{C}HOH$	<250	$\varepsilon_{255}=0.87\pm0.07$	p.r. of ethanol	214
$CH_3\dot{C}HOH$	<210	~1	r. of ethanol, 77 K	215
$CH_3\dot{C}HOH$	<210	$\varepsilon_{230}G=7.63$	r. of ethanol, 80 K	206
$CH_3\dot{C}HOH$	266, 257, 247	$\varepsilon_{297}=0.23\pm0.055$	p.r. of ethanol	216
$CH_3\dot{C}HOH$	~290	—	p.r. of ethanol in water	216
$CH_3\dot{C}HOH$	—	$\varepsilon_{297}=0.24\pm0.045$	p.r. of ethanol in water, 296 K	217
$CH_3\dot{C}HOH$	—	$\varepsilon_{260}=0.23$	r. of ethanol, 77 K	192
$CH_3\dot{C}HOH$	<210	—	p.r. of ethanol in water	204
$CH_3\dot{C}HOH$	<220	—	r. of ethanol, 77 K	211
$CH_3\dot{C}HOH$	—	$\varepsilon_{254}=0.71\pm0.17$	p. of H_2O_2 in ethanol, 77 K	218
$CH_3\dot{C}HOH$	<200	—	r. of ethanol, 77 K	212
$CH_3\dot{C}HOH$	<210	$\varepsilon_{200}=0.1$	r. of ethanol, 77 K	219
$CH_3CH_2\dot{C}HOH$	232	$\varepsilon_{25}G=7.28$	r. of 1-propanol, 80 K	206
$CH_3CH_2\dot{C}HOH$	230	—	p.r. of 1-propanol, 147 and 300 K	220
$(CH_3)_2\dot{C}OH$	330	—	p. of H_2O_2 in isopropyl alcohol, 77 K	221
$(CH_3)_2\dot{C}OH$	<210	—	p.r. of isopropyl alcohol in water	204
$(CH_3)_2\dot{C}OH$	<260	0.87	p.r. of isopropyl alcohol in water	222
$(CH_3)_2\dot{C}OH$	230	—	p.r. of acetone in water, 298 K	223
$(CH_3)_2\dot{C}OH$	<250	—	r. of isopropyl alcohol, 77 K	224
$(CH_3)_2\dot{C}OH$	—	$\varepsilon_{325}=0.38$	f.p. of acetone in hydrocarbons	225
$CH_3(CH_2)_2\dot{C}HOH$	222	~1	p.r. of 1-butanol in water	204
$CH_3(CH_2)_2\dot{C}HOH$	~238	$\varepsilon_{245}G=6.21$	r. of 1-butanol, 80 K	206
$CH_3(CH_2)_2\dot{C}HOH$	<220	—	r. of 1-butanol, 77 K	211
$(CH_3)_2CH\dot{C}HOH$	225	~1	p.r. of isobutyl alcohol in water	204
$(CH_3)_2CH\dot{C}HOH$	220	—	r. of isobutyl alcohol, 77 K	211
$CH_3(CH_3)_2\dot{C}OH$	225	0.9	p.r. of t-butyl alcohol in water	204
n-$C_4H_9\dot{C}HOH$	<256	$\varepsilon_{270}G=4.08$	r. of 1-pentanol, 77 K	206
$(CH_3)_3C\dot{C}HOH$	~238	—	p.r. of neopentyl alcohol in water	204
n-$C_5H_{11}\dot{C}HOH$	<300	$\varepsilon_{313}G=2.7$	r. of 1-hexanol, 77 K	206
$HO\dot{C}HOH$	—	$\varepsilon_{240}=0.2$	p.r. of formaldehyde in water	226
$HO\dot{C}HCH_2OH$	—	$\varepsilon_{250}=0.61$	p.r. of ethylene glycol in water	227
$HO\dot{C}HCH(OH)CH_2OH$ or $HOCH_2\dot{C}(OH)CH_2OH$	250	$\varepsilon_{270}=0.2$	p.r. of glycerol in water	228
cyclo-$\dot{C}_6H_{10}OH$	<290	—	p.r. of cyclohexanol, 298 K	204
cyclo-$\dot{C}_6H_{10}OH$	230	1	p.r. of cyclohexanol in water	204
~$CH_2\dot{C}(OH)CH_2$~	225—235	1.7±0.5	r. of poly(vinyl) alcohol), 77 K	229, 230
~$CH_2\dot{C}(CH_3)OH$	286	—	r. of poly(propylene oxide), 77 K	231
$CH_3\dot{C}HOC_2H_5$	—	$\varepsilon_{260}=0.39$	r. of $C_2H_5OC_2H_5$, 77 K	218
~$CH_2\dot{C}HO$~	<220	$\varepsilon_{235}=1.5\pm0.1$	p.r. of poly(ethylene oxide) in water	232

*The notation is the same as in Table 1.

The greatest number of studies have been devoted to the photochemical reactions of radicals in methanol, ethanol, and diethyl ether. The benzene-sensitised and hydrogen peroxide-initiated photolysis of methanol and ethanol at 77 K has been investigated[162,237,238] and, on the basis of the study of the kinetics of the accumulation and interconversion of the radicals, a mechanism has been proposed for the photochemical reactions of the alcohol radicals. Under the influence of the ultraviolet radiation of a high-pressure mercury lamp on the $CH_3OH + H_2O_2$ system, the formation of the radicals $\dot{C}H_3$ and $H\dot{C}O$ was recorded by EPR, their concentration rising to a limit. The amount of gaseous photolysis products increased continuously and their composition was independent of the duration of photolysis (57% H_2, 26% CO, and 17% CH_4). At the same time the increase of the concentration of free radicals was accompanied by a decrease of the rate of consumption of hydrogen peroxide, indicating the occurrence of hydrogen peroxide-initiated reactions, which continued for some time even without the participation of the initiator. Two possible mechanisms of the photolysis of alcohol radicals, taking into account the experimental results obtained, have been examined[237]. The first presupposes the formation of the radicals $\dot{C}H_3$ and $H\dot{C}O$ in parallel reactions:

$$\dot{C}H_2OH \xrightarrow{h\nu} \begin{cases} \ddot{C}H_2 + \dot{O}H \xrightarrow{2CH_3OH} \dot{C}H_3 + 2\dot{C}H_2OH + H_2O \\ H\dot{C}O + H_2 \end{cases} \quad (1)$$

The second involves the photolysis of the radicals $\dot{C}H_2OH$ linked by hydrogen bonds to the surrounding alcohol molecules:



(2)

The necessity for hydrogen bonds to permit the formation of the radicals $\dot{C}H_3$ in the photolysis of methanol radicals was confirmed by a study[239] where the authors failed to observe the formation of methyl radicals when methanol radicals were photolysed in a sulphuric acid matrix. Data[162,240], according to which an increase of the concentration of free radicals (to 30%) was observed when the radicals $\dot{C}H_2OH$, obtained by the benzene-sensitised photolysis of methanol at 77 K, were irradiated at wavelengths in the range $290 \leq \lambda \leq 320$ nm and γ-irradiated methanol was exposed to light at wavelengths in the range $240 \leq \lambda \leq 400$ nm, can serve as evidence in support of the possibility of reactions (1) and (2). However, in the majority of studies, for example those[161,180,192,210] where the alcohol radicals were obtained by γ-radiolysis, an increase of the radical concentration was not observed when the radicals $\dot{C}H_2OH$ were exposed to ultraviolet radiation.

An ESR study of the radicals obtained as a result of the irradiation at $\lambda = 253.7$ nm at 77 K of ethanol deuterated in various positions resulted in the measurement of the spectra of the radicals $\dot{C}_2H_5(C_2H_5OH)$, $\dot{C}_2H_5(C_2H_5OD)$, $CD_3\dot{C}H_2(CD_3.CH_2OH)$, and $CH_3\dot{C}D_2(CH_3CD_2OH)$.[241] Evidently, when a quantum of radiation is absorbed by an alcohol radical, ethyl radicals are formed from alcohol molecules linked to the radicals by hydrogen bonds.

The photochemical reactions of radicals in ethanol and diethyl ether in the hydrogen peroxide-initiated and naphthalene-sensitised photolysis have been investigated in detail[171] When light was allowed to act on ethanol and diethyl ether containing added hydrogen peroxide at 77 K, the radicals $\dot{C}H_3$ and $\dot{C}_2H_5$ were detected in the ESR spectra. In the dark, the alkyl radicals were converted into the radicals $CH_3\dot{C}HOR$ ($R = H$ or C_2H_5) and in addition a radical giving rise to a

singlet ESR spectrum appeared. In the naphthalene-sensitised photolysis the ESR spectra revealed the presence of the radicals $\dot{C}H_3$, $\dot{C}_2H_5$, $CH_3\dot{C}HOR$, and, after prolonged photolysis, $CH_3\dot{C}O$, to which a singlet ESR spectrum was assigned. Analysis of the gaseous products, carried out simultaneously with the ESR study of the radicals, showed that in diethyl ether the ratio of the amount of hydrogen to that of ethane diminished with increasing duration of the exposure to radiation, while in ethanol it increased. On this basis, it was concluded that the photolysis of the radicals $CH_3\dot{C}HOH$ results in the formation of hydrogen, while the photolysis of the radicals $C_2H_5O\dot{C}HCH_3$ leads to ethane. The following mechanism has been proposed to account for the results[171]:

$$CH_3\dot{C}HOR \xrightarrow{h\nu} CH_3CHO + \dot{R} \ , \qquad (3)$$

$$CH_3\dot{C}H(H)-O-OCH_2CH_3 \xrightarrow{h\nu} CH_3CHO + H_2O + \dot{C}_2H_5 \ , \qquad (4)$$

$$CH_3\dot{C}HOR \xrightarrow{h\nu} \dot{C}H_3 + \ddot{C}HOR \ , \qquad (5)$$

$$\ddot{C}HOR \xrightarrow{h\nu} CO + RH \ ,$$

$$\ddot{C}HOR \rightarrow RCHO \ ,$$

$$\dot{C}H_3\ (\dot{C}_2H_5) + CH_3CH_2OR \rightarrow CH_4\ (C_2H_6) + CH_3\dot{C}HOR \ ,$$

$$\dot{R} + CH_3CHO \rightarrow RH + CH_3\dot{C}O \ ,$$

$$CH_3\dot{C}O \xrightarrow{h\nu} \dot{C}H_3 + CO \ . \qquad (6)$$

This mechanism explained many experimental results; however, the preferential occurrence of reaction (5) compared with reaction (6), which the authors[171] postulated, conflicted with the detection[164] of $\dot{C}_2H_5$ and species giving rise to a singlet ESR spectrum rather than methyl radicals when ethanol radicals $CH_3\dot{C}HOH$ were irradiated at a wavelength in the range $300 \leq \lambda \leq 400$ nm.

The mechanism of the photolysis of alcohol and ether radicals has been studied in greatest detail by Chervonenko and coworkers[180,192]. According to these investigators, the principal reaction of alcohol radicals is their dissociation reaction (3). This mechanism is supported by a number of factors.

1. The main product when alcohol radicals are irradiated is hydrogen.

2. The formation of ethyl radicals is observed in the photolysis of the radicals $\dot{C}H_2OH$ in methanol in the presence of ethylene, which is an effective acceptor of hydrogen atoms, while the rate of consumption of $\dot{C}H_2OH$ radicals increases markedly as a result of the suppression of the process

$$CH_3OH + H \rightarrow \dot{C}H_2OH + H_2 \ .$$

3. Calculation on the $\dot{C}H_2OH$ radical by the CNDO method showed[192] that, after the excitation of the π-electron to the lowest vacant σ-orbital, the O–H bond order diminishes, i.e. the bond is weakened. The dissociation of ether radicals takes place similarly. The quantum yields of reaction (3), determined from the initial linear sections of the kinetic curves for the accumulation of hydrogen in ethanol and of ethane in diethyl ether under the influence of light at a wavelength $\lambda = 310$ nm at 77 K on the corresponding radicals proved to be 0.3 ± 0.2.

The formation of the radicals $R_1R_2\dot{C}H$ in the photolysis of the alcohol radicals $R_1R_2\dot{C}OH$ has been explained[180,192] by reaction (4). The quantum yield of this process, measured in ethanol under the influence of light at a wavelength $\lambda = 310$ nm is 0.03 ± 0.02. Hydrogen bonds play an important role in reaction (4), but one should note that the mechanism proposed requires the transfer of excitation energy over a considerable distance, which imposes severe limitations on the probability of its occurrence. At the same time CNDO calculations for the $\dot{C}H_2OH$ radical showed that the C–O bond is strengthened in the excited state, so that the occurrence of reactions (1) and (2) is unlikely.

Studies have been published recently[114,218,242-244] in which a fundamentally different mechanism is proposed for the formation of the radicals $R_1R_2\dot{C}H$ in the photolysis of alcohol radicals, involving their photoionisation. According to theoretical estimates[245], the ionisation potential of the alcohol radicals $CH_3\dot{C}HOH$ in a solid acetaldehyde matrix can be reduced to 2.5 eV, which corresponds to the energy of a light quantum with a wavelength $\lambda = 495$ nm.

A study of the influence of radiation at a wavelength $\lambda = 253.7$ nm on ethanol radicals, obtained in the photolysis of hydrogen peroxide solutions in ethanol at 77 K in the presence of N_2O, established[218] that the gaseous reaction products contain nitrogen, the formation of which is associated with photoionisation of the alcohol radical:

$$CH_3\dot{C}HOH \xrightarrow{h\nu} CH_3CHOH^+ + e^- \ ,$$

$$e^- + N_2O \rightarrow N_2 + O^- \ .$$

The accumulation of ethyl radicals formed in the photolysis by light at wavelengths in the range $250 \leq \lambda \leq 350$ nm of the alcohol radicals $CH_3\dot{C}HOH$ in γ-irradiated neutral, acid, and alkaline ethanol solutions at 77 K, has been investigated. It has been observed that the initial rate of accumulation of $\dot{C}_2H_5$ is almost independent of the concentration of added acid (H_2SO_4), but decreases sharply with increase of the amount of added alkali (NaOH), At the same time the limiting yield of $\dot{C}_2H_5$ is a maximum in neutral solutions and decreases both with increase of the concentration of alkali and with increase of the concentration of the acid. In order to explain the experimental data obtained, the following reactions have been postulated[242]:

$$CH_3\dot{C}HOH \rightarrow CH_3CHOH^+ + e^- \ ,$$

$$C_2H_5OH + CH_3CHOH^+ \rightarrow CH_3CHO + C_2H_5OH_2^+ \ ,$$

$$e^- + C_2H_5OH_2^+ \rightarrow \dot{C}_2H_5 + H_2O \ .$$

Furthermore, in alkaline media, the reactions

$$C_2H_5O^- + C_2H_5OH_2^+ \rightarrow 2C_2H_5OH \ ,$$

$$OH^- + C_2H_5OH_2^+ \rightarrow C_2H_5OH + H_2O \ ,$$

can occur, while in acid matrices there is a possibility of the reactions

$$e^- + HSO_4^- \rightarrow SO_4^{2-} + H \ ,$$

$$H + C_2H_5OH \rightarrow CH_3\dot{C}HOH + H_2 \ .$$

The possibility of the photoionisation of alcohol radicals has been considered in a number of studies[114,243,244] to explain the results obtained when radicals were u.v. irradiated in water–methanol mixtures, ethylene glycol–water mixtures[243], and ethanol[244] irradiated at 77 K. However, according to the authors[244], it remains obscure why the radicals $R_1R_2\dot{C}H$ are not formed on annealing stabilised electrons in irradiated specimens.

Thus the main process associated with the action of radiation on alcohol and ether radicals is their dissociation. On the other hand, the problem of the mechanism of the formation of the radicals $R_1R_2\dot{C}H$ in the photolysis of alcohol radicals requires additional study.

The occurrence of the photochemical reactions of radicals in poly(vinyl alcohol)[229,230] and poly(ethylene oxide)[246] at 77 K and higher temperatures lead to an effective degradation of the polymers.

VI. PHOTOCHEMICAL REACTIONS OF RADICALS DERIVED FROM ESTERS, ALDEHYDES, KETONES, ACIDS, AND ACID ANHYDRIDES

Data for the absorption spectra of ester, aldehyde, ketone, acid, and acid anhydride radicals are presented in Table 7. The photochemical reactions of ester radicals were first

reported in a study[211] where the appearance of a doublet signal with a splitting of 129 G was observed in the ESR spectra of methyl acetate (γ-irradiated at 77 K) after its exposure to ultraviolet radiation.

Table 7. Absorption spectra of radicals derived from esters, aldehydes, ketones, acids, and acid anhydrides.

Radical	λ_{max}	$10^{-3}\varepsilon_{\lambda max}$, litre mol^{-1} cm^{-1}	Conditions of generation*	Refs.
$\dot{C}H_2COOCH_3$	320	—	p.r. of methyl thioglycolate in water	270
$\dot{C}H_2COOCH_3$	320	0.8	p.r. of chloromethyl acetate in water	271
$\dot{C}H_2COOCH_3$	320	—	p.r. of glycylmethyl acetate in water	271
$\dot{C}H_2COOC_2H_5$	300	—	p.r. of ethyl acetate with N_2O	272
	310	—	p.r. of ethyl acetate	272
$CH_3COO\dot{C}HCH_2OH$	300	1.56	p.r. of 2-hydroxyethyl acetate	263
$\sim CH_2-\dot{C}(COOCH_3)-CH_2\sim$	314	—	r. of poly(methyl methacrylate)	273
$\dot{C}H_2CHO$	~300	0.26	p.r. of ethylene glycol in water	227
$\dot{C}H_2CHO$	—	$\varepsilon_{360}=0.26$	p.r. of 2-hydroxyethyl acetate	263
$\dot{C}H_2COCH_3$	~285	—	r. of acetone, 77 K	264
$\dot{C}H_2COCH_3$	295	0.85±0.15	p.r. of acetone, 293 K	222
$CH_3\dot{C}HCOCH_3$	315	—	r. of ethyl methyl ketone, 77 K	265
$CH_3CO\dot{C}HCH_2OH$	230—350	—	p.r. of methyl vinyl ketone in water	274
$\dot{C}OOH$	250±5	—	p.r. of formic acid	267
$\dot{C}H_2COOH$	320	0.65	p.r. of acetic acid in water	268
$\dot{C}H_2COOH$	240, 365	—	r. of glycine and alanine	269
$\dot{C}H_2COOH$	310	0.31	r. of acetic acid in 10 M H_2SO_4, 80 K	192
$\dot{C}H_2COOH$	320	0.67	p.r. of thioglycolic acid in water	270
$\dot{C}H_2COOH$	300	—	p.r. of acetic acid in water	271
$CH_3\dot{C}HCOOH$	300	0.7	p.r. of propionic acid in water	268
$CH_3CH_2\dot{C}HCOOH$	280	—	p.r. of butyric acid in water	268
$HOOC\dot{C}HCOOH$	340	0.4	p.r. of malonic acid in water	268

*The notation is the same as in Table 1.

The photochemical reactions of the radicals in methyl formate and methyl acetate in the toluene-sensitised or hydrogen peroxide-initiated photolysis at 77 K have been investigated[275]. When the radicals $RCOO\dot{C}H_2$ were irradiated at a wavelength in the range $290 \leq \lambda \leq 380$ nm, the formation of methyl and formyl radicals as well as radicals giving rise to a singlet ESR line was observed. The total number of free valences then increases, which was attributed to the following reactions:

$$RCOO\dot{C}H_2 \xrightarrow{h\nu} \begin{cases} \rightarrow H\dot{C}O + RCHO \\ \rightarrow \ddot{C}H_2 + RCOO\dot{} \end{cases},$$

$$\ddot{C}H_2 + RCOOCH_3 \rightarrow \dot{C}H_2 + RCOO\dot{C}H_2 .$$

The singlet line in the ESR spectra was assigned to radicals of the type RCOO (resistant to the action of light according to the authors), RO, and ROCO (which enter into photochemical reactions). This interpretation of the spectra is open to serious objections, because it is known[276] that radicals of type RCOO are unstable and decompose spontaneously, while radicals of the type RO cannot be stabilised in ester matrices. Analogous changes in the ESR spectra were observed in the photolysis of methyl acetate, sensitised by aromatic compounds, at 77 K.[277]

The photochemical reactions of the free radicals formed in the photolysis sensitised by aromatic compounds and γ-radiolysis of alkyl acetates at 77 K have been studied in detail[182, 278-280]. It was established that the radicals formed as a result of the abstraction of a hydrogen atom from the alcohol moiety of the molecule are effectively photolysed by light at a wavelength $\lambda = 365$ nm, giving rise to acetyl radicals and the molecules of the corresponding aldehydes and ketones;

$$CH_3COO\dot{C}R_1R_2 \xrightarrow{h\nu} CH_3\dot{C}O + O{=}CR_1R_2 .$$

The action of light at a wavelength $\lambda \geq 300$ nm on the radicals arising following the abstraction of a hydrogen atom from the acid moiety of the molecules obtained on γ-irradiation (at 77 K) of α-halogenoacid esters did not lead to an appreciable change of the ESR spectra[280]. Possibly in this case the reaction proceeds via the following mechanism:

$$R_1R_2\dot{C}COOR \rightarrow R_1R_2C{=}C{=}O + \dot{O}R .$$

However the lack of data for the photolysis products precludes a final determination of its mechanism at the present time.

The study of the photochemical reactions of ester radicals in polymeric matrices [poly(vinyl acetate) (PVA), poly(methyl methacrylate) (PMMA), and others] is of considerable interest. It has been established[76,155,281-283] that the action of light at a wavelength $\lambda \leq 380$ nm on the radicals $\sim CH_2\dot{C}(OCOCH_3)CH_2\sim$, which are formed in PVA γ-irradiated at 77 K, leads to the formation of radicals giving rise to a 4-line ESR spectrum with a splitting of 23 G and intensity ratios of 1 : 3 : 3 : 1. When PVA specimens are kept at 77 K, the initial ESR spectrum is restored. The observed reactions of the radicals of PVA were explained by the isomerisation of the macroradicals[76,155,282]:

$$\sim CH_2\dot{C}(OCOCH_3)CH_2\sim \underset{}{\overset{h\nu}{\rightleftarrows}} \sim CH(OCOCH_3)\dot{C}HCH(OCOCH_3)\sim .$$

However, the study of the gaseous products formed in the photolysis of the radicals $\sim CH_2\dot{C}(OCOCH_3)CH_2\sim$ by light at a wavelength $\lambda \geq 360$ nm showed[283] that this involves the accumulation of considerable amounts of methane and carbon monoxide. Consequently macroradicals undergo photodissociation in this instance too:

$$\sim CH_2\dot{C}(OCOCH_3)CH_2\sim \xrightarrow{h\nu} \sim CH_2\underset{\underset{O}{\|}}{C}CH_2\sim + CH_3\dot{C}O ,$$

with subsequent photolysis of the acetyl radicals. Thus the 4-line ESR spectrum observed in a number of studies[76,155,281,282] refers to the methyl radical and not to $\sim CH(OCOCH_3)\dot{C}HCH.(OCOCH_3)\sim$.

When PMMA,[282,284] poly(methyl acrylate), and poly(n-hexyl methacrylate)[284] specimens γ-irradiated at 77 K were exposed to radiation, changes were observed in the ESR spectra, which were explained by the occurrence of a number of photochemical reactions of free radicals. However, the mechanism proposed by the authors[284] for these processes is inaccurate owing to the erroneous interpretation of certain signals in the ESR spectra.

When poly(ethyl acrylate) γ-irradiated at 77 K is exposed to light[285], the radical species giving rise to a singlet ESR spectrum vanishes and ethyl radicals are formed:

$$\sim CH_2-\underset{\dot{O}-\underset{\dot{O}-C_2H_5}{\overset{|}{C}}-C_2H_5}{\overset{|}{CH}}\sim \xrightarrow{h\nu} \dot{C}_2H_5 + \sim CH_2-\underset{\underset{\dot{O}-C_2H_5}{\overset{|}{C}}=O}{\overset{|}{CH}}\sim .$$

However, the observed changes in the ESR spectra are most probably associated either with the photochemical reactions of the acyl radicals or with the photolysis of the corresponding radical-anion, which can be stabilised in the ester matrix on γ-radiolysis[286,287].

The mechanism of the photochemical reactions of radicals in PMMA has been studied in greatest detail by Toptygin and coworkers[198,199,288]. Analysis of the ESR spectra established

that the radicals in PMMA enter into the following photochemical reactions:

$$\sim (CH_3)\,C\,(COOCH_3)\,\dot{C}H\,(CH_3)\,C\,(COOCH_3) \sim \xrightarrow{h\nu} \rightarrow \sim (CH_3)\,C\,(COOCH_3)\,CH{=}C\,(CH_3) + O\dot{C}OCH_3 \ .$$

The radicals $O\dot{C}OOCH_3$ dissociate under the influence of light at a wavelength $\lambda \leq 380$ nm with formation of $\dot{C}H_3$ and CO_2 (it has been established[289] that the radicals $O\dot{C}OR$ have an absorption maximum at $\lambda = 330$–335 nm; $\varepsilon \cong 10^3$ litre mol^{-1} cm^{-1}; the quantum yield of photolysis by light at a wavelength $\lambda = 313$ nm at 77 K is 0.24).

The radicals formed as a result of the abstraction of a hydrogen atom from the alcohol moiety in PMMA dissociate under the influence of radiation to form the radicals $H\dot{C}O$:

$$\sim CH_2\,(CH_3)\,C\,(COO\dot{C}H_2)\,CH_2 \sim \xrightarrow{h\nu} [\sim CH_2\,(CH_3)\,C\,(\dot{C}{=}O)\,CH_2 \sim + H_2CO] \rightarrow \rightarrow \sim CH_2\,(CH_3)\,C\,(CHO)\,CH_2 \sim + H\dot{C}O \ .$$

Furthermore, it might have been expected that photochemical reactions of central macroradicals can occur in PMMA with dissociation of the main polymer chain, for example:

$$\sim (CH_3)C(COOCH_3)\,\dot{C}H\,(CH_3)C(COOCH_3) \sim \xrightarrow{h\nu} \dot{C}H_2 \sim (CH_3)C(COOCH_3) \sim + + \sim (CH_3)C(COOCH_3)\,CH{=}(CH_3)C(COOCH_3) \ .$$

The study of the degradation of PMMA in its photolysis initiated by iron(III) chloride and potassium hexacyanoferrate(II) [290,291] and in the direct photolysis and photolysis sensitised by aromatic compounds[287,292,293] showed that the decomposition of the main polymer chain occurs mainly in thermal and not photochemical reactions of radicals.

An ESR study of the photolysis of liquid acetone in the presence of various additives established that, together with the spectrum due to the radical $\dot{C}H_2COCH_3$, there are lines associated with the methyl radical[294]. On this basis, the authors suggested that the following reaction occurs on irradiation:

$$\dot{C}H_2COCH_3 \xrightarrow{h\nu} \dot{C}H_3 + CH_2{=}C{=}O \ . \qquad (7)$$

The action of light at a wavelength $\lambda \leq 340$ nm on the radicals $\dot{C}H_2COCH_3$, stabilised in acetone γ-irradiated at 77 K, led to a decrease of their concentration and to a simultaneous increase of the concentration of methyl radicals $\dot{C}H_3$ and acetyl radicals, giving rise to a singlet ESR spectrum[264]. The rate constants for the destruction of acetonyl radicals and the accumulation of $\dot{C}H_3$ radicals, obtained from the linear sections of the kinetic curves, proved to be approximately equal. These data confirm that the acetonyl radical decomposes via reaction (7). The appearance of the radicals $CH_3\dot{C}O$ may be caused by the photolysis of keten and by the subsequent dark reactions involving CO. Analogous results were obtaineed in a study of the photolysis of acetone in the presence of hydrogen peroxide[295].

The mechanisms of the photolysis of aliphatic aldehydes and ketones at 77 K (acetaldehyde, propionaldehyde, and isobutyraldehyde; ethyl methyl ketone, isopropyl methyl ketone, and diethyl ketone) have been investigated. It has been observed[173,265,296] that, when radicals are irradiated at a wavelength $\lambda \leq 340$ nm in aldehydes and ketones, changes occur in the ESR spectra, associated, according to the authors, with the following reactions:

$$R_1R_2\dot{C}CHO \xrightarrow{h\nu} R_1R_2\dot{C}H + CO \ ,$$
$$R_1R_2\dot{C}COR \xrightarrow{h\nu} R_1R_2\dot{C}H + R'{=}C{=}O \ .$$

It is important to note that the reaction mechanism has been proposed solely on the basis of the analysis of complex ESR spectra and apparently consists of many stages. When solutions of hydrogen peroxide in acetic acid were acted upon by the total radiation of the high-pressure mercury lamp at 77 K, the formation of methyl and formyl radicals as well as species giving rise to a singlet ESR spectrum was observed by ESR. The authors[275] believe that, under the influence of light at a wavelength $\lambda \leq 400$ nm, the $\dot{C}H_2COOH$ radicals undergo a branched-chain photolysis with formation of the radicals $\dot{C}H_3$, $H\dot{C}O$, and $\dot{C}OOH$:

$$\dot{C}H_2COOH \xrightarrow{h\nu} \begin{cases} \rightarrow H\dot{C}O + CH_2O \\ \rightarrow \dot{C}H_2 + \dot{C}OOH \end{cases} \ , \qquad (8)$$
$$\dot{C}H_2 + CH_3COOH \rightarrow \dot{C}H_3 + CH_2COOH \ .$$

The formation of methyl radicals in the photolysis by radiation at a wavelength $\lambda \geq 270$ nm of the radicals $\dot{C}H_2COOH$, obtained by the γ-radiolysis of aqueous acetic acid solutions at 77 K, has been observed[297]. Calculation of the electronic structure of the $\dot{C}H_2COOH$ radicals by the CNDO method showed[192] that, on σ–π^* excitation, the dissociation of the C–OH bond is most probable (bond energy approximately 2.5 eV). The probability of dissociation at the C–C bond diminishes, which throws doubt on the possibility of reaction (8).

The photochemical reactions of monocarboxylic acid radicals have been studied in greatest detail by Chervonenko and Roginskii[192,298], who established that irradiation at a wavelength in the range $300 \leq \lambda \leq 400$ nm of the $R\dot{C}HCOOH$ radicals, formed in γ-irradiated acetic, propionic, butyric, and isovaleric acids, leads to the formation (among other reaction products) of CO_2 and the hydrocarbons RCH_3 in approximately equal yields. The fact that methyl radicals are formed in the CH_3COOD matrix on photolysis of the radicals $\dot{C}H_2COOD$ at 77 K shows that the radicals $R\dot{C}HCOOH$ in the excited state react with the surrounding molecules:

$$R\dot{C}HCOOH + RCH_2COOH \xrightarrow{h\nu} RCH{=}C\,(OH)_2 + RCH_2C\dot{O}O \ , \qquad (9)$$
$$RCH{=}C\,(OH)_2 \rightarrow RCH{=}C{=}O + H_2O \ ,$$
$$RCH_2C\dot{O}O \rightarrow R\dot{C}H_2 + CO_2 \ . \qquad (10)$$

The quantum yield of reaction (9), determined from the initial linear section of the curve for the accumulation of methyl radicals in 10 and 25% acetic acid solutions in 10 M H_2SO_4 on irradiation at a wavelength $\lambda = 310$ nm, proved to be $(4 \pm 2) \times 10^{-3}$.

Apart from reaction (9), the photolysis of the radicals $R\dot{C}HCOOH$ may be expected to involve processes which are difficult to detect by ESR and by analysing stable reaction products, particularly the reaction

$$R\dot{C}HCOOH \xrightarrow{h\nu} RCH{=}C{=}O + \dot{O}H \ . \qquad (11)$$

The study of the photolysis by light at a wavelength $\lambda \geq 360$ nm of the radicals $\dot{C}H_2COOH$, obtained by the γ-irradiation of a 10% monochloroacetic acid solution in 1-propanol at 77 K, showed that 1-propanol radicals then accumulate. The quantum yield of the reaction for light at a wavelength $\lambda = 310$ nm is 0.3 ± 0.2.

When the radicals stabilised on γ-irradiation in acetic, propionic, and butyric anhydrides at 77 K are acted upon by light, the main process is their dissociation[299]:

$$R\dot{C}HCOOCOCH_2R \xrightarrow{h\nu} RCH{=}C{=}O + RCH_2C\dot{O}O \ . \qquad (12)$$

The dissociation is followed by the spontaneous decomposition of $RCH_2C\dot{O}O$ via reaction (10). The quantum yield of reaction (12), determined from the linear section of the kinetic curve for the accumulation of the radicals $\dot{C}H_3$ in acetic anhydride on irradiation at a wavelength $\lambda = 313$ nm at 77 K, is 0.9 ± 0.1.

Thus the main process when ester, aldehyde, ketone, acid, and acid anhydride radicals are acted upon by light at the wavelengths corresponding to their absorption bands is their dissociation.

VII. CONCLUSION

Despite the apparent wide variety of the photochemical reactions of radicals in different systems, there are certain characteristics which make it possible to predict with a particular degree of probability the type of reaction as a function of the type of excitation[5]. Table 8 shows that radicals subjected to $\pi-\sigma^*$ and $\sigma-\pi^*$ excitation undergo virtually only the photodissociation reaction and the quantum yields of these processes are high. Less definite conclusions can be reached concerning the mode of the photochemical reactions with $n-\pi^*$ excitation; here it is necessary to obtain additional experimental and calculated data.

Table 8. Photochemical reactions of free radicals of different types.

Radicals	Excitation	Type of reaction	Quantum yield	Refs.
Alkyl	$\pi \rightarrow \sigma^*$	dissociation	0.01	30
Alkyl	$\pi \rightarrow \sigma^*$	substitution	0.5 ± 0.15	30
Peroxy	$n \rightarrow \pi^*$	dissociation, substitution	$(0.04\pm0.01)\times(0.7\pm0.3)$	150, 151
Acyl	$\sigma \rightarrow \pi^*$	dissociation	—	—
From alcohols	$\pi \rightarrow \sigma^*$	dissociation, ionisation (?)	0.3 ± 0.2	180, 192
From ethers	$\pi \rightarrow \sigma^*$	dissociation	0.3 ± 0.2	180, 192
From esters	$\pi \rightarrow \sigma^*$	dissociation	—	—
From aldehydes	$\pi \rightarrow \sigma^*$	dissociation	—	—
From ketones	$\pi \rightarrow \sigma^*$	dissociation	—	—
From acids	$\pi \rightarrow \sigma^*$	dissociation	0.3 ± 0.2	192, 298
From acid anhydrides	$\pi \rightarrow \sigma^*$	dissociation	0.9 ± 0.1	192, 299

REFERENCES

1. V.S.Chervonenko and S.Ya.Pshezhetskii, Khim.Vys. Energii, **9**, 559 (1975).
2. A.Habersbergerova, I.Janovsky, and J.Teply, Radiat. Res.Rev., **1**, 109 (1968); **4**, 123 (1972).
3. S.Ya.Pshezhetskii, A.G.Kotov, V.K.Milinchuk, V.A.Roginskii, and V.I.Tupikov, "EPR Svobodnykh Radikalov v Radiatsionnoi Khimii" (EPR of Free Radicals in Radiation Chemistry), Izd.Khimiya, Moscow, 1972, p.381
4. S.Ya.Pshezhetskii, A.G.Kotov, V.K.Milinchuk, and V.I.Tupikov, Int.J.Radiat.Phys.Chem., **6**, 159 (1974).
5. S.Ya.Pshezhetskii, Zhur.Vses.Khim.Obshch.im. Mendeeleva, **20**, 84 (1975).
6. A.I.Bogatyreva and A.L.Buchachenko, Uspekhi Khim., **44**, 2171 (1975) [Russ.Chem.Rev., No.12 (1975)].
7. E.R.Klinshpont and V.K.Milinchuk, "Obzory po Otdel'nym Proizvodstvam Khimicheskoi Promyshlennosti" (Reviews on Individual Manufacturing Processes in Chemical Industry), Izd.NIITEKhIM, Moscow, 1976, No.6.
8. G.Herzberg, "The Spectra and Structures of Simple Free Radicals" (Translated into Russian), Izd.Mir, Moscow, 1974, p.161.
9. G.Herzberg and J.Shoosmith, Can.J.Phys., **34**, 523 (1956).
10. G.Herzberg, Proc.Roy.Soc.A, **262**, 291 (1961).
11. D.A.Parkes, D.M.Paul, C.P.Quinn, and R.C.Robson, Chem.Phys.Letters, **23**, 425 (1973).
12. P.D.Pacey, Chem.Phys.Letters, **23**, 394 (1973).
13. R.Harvey and P.F.Jessen, Nature (Phys.Sci.), **241**, 102 (1973).
14. G.C.Stevens, R.M.Clarke, and E.J.Hart, J.Phys. Chem., **76**, 3863 (1972).
15. H.C.Christensen, G.Nilsson, K.A.Thomas, and T.Reitberger, Chem.Phys.Letters, **22**, 533 (1973).
16. H.E.van den Berg and A.B.Callear, Trans.Faraday Soc., **66**, 2681 (1970).
17. D.G.Horne and R.G.W.Norrish, Proc.Roy.Soc.A, **315**, 301 (1971).
18. M.L.Pohjonen, L.Leinonen, H.Lemmetyinen, and J.Kashikallio, Finn.Chem.Letters, 207 (1974).
19. B.Hickel, J.Phys.Chem., **79**, 1054 (1975).
20. D.A.Parkes, D.M.Paul, and C.P.Quinn, J.Chem.Soc., Faraday Trans.I, **72**, 1935 (1976).
21. J.J.McCarvey and W.P.McGrath, Trans.Faraday Soc., **60**, 2196 (1964).
22. C.J.Hochanadel, J.A.Ghormley, J.W.Boyle, and P.J.Ogren, J.Phys.Chem., **81**, 3 (1977).
23. F.C.James, J.A.Kerr, and J.P.Symons, Ber. Bunsenges.Phys.Chem., **78**, 204 (1974).
24. M.Levy and J.P.Simons, J.Chem.Soc., Faraday Trans. II, **71**, 561 (1975).
25. D.A.Parkes, D.M.Paul, and C.P.Quinn, J.Chem.Soc., Faraday Trans.I, **72**, 1952 (1976).
26. A.G.Gaydon, G.N.Spokes, and J.van Suchtelen, Proc. Roy.Soc.A, **256**, 323 (1960).
27. H.R.Wendt, D.Wyrsch, and H.E.Hunziker, Ber. Bunsenges Phys.Chem., **78**, 201 (1974).
28. R.W.F.Lonwrier and W.H.Hamill, J.Phys.Chem., **73**, 1707 (1969).
29. D.A.Parkes and C.P.Quinn, Chem.Phys.Letters, **33**, 483 (1975).
30. M.Ya.Mel'nikov and N.V.Fok, "Tezisy Dokladov III Vsesoyuznogo Soveshchaniya po Fotokhimii, Rostov-na-Donu, 1977" (Abstracts of Reports at the IIIrd All-Union Conference on Photochemistry, Rostov-on-Don, 1977), p.201.
31. L.W.Burggraf and R.F.Firestone, J.Phys.Chem., **75**, 508 (1971).
32. M.C.Sauer and I.Mani, J.Phys.Chem., **72**, 3856 (1968).
33. J.E.Jordan and D.W.Pratt, J.Amer.Chem.Soc., **96**, 5588 (1974).
34. A.Ekstrom, R.Suenram, and J.E.Willard, J.Phys. Chem., **74**, 1888 (1970).
35. V.I.Sklyarenko, M.Ya.Melnikov, and N.V.Fock, Chem. Comm., 167 (1975).
36. M.Ya.Mel'nikov, V.I.Sklyarenko, and N.V.Fok, Dokl. Akad.Nauk SSSR, **218**, 758 (1974).
37. R.H.Schuler and L.K.Patterson, Chem.Phys.Letters, **27**, 369 (1974).
38. T.Soylemez and R.H.Schuler, J.Phys.Chem., **78**, 1052 (1974).
39. J.Rabani, M.Pick, and M.Simic, J.Phys.Chem., **78**, 1049 (1974).
40. M.Ebert, J.P.Keeme, E.J.Land, and A.J.Swallow, Proc.Roy.Soc.A, **287**, 1 (1965).
41. M.Simic and R.Hayon, J.Phys.Chem., **75**, 1677 (1971).
42. T.Reitberger, Radiochem.Radioanal.Letters, **5**, 349 (1970).
43. R.H.Partridge, J.Chem.Phys., **52**, 1277 (1970).
44. D.C.Waterman and M.Dole, J.Phys.Chem., **71**, 1906 (1970).
45. D.M.Bodily and M.Dole, J.Chem.Phys., **45**, 1428, 1433 (1966).
46. V.V.Vasilenko, E.R.Klinshpont, and V.K.Malinchuk, Khim.Vys.Energii, **8**, 273 (1974).
47. B.Lesique, L.Gilles, and R.J.Woods, Can.J.Chem., **52**, 1135 (1974).

48. Yu.A.Kiryushin and V.A.Poluektov, Zhur.Fiz.Khim., **46**, 1764 (1972) [Russ.J.Phys.Chem., No.7 (1972)].
49. M.Iwasaki and K.Toriyama, J.Chem.Phys., **47**, 559 (1967).
50. M.Iwasaki and K.Toriyama, J.Chem.Phys., **46**, 2852 (1967).
51. P.B.Ayscough and C.Thomson, Trans.Faraday Soc., **58**, 1477 (1962).
52. P.B.Ayscough, K.J.Ivin, J.M.O'Donnel, and C.Thomson, V Int.Symp.on Free Radicals, Uppsala, 1961.
53. N.Leray and J.Roncin, Int.J.Radiat.Phys.Chem., **4**, 347 (1972).
54. N.F.Shamonina and A.G.Krotov, Khim.Vys.Energii, **6**, 478 (1972).
55. Y.Kidani, S.Uno, H.Koike, and M.Iwasaki, Ann.Rept.Fac.Parm.Nagoya Sity Univ., **19**, 22 (1971).
56. M.Iwasaki, T.Ichikawa, and K.Toriyama, J.Polymer Sci., B**5**, 423 (1967).
57. K.Tsuji and T.Seiki, Polymer J., 1, 133 (1970).
58. E.R.Klinshpont, V.K.Milinchuk, and S.Ya.Pshezhetskii, Vysokomol.Soed., A**15**, 1963 (1973).
59. E.N.Teleshov, V.A.Sharpatyi, A.N.Pravednikov, and S.S.Medvedev, Zhur.Strukt.Khim., **5**, 627 (1964).
60. H.Nishimura, N.Tamura, Y.Tabata, and K.Oshima, J.Chem.Soc.Japan (Ind.Chem.Sect.), **73**, 1227, 1233 (1970).
61. H.Nishimura, N.Tamura, Y.Tabata, and K.Oshima, J.Chem.Soc.Japan (Pure Chem.Sect.), **91**, 787 (1970).
62. F.C.Adam and I.R.H.Marshall, Can.J.Chem., **54**, 3833 (1976).
63. E.M.Burbo, Candidate's Thesis, Moscow State University, Moscow, 1975.
64. F.J.Adrian, V.A.Bowers, and E.L.Cochran, J.Chem. Phys., **63**, 919 (1975).
65. A.A.Ovchinnikov and V.G.Plotnikov, "Tezisy Dokladov III Vsesoyuznogo Soveshchaniya po Fotokhimii, Rostov-na-Donu, 1977" (Abstracts of Reports at the IIIrd All-Union Conference on Photochemistry, Rostov-on-Don, 1977), p.7.
66. K.Tsuji and F.Williams, J.Phys.Chem., **73**, 4017 (1969).
67. V.S.Pudov, A.I.Bogatyreva, A.L.Buchachenko, and M.B.Neiman, Vysokomol.Soed., B**9**, 622 (1967).
68. A.I.Bogatyreva, A.G.Sklyarova, and A.L.Buchachenko, Khim.Vys.Energii, **5**, 37 (1971).
69. L.M.Baider, Candidate's Thesis, Moscow State University, Moscow, 1971.
70. L.M.Baider, M.V.Voevodskaya, and N.V.Fok, Khim. Vys.Energii, **5**, 422 (1971).
71. V.P.Malinskaya, L.M.Baider, and N.V.Fok, Khim.Vys. Energii, **3**, 91 (1969).
72. H.Joshida and B.Ranby, J.Polymer Sci., B**12**, 1155 (1964).
73. B.Ranby and H.Joshida, J.Polymer Sci., C**10**, 236 (1966).
74. H.L.Browning, I.R.H.Ackerman, and H.W.Patton, J.Polymer Sci., A-1, **4**, 1433 (1966).
75. V.K.Milichuk, Vysokomol.Soed, **7**, 1293 (1965).
76. V.K.Milinchuk and E.R.Klinshpont, Khim.Vys.Energii, **1**, 352 (1967).
77. K.Tsuji and T.Seiki, J.Polymer Sci.Polymer Letters, **10**, 139 (1972).
78. V.V.Vasilenko, E.R.Klinshpont, and V.K.Milinchuk, "Tezisy Dokladov III Vsesoyuznogo Soveshchaniya po Fotokhimii, Rostov-na-Donu, 1977" (Abstracts of Reports at the IIIrd All-Union Conference on Photochemistry, Rostov-on-Don, 1977), p.167.
79. K.Tsuji and S.Okamura, Bull.Chem.Soc.Japan, **42**, 2827 (1969).
80. K.Tsuji, H.Yoshida, K.Hayashi, and S.Okamura, Ann. Rept.of Japanese Association for Radiation Research on Polymers, **7**, 119 (1965–1966).
81. D.J.Henderson and J.E.Willard, J.Amer.Chem.Soc., **91**, 3014 (1969).
82. M.Ya.Mel'nikov, Vestnik Moskov.Gos.Univ., Ser.Khim., 55 (1975).
83. M.Ya.Mel'nikov, Vestnik Moskov.Gos.Univ., Ser.Khim., 495 (1976).
84. T.Ichikawa and N.Ohta, J.Phys.Chem., **81**, 560 (1977).
85. D.P.Lin, J.Chin.Chem.Soc., **21**, 201 (1974).
86. A.J.Elliot and F.C.Adam, Can.J.Chem., **52**, 102 (1974).
87. D.D.Wilkey, H.W.Fenrick, and J.E.Willard, J.Phys. Chem., **81**, 220 (1977).
88. E.D.Sprague and J.E.Willard, J.Chem.Phys., **63**, 2603 (1975).
89. G.K.Vasil'ev and V.L.Tal'roze, Kinetika i Kataliz, **4**, 497 (1963).
90. D.H.Ellison, G.A.Salmon, and F.Wilkinson, Proc. Roy.Soc.A, **328**, 23 (1972).
91. V.E.Zubarev, "Tezisy Dokladov Konferentsii Molodykh Uchenykh g Moskvy" (Abstracts of Reports at the Conference of Young Scientists from the City of Moscow), Moscow, 1978, p.116.
92. V.E.Zubarev, V.N.Belevskii, and L.T.Bugaenko, Uspekhi Khim., **48**, 1361 (1979) [Russ.Chem.Rev., No.8 (1979)].
93. C.Chachaty and A.Forchioni, Compt.rend., C**268**, 300 (1969).
94. Y.Takegami, S.Imamura, F.Masuda, and Y.Watanabe, J.Chem.Soc., Japan, Ind.Chem.Sect., **72**, 1876 (1969).
95. V.I.Kurlyankina, V.N.Shadrin, E.N.Kazbekov, V.A.Molotkov, and M.K.Burkina, Zhur.Obshch.Khim., **44**, 1593 (1974).
96. T.A.Garibyan, A.A.Mantashyan, A.B.Nalbandyan, and A.S.Saakyan, Arm.Khim.Zhur., **24**, 13 (1971).
97. S.Ya.Pshezhetskii, A.G.Kotov, V.K.Milinchuk, V.A.Roginskii, and V.N.Tupikov, "EPR Svobodnykh Radikalov v Radiatsionnoi Khimii" (ESPR of Free Radicals in Radiation Chemistry), Izd.Khimiya, Moscow, 1972, p.124.
98. J.A.Chromley and A.C.Stewart, J.Amer.Chem.Soc., **78**, 2934 (1956).
99. D.N.Sitharamoto and J.F.Dunkan, J.Phys.Chem., **67**, 2126 (1963).
100. O.F.Khodzhaev, B.T.Ershov, and A.K.Pikaev, Izv. Akad.Nauk SSSR, Ser.Khim., 246 (1968).
101. I.A.Taub and K.Eiben, J.Chem.Phys., **49**, 2499 (1968).
102. J.W.Boyle, J.A.Chromley, C.J.Hochanadel, and J.F.Riley, J.Phys.Chem., **73**, 2886 (1969).
103. P.Pagsberg, H.Christenen, J.Rabani, G.Nilsson, J.Fenger, and S.O.Nielsen, J.Phys.Chem., **73**, 1029 (1969).
104. J.K.Thomas, J.Rabani, M.S.Matheson, E.J.Hart, and S.Gordon, J.Phys.Chem., **70**, 2409 (1966).
105. D.M.Bradley, in Pulse Radiolysis, Acad.Press, London, 1965, p.289.
106. D.M.Brown, F.S.Dainton, D.C.Walker, and J.P.Keene, in Pulse Radiolysis, Acad.Press, London, 1965, p.221.
107. J.Rabani, Adv.Chem.Ser., **81**, 131 (1968).
108. H.Büchler, R.E.Buhler, and R.Cooper, J.Phys. Chem., **80**, 1549 (1976).
109. G.G.Jayson, B.J.Parsons, and A.J.Swallow, J.Chem.Soc., Faraday Trans.I, **69**, 1597 (1973).

110. S.O.Nielsen, Proc.X, Czech.Ann.Meeting on Radiation Chemistry, Marianske Lazne, 1970, p.406.
111. W.D.McGrath and J.J.McGarvey, Nature, **201**, 991 (1964).
112. J.J.McGarvey and W.D.McGrath, Trans.Faraday Soc., **60**, 2196 (1964).
113. F.Lenci and H.Neubacher, Chem.Phys.Letters, **16**, 28 (1972).
114. J.Moan, Photochem.Photobiol., **22**, 111 (1975).
115. G.Czapski and L.M.Dorfman, J.Phys.Chem., **68**, 1169 (1964).
116. S.Gordon, E.J.Hart, and J.K.Thomas, J.Phys.Chem., **68**, 1262 (1964).
117. G.E.Adams, J.W.Boag, and B.D.Michael, Proc.Roy. Soc.A, **289**, 321 (1966).
118. T.T.Pankert and H.S.Johnston, J.Chem.Phys., **56**, 2824 (1972).
119. B,H.Bielski and H.A.Schwarz, J.Phys.Chem., **72**, 3836 (1968).
120. J.Rabani and S.O.Nielsen, J.Phys.Chem., **72**, 3736 (1969).
121. H.Kijewski and J.Troe, Int.J.Chem.Kinet., **3**, 223 (1971).
122. D.Behar and G.Czapski, Isr.J.Chem., **8**, 699 (1970).
123. H.Kijewski and J.Troe, Ber.Bunsenges.Phys.Chem., **75**, 1131 (1971).
124. C.J.Hochanadel, J.A.Chormley, and P.J.Ogren, J.Chem.Phys., **56**, 4426 (1972).
125. H.Kijewski and J.Troe, Helv.Chim.Acta, **55**, 205 (1972).
126. G.M.Zimina and N.A.Bakh, Khim.Vys.Energii, **8**, 56 (1974).
127. G.M.Zimina, A.L.Karasev, and N.A.Bakh, Khim.Vys. Energii, **5**, 176 (1971).
128. R.L.McCarthy and A.MacLachlan, Trans.Faraday Soc., **56**, 1187 (1960).
129. R.L.McCarthy and A.MacLachlan, Trans.Faraday Soc., **57**, 1107 (1961).
130. R.L.McCarthy and A.MacLachlan, J.Chem.Phys., **35**, 1625 (1961).
131. N.A.Bakh and G.M.Zimina, Khim.Vys.Energii, **3**, 92 (1969).
132. K.Stockhausen, A.Fojtik, and A.Henglein, Ber. Bunsenges.Phys.Chem., **74**, 34 (1970).
133. J.Rabani and D.Klug-Roth, J.Phys.Chem., **78**, 2089 (1974).
134. K.Stockhausen, A.Henglein, and G.Beek, Ber. Bunsenges.Phys.Chem., **73**, 567 (1969).
135. Y.Ilan, J.Rabani, and A.Henglein, J.Phys.Chem., **80**, 1558 (1976).
136. L.M.Dorfman, I.A.Taub, and R.E.Buhler, J.Chem. Phys., **36**, 3051 (1962).
137. E.Hayon and M.Simic, J.Amer.Chem.Soc., **95**, 6681 (1973).
138. L.R.Josimovic, I.G.Draganic, and V.M.Markovic, Glasnik Hem.Brus.Beograd, **41**, 75 (1976).
139. Yu.A.Kiryushin and V.A.Poluektov, Kinetika i Kataliz, **16**, 1118 (1975).
140. V.K.Milinchuk and S.Ya.Pshezhetskii, Dokl.Akad.Nauk SSSR, **152**, 665 (1963).
141. E.R.Klinshpont, V.K.Milinchuk, and S.Ya.Pshezhetskii, Vysokomol.Soed., **B12**, 88 (1970).
142. Yu.A.Ershov, A.F.Lukovnikov, and A.A.Baturina, Kinetika i Kataliz, **7**, 601 (1966).
143. Yu.A.Ershov and Yu.V.Gak, Izv.Akad.Nauk SSSR, Ser.Khim., 778 (1967).
144. M.Ya.Mel'nikov, L.M.Baider, and N.V.Fok, Khim.Vys. Energii, **11**, 338 (1977).
145. J.T.Martin and R.G.W.Norrish, Proc.Roy.Soc.A, **220**, 322 (1953).
146. M.A.Pospelova, V.G.Belokon', and V.S.Gurman, Dokl. Akad.Nauk SSSR, 212, 414 (1973).
147. V.S.Gurman and G.B.Sergeev, Zhur.Fiz.Khim., **44**, 1086 (1970) [Russ.J.Phys.Chem., No.4 (1970)].
148. E.R.Klinshpont, V.K.Milinchuk, S.M.Dmitriev, and A.I.Kurilenko, Vysokomol.Soed., A14, 1596 (1972).
149. E.R.Klinshpont and V.K.Milinchuk, Vysokomol.Soed., **B15**, 35 (1973).
150. V.V.Vasilenko, E.R.Klinshpont, and V.K.Milinchuk, Khim.Vys.Energii, **10**, 428 (1976).
151. V.K.Milinchuk, E.R.Klinshpont, and V.V.Vasilenko, J.Polymer Sci., Polymer Chem.Ed., **14**, 1419 (1976).
152. E.R.Klinshpont, V.K.Milinchuk, and S.Ya.Pshezhetskii, Vysokomol.Soed., A12, 1505 (1970).
153. S.Siegel and H.Hedgpeth, J.Chem.Phys., **46**, 3904 (1967).
154. P.Hedvig, J.Polymer Sci., A1, 1145 (1969).
155. V.K.Milinchuk, E.R.Klinshpont, and S.Ya.Pshezhetskii, Symposium, "Radiatsionnaya Khimiya Polimerov" (Radiation Chemistry of Polymers), Izd.Nauka, Moscow, 1966, p.211.
156. E.R.Klinshpont and V.K.Milinchuk, Khim.Vys.Energii, **1**, 242 (1967).
157. T.Tagawa, H.Amemiya, I.Shinochara, M.Hagiwara, and T.Kagia, J.Polymer Sci., Polymer Chem.Ed., **13**, 2843 (1975).
158. M.Hagiwara, T.Tagawa, H.Amemiya, K.Araki, I.Shinochara, and T.Kagia, J.Polymer Sci., Polymer Chem.Ed., **14**, 2167 (1976).
159. V.K.Milinchuk and E.R.Klinshpont, J.Polymer Sci., C40, 1 (1973).
160. C.Chachaty and E.Hayon, Nature, **200**, 59 (1963).
161. C.Chachaty and E.Hayon, J.Chim.Phys., **61**, 1115 (1964).
162. B.N.Shelimov, N.V.Fok, and V.V.Voevodskii, Kinetika i Kataliz, **5**, 1008 (1964).
163. A.K.Piskunov and D.N.Shigorin, Teor.Eksper.Khim., **3**, 266 (1967).
164. A.K.Piskunov, N.V.Verein, and G.A.Ozerov, Zhur. Fiz.Khim., **41**, 1524 (1967) [Russ.J.Phys.Chem., No.6 (1967)].
165. F.S.Dainton, G.Salmon, and P.Wardman, Proc.Roy. Soc., A313, 1 (1969).
166. H.Hirai and M.Fujwara, J.Chem.Soc.Japan, 968 (1972).
167. C.Chachaty and A.Forchioni, J.Chim.Phys., 66, 929 (1969).
168. H.S.Judeikis and S.Siegel, J.Chem.Phys., **43**, 3625 (1965).
169. J.E.Bennett, B.Mile, and B.Ward, Chem.Comm., 13 (1969).
170. J.E.Bennett, B.Mile, A.Thomas, and B.Ward, Adv. Phys.Org.Chem., **8**, 1 (1970).
171. J.E.Bennett and B.Mile, Trans.Faraday Soc., **67**, 1587 (1971).
172. N.D.Chuvylkin and G.M.Zhidomirov, Zhur.Strukt. Khim., **13**, 236 (1972).
173. M.Ya.Mel'nikov, L.M.Baider, and N.V.Fok, Dokl.Akad. Nauk SSSR, **206**, 122 (1973).
174. H.M.Heuvel and K.C.Lind, J.Polymer Sci., A-2, **8**, 401 (1970).
175. K.Tsuji and T.Seiki, J.Polymer Sci., A-1, **9**, 3063 (1971).
176. Y.Hama, K.Hosono, Y.Furui, and K.Shinochara, J.Polymer Sci., A-1, **9**, 1411 (1971).
177. Y.Hama, T.Ooi, and K.Shinochara, Polymer, 15, 787 (1974).

178. Y.Hama and K.Shinochara, Mol.Phys., **18**, 279 (1970).
179. J.E.Guillet, Polymer Eng.Sci., **14**, 482 (1974).
180. V.S.Chervonenko, V.A.Roginskii, and S.Ya.Pshezhetskii, Khim.Vys.Energii, **4**, 450 (1970).
181. G.B.Pariiskii, L.M.Postnikov, E.Ya.Davydov, and D.Ya.Toptygin, Vysokomol.Soed., **A16**, 482 (1974).
182. T.Bettger, V.K.Fuki, and N.V.Fok, Dokl.Akad.Nauk SSSR, **207**, 632 (1972).
183. G.E.Ewing, W.E.Thompson, and G.C.Pimentel, J.Chem.Phys., **32**, 927 (1960).
184. D.A.Ramsay, J.Chem.Phys., **21**, 960 (1953).
185. J.W.C.Johns, S.H.Priddle, and D.A.Ramsay, Discuss. Faraday Soc., **35**, 90 (1963).
186. D.E.Milligan and M.E.Jacox, J.Chem.Phys., **51**, 277 (1969).
187. D.E.Milligan, M.E.Jacox, A.M.Bass, J.J.Comeford, and D.E.Mann, J.Chem.Phys., **42**, 3187 (1965).
188. D.K.W.Wang and W.E.Jones, J.Photochem., 1, 147 (1972).
189. M.E.Jacox and D.E.Milligan, J.Chem.Phys., **43**, 866 (1966).
190. S.Noda, K.Fueki, and Z.Kuri, J.Chem.Phys., **49**, 3287 (1968).
191. L.Josimovic, J.Teply, and O.I.Micic, J.Chem.Soc., Faraday Trans.I, **72**, 285 (1976).
192. V.S.Chervonenko, Candidate's Thesis, Karpov Physicochemical Institute, Moscow, 1973.
193. F.S.Dainton, G.A.Salmon, and U.F.Zucker, Proc.Roy. Soc.A, **320**, 1 (1970).
194. T.Yashitake, Kobunshi Kagaky, **29**, 467 (1972).
195. R.H.Walsh and S.W.Benson, J.Phys.Chem., **70**, 3751 (1966).
196. S.W.Benson, J.Chem.Educ., **42**, 502 (1965).
197. J.A.Kerr and A.C.Lloyd, Trans.Faraday Soc., **63**, 2480 (1967).
198. G.B.Pariiskii, E.Ya.Davydov, and D.Ya.Toptygin, Izv. Akad.Nauk SSSR, Ser.Khim., 2207 (1973).
199. E.Ya.Davydov, G.B.Pariiskii, and D.Ya.Toptygin, Vysokomol.Soed., A17, 1504 (1975).
200. G.P.Pariiskii, E.Ya.Davydov, and D.Ya.Toptygin, Izv. Akad.Nauk SSSR, Ser.Khim., 1054 (1973).
201. G.B.Pariysky, L.M.Postnikov, D.Ya.Toptygin, and E.Ya.Davidov, J.Polymer Sci., C1287 (1973).
202. Ya.N.Malkin, M.Ya.Mel'nikov, and N.V.Fok, Khim.Vys. Energii, **9**, 281 (1975).
203. V.V.Pervukhin, S.V.Kamyshan, A.A.Obynochnyi, and R.Z.Sagdeev, Khim.Vys.Energii, **11**, 283 (1977).
204. M.Simic, P.Neta, and E.Hayon, J.Phys.Chem., **73**, 3794 (1969).
205. M.C.Sauer and B.Ward, J.Phys.Chem., **71**, 3971 (1967).
206. A.Habersbergerova, L.Josimovic, and J.Teply, Trans. Faraday Soc., **66**, 669 (1970).
207. A.Habersbergerova, L.Josimovic, and J.Telpy, Trans. Faraday Soc., **66**, 656 (1970).
208. J.H.Baxendale, M.A.J.Rodgers, and M.D.Ward, J.Chem.Soc.A, 1246 (1970).
209. F.S.Dainton, J.P.Keene, T.J.Kemp, G.A.Salmon, and J.Teply, Proc.Chem.Soc., 265 (1964).
210. F.S.Dainton, G.A.Salmon, and J.Teply, Proc.Roy.Soc. A, **286**, 27 (1965).
211. R.S.Alger, T.H.Anderson, and L.A.Webb, J.Chem. Phys., **30**, 695 (1959).
212. S.Fujii and J.E.Willard, J.Phys.Chem., **74**, 4313 (1970).
213. C.F.Cullis, J.M.Francis, Y.Raef, and A.J.Swallow, Proc.Roy.Soc.A, **300**, 443 (1967).
214. J.W.Fletcher, P.J.Richards, and W.Seddom, Can.J. Chem., **48**, 3765 (1970).
215. A.Bernas, D.Grand, and C.Chachaty, Proc.X Czech. Ann.Meeting on Radiation Chemistry, Marianske Lazne, 1970, p.358.
216. T.A.Taub and L.M.Dorfman, J.Amer.Chem.Soc., **84**, 4053 (1962).
217. L.M.Dorfman and I.A.Taub, J.Amer.Chem.Soc., **85**, 2370 (1963).
218. C.Chachaty, A.Forchioni, and J.Desalos, Compt.rend., C270, 449 (1970).
219. A.Bernas, D.Grand, and C.Chachaty, Chem.Comm., 1667 (1970).
220. L.Gilles and A.W.Boyd. Can.J.Chem., **54**, 531 (1976).
221. V.S.Gurman and V.I.Papisova, Dokl.Akad.Nauk SSSR, 196, 1117 (1971).
222. M.Nakashima and E.Hayon, J.Phys.Chem., **75**, 1910 (1971).
223. S.Gordon, E.J.Hart, and J.K.Thomas, J.Phys.Chem., 68, 1263 (1964).
224. F.Kish and Kh.S.Bagdasar'yan, Zhur.Fiz.Khim., **40**, 1339 (1966) [Russ.J.Phys.Chem., No.6 (1966)].
225. G.Porter, S.K.Dogra, R.O.Lanffy, S.E.Sugamori, and R.W.Yip, J.Chem.Soc., Faraday Trans.I, **69**, 1462 (1973).
226. Y.Raef and A.J.Swallow, J.Phys.Chem., **70**, 4072 (1966).
227. K.M.Bansal, M.Gratzel, A.Heuglein, and E.Janata, J.Phys.Chem., **77**, 16 (1973).
228. J.S.Moore and A.F.Norris, Int.J.Radiat.Biol., **29**, 489 (1976).
229. V.S.Chervonenko, Khim.Vys.Energii, **10**, 458 (1976).
230. V.S.Chervonenko and S.Ya.Pshezhetskii, Vysokomol. Soed., B19, 783 (1977).
231. G.R.Roberts, M.Budzal, and M.Dole, J.Polymer Sci., A-2, 9, 1729 (1971).
232. U.Borgwardt, W.Schnabel, and A.Henglein, Makromol. Chem., **127**, 176 (1969).
233. V.V.Voevodsky, "IV Symp.on Free Radical Stabilization, Washington, 1959".
234. V.V.Voevodskii, Kinetika i Kataliz, 1, 45 (1960).
235. R.H.Johnsen, J.Phys.Chem., 63, 2088 (1959).
236. R.H.Johnsen, J.Phys.Chem., **65**, 2144 (1961).
237. B.N.Shelimov, N.V.Fok, and V.V.Voevodskii, Kinetika i Kataliz, **4**, 539 (1963).
238. B.N.Shelimov, Candidate's Thesis, Moscow State University, Moscow, 1964.
239. N.M.Bazhin, E.N.Kuznetsov, N.N.Bubnov, and V.V.Voevodskii, Kinetika i Kataliz, **7**, 732 (1966).
240. S.B.Milliken and R.H.Johnsen, J.Phys.Chem., **71**, 2116 (1967).
241. P.J.Sullivan and W.S.Koski, J.Amer.Chem.Soc., **86**, 159 (1964).
242. M.Shiotani and C.Chachaty, Bull.Chem.Soc.Japan, **47**, 28 (1974).
243. J.Moan, Int.J.Radiat.Phys.Chem., **5**, 293 (1973).
244. J.Moan, J.Phys.Chem., **79**, 2220 (1975).
245. E.I.Finkel'shtein, Vysokomol.Soed., **A9**, 70 (1967).
246. T.V.Ivanova, M.Ya.Mel'nikov, and N.V.Fok, Dokl. Akad.Nauk SSSR, **231**, 649 (1976).
247. M.C.R.Symons and M.G.Townsend, J.Chem.Soc., **263**, 277 (1959).
248. R.S.Alger, T.H.Anderson, and L.A.Webb, J.Chem. Phys., **35**, 49 (1961).
249. J.A.Brivati, N.Keen, and M.C.R.Symons, J.Chem. Soc., 237 (1962).
250. P.J.Sullivan and W.S.Koski, J.Amer.Chem.Soc., 84, 1 (1962).
251. P.J.Sullivan and W.S.Koski, J.Amer.Chem.Soc., **85**, 384 (1963).

252. V.I.Mal'tsev and A.A.Petrov, Zhur.Org.Khim., 1, 2140 (1965).
253. V.I.Mal'tsev and A.A.Petrov, Zhur.Org.Khim., 2, 1182 (1966).
254. K.Shimokashi, Y.Mori, and J.Tanaka, Bull.Chem.Soc., Japan, **40**, 302 (1967).
255. R.H.Johnsen and D.A.Becker, J.Phys.Chem., **67**, 871 (1963).
256. T.Ohmae, S.Ohnishi, H.Sakurai, and I.Nitta, J. Chem.Phys., 42, 4053 (1965).
257. E.Ya.Davydov, G.B.Pariiskii, and D.Ya.Toptygin, Izv. Akad.Nauk SSSR, Ser.Khim., 1747 (1974).
258. I.E.Makarov and B.G.Ershov, Izv.Akad.Nauk SSSR, Ser.Khim., 530 (1970).
259. N.-S.Non, J.Polymer Sci., Polymer Chem.Ed., 14, 2497 (1976).
260. Yu.V.Gak and A.F.Lukovnikov, Vysokomol.Soed., A12, 2415 (1970).
261. C.Chachaty, Compt.rend., C259, 2423 (1964).
262. S.Noda, K.Torimoto, K.Fueki, and Z.Kuri, Bull. Chem.Soc.Japan, **44**, 273 (1971).
263. T.Matsushige, G.Koltzenburg, and D.Schulte-Frohlinde, Ber.Bunsenges.Phys.Chem., **79**, 657 (1975).
264. G.V.Pukhal'skaya, A.G.Kotov, and S.Ya.Pshezhetskii, Zhur.Fiz.Khim., **40**, 714 (1966) [Russ.J.Phys.Chem., No.3 (1966)].
265. M.Ya.Mel'nikov and N.V.Fok, Dokl.Akad.Nauk SSSR, **206**, 1391 (1972).
266. D.M.Camaioni, H.F.Waiter, J.E.Jordan, and D.W.Pratt, J.Amer.Chem.Soc., **95**, 7978 (1973).
267. G.V.Buxton and R.M.Sellers, J.Chem.Soc., Faraday Trans.I, **69**, 555 (1973).
268. P.Neta, M.Simic, and E.Hayon, J.Phys.Chem., **73**, 4207, 4214 (1969).
269. H.W.Shields, W.Marsh, and P.J.Hamrich, J.Chem.Phys., **52**, 6437 (1970).
270. M.Z.Hoffman and E.Hayon, J.Phys.Chem., 77, 990 (1973).
271. M.Simic and E.Hayon, Radiat.Res., **48**, 244 (1971).
272. G.Ramanan, J.Phys.Chem., **80**, 1553 (1976).
273. J.J.Ten Bosch, W.F.Verhelst, and K.H.Chadwick, J.Polymer Sci., A-1, 10, 1679 (1972).
274. L.Josimovic and I.Draganic, Int.J.Radiat.Phys. Chem., **5**, 505 (1973).
275. V.I.Mal'tsev, B.N.Shelimov, and A.N.Petrov, Zhur. Org.Khim., **4**, 545 (1968).
276. A.L.Buchachenko, "Khimicheskaya Polyarizatsiya Elektronov i Yader" (Chemically Induced Polarisation of Electrons and Nuclei), Izd.Nauka, Moscow, 1974, p.95.
277. S.Mizutan, Y.Nakajima, and S.Sato, Bull.Chem.Soc. Japan, **43**, 2002 (1970).
278. V.K.Fuki, E.B.Glazman, N.Ya.Mel'nikov, and N.V.Fok, Vestnik Moskov.Gos.Univ., Ser.Khim., 706 (1974).
279. V.K.Fuki, E.B.Glazman, N.Ya.Mel'nikov, and N.V.Fok, Vestnik Moskov.Gos.Univ., Ser.Khim., 77 (1976).
280. V.K.Fuki, Candidate's Thesis, Moscow State University, Moscow, 1975.
281. N.A.Bakh, A.V.Vannikov, and A.D.Grishina, "Elektroprovodnost' i Paramagnetizm Polimernykh Poluprovodnikov" (The Conductivity and Paramagnetism of Polymeric Semiconductors), Izd.Nauka, Moscow, 1971, p.35.
282. V.K.Milinchuk and S.Ya.Pshezhetskii, Vysokomol. Soed., **6**, 1605 (1964).
283. V.K.Fuki, O.V.Zin'kovskaya, T.Bettger, M.Ya.Mel'nikov, and N.V.Fok, Dokl.Akad.Nauk SSSR, **221**, 1136 (1975).
284. V.G.Vinogradova, B.N.Shelimov, and N.V.Fok, Khim. Vys.Energii, 2, 128 (1968).
285. P.Hesse, A.Rosenberg, and H.Heusinger, Europ. Polymer J., 9, 581 (1973).
286. A.Torikai, H.Kato, and Z.Kuri, J.Polymer Sci., Polymer Chem.Ed., **14**, 1606 (1976).
287. M.Ya.Mel'nikov and N.V.Fok, Khim.Vys.Energii, 11, 277 (1977).
288. Yu.A.Mikheev, T.S.Popravko, L.L.Yasina, and D.Ya.Toptygin, Vysokomol.Soed., A15, 2470 (1973).
289. M.Ya.Mel'nikov, E.M.Lipskerova, O.M.Mikhailik, and N.V.Fok, "Tezisy Dokladov VII Vsesoyuznogo Soveshchaniya po Kinetike i Mekhanizmu Reaktsii v Tverdom Tele, Chernogolovka, 1978" (Abstracts of Reports at the VIIth All-Union Conference on the Kinetics and Mechanisms of Solid-State Reactions, Chernogolovka, 1978), p.350.
290. N.I.Zaitseva, T.V.Pokholok, G.B.Pariiskii, and P.Ya.Toptygin, Dokl.Akad.Nauk SSSR, **229**, 906 (1976).
291. E.Ya.Davydov, G.B.Pariiskii, and D.Ya.Toptygin, Vysokomol.Soed., A19, 977 (1977).
292. M.Ya.Mel'nikov and N.V.Fok, Dokl.Akad.Nauk SSSR, 231, 388 (1976).
293. O.V.Zinkovskaya, V.K.Fuki, M.Ya.Melnikov, and N.V.Fock, J.Polymer Sci., Polymer Letters, **16**, 41 (1978).
294. H.Zeldes and D.Livingston, J.Chem.Phys., **45**, 1946 (1966).
295. V.I.Mal'tsev, Zhur.Org.Khim., 3, 486 (1967).
296. M.Ya.Mel'nikov, Candidate's Thesis, Moscow State University, Moscow, 1973.
297. V.I.Spitsyn, G.P.Chernova, B.G.Ershov, and A.K.Pikaev, Izv.Akad.Nauk SSSR, Ser.Khim., 777 (1972).
298. V.S.Chervonenko and V.A.Roginskii, Khim.Vys. Energii, 7, 53 (1973).
299. V.S.Chervonenko and V.A.Roginskii, Khim.Vys. Energii, **6**, 95 (1972).

Faculty of Chemistry,
Moscow State University

Translated from *Uspekhi Khimii*, 49, 283-326 (1980) U.D.C. 547.431 : 547.481

Cobalt Complexes of Carbaboranes

E.V.Leonova

The results of studies on the chemical behaviour and methods of synthesis of cobalt complexes of carbaboranes are surveyed and described systematically. The methods of synthesis are classified and the applications of each method are considered. A systematic account is given of methods for the identification of cobalt complexes of carbaboranes. The chemical properties of such complexes are determined by the structure and properties of the carbaborane ligand. The electronic configuration of the cobalt atom in different cobalt complexes of carbaboranes varies within wide limits (d^8–d^5). The review deals with studies in the period 1965-1978 and partially in 1979.
There are 229 references.

CONTENTS

I. Introduction 147
II. General characteristics of the complexes 147
III. Synthesis of cobalt complexes of carbaboranes 151
IV. Properties of polyhedral π-complexes of cobalt 157
V. Polyhedral cobalt complexes of *nido*-carbaboranes 164
VI. Carbaborane-containing three-layer sandwich structures 165
VII. Cobalt σ-complexes of carbaboranes 166
VIII. Cobalt-containing boranes 166

I. INTRODUCTION

Polyhedral π-complexes of metals belonging to the Cu, Cr, Mn, Fe, Co, and Ni subgroups, based on the highest and lowest carbaboranes, are now known. Preparative methods have been developed for their synthesis and their properties are being vigorously investigated. The principal achievements in this field have been described in a number of reviews[1-11]. Exhaustive information about the period from 1965 to 1972 is presented in the review of Zakharkin and Kalinin[12]. The aim of the present publication is to isolate cobalt complexes from the overall wide variety of polyhedral and transition metal π-complexes as the most typical representatives of compounds of this class which have attracted the attention of investigators.

II. GENERAL CHARACTERISTICS OF THE COMPLEXES

Carborane π-complexes of iron and cobalt having the general formula $[(B_9C_2H_{11})_2M]^{z-}$ (M = Fe or Co, $z = 2$ or 1), the formal analogues of compounds of the type of ferrocene and the cobaltocenium cation, were synthesised for the first time in 1965. In these complexes the iron and cobalt atoms are coordinated to the dicarbollide dianion[13,14]. The results of X-ray diffraction studies on metal complexes of carbaboranes[15,16], ^{11}B and ^1H NMR and NQR data[17] for these compounds, as well as their magnetic, electronic[18] and electrochemical properties agree with the hypothesis of the sandwich nature of the metal–ligand bond in these π-complexes. The possibility of the existence of metal complexes of carbaboranes follows from the quantum-mechanical description of the dicarbollide ion[19,20]. The calculation is based on the hypothesis of the formation by the five atomic orbitals of the open pentagonal B_3C_2 surface of three bonding and two antibonding molecular orbitals[19,20]. The filling of the bonding molecular orbitals with six electrons makes the dicarbollide ion an isoelectronic and isostructural analogue of the Cp anion (Cp = C_5H_5) (see also Zakharkin and Kalinin[12]).

Apart from compounds of the type $[(B_nC_2H_{n+2})_2Co]^-$, Cp-containing complexes having the general formula $(\eta^5\text{-CpCo})_mB_nC_2H_{n+2}$ ($m = 1$–4; $n = 3$–10) are also known at the present time.

One of the qualitative features of the stability of metal complexes of carbaboranes is the validity of the empirical rule concerning the number of electrons required for the formation of the π-complex with participation of bonds in the ligand. It has been shown[21] that this number is given by the formula $2k + 14$, where k is the number of vertices in the polyhedron of the metal carbaborane complex. For example, in $CpCo.B_3C_2H_{11}$ ($m = 1$, $n = 9$; 12 vertices) there are altogether 60 electrons, which include five electrons from the Cp ligand, 9 electrons from the cobalt atom, 11 electrons from the 11 hydrogen atoms, 27 electrons from the 9 boron atoms, and 8 electrons from the 2 carbon atoms. The formation of all the CH and BH bonds requires 22 electrons, while the remaining 38 electrons are involved in the formation of bonds in the π-complex and their number can be calculated from the empirical formula $2k + 14$ ($k = 12$).[21] For bimetallic carbaborane complexes $(\eta^5\text{-CpCo})_2B_nC_2H_{n+2}$, the formula $2k + 26$ is used[21].

The stability of the complexes and their chemical properties depend on the formal degree of oxidation (f.d.o.) of the metal and the overall charge of the π-complex. Complexes whose overall charge is smaller and whose metal atom has the usual f.d.o. are more stable. On the other hand, a high molecular charge of the π-complex and an uncharacteristic f.d.o. of the metal reduce the stability of the compound[21] (see also Section IV). The molecular geometry of the cobalt complex of a carbaborane also influences its stability. The most stable compounds are those whose polyhedron is an icosahedron[22]. In dicobalt complexes of carbaboranes the direct Co–Co interaction stabilises the system[23], but, at an elevated temperature, compounds in the polyhedron of which cobalt atoms do not occupy neighbouring vertices are more stable. Such a disposition of cobalt atoms does not interfere with the more vigorous vibration of the Cp rings[23].

There exists the view[21] that a complex of the type $CpCo.B_nC_2H_{n+2}$ can be regarded as a heterocarbaborane in which the BH fragment has been replaced by the isoelectronic CpCo fragment. It is suggested that, like the BH fragment, the CpCo group supplies three orbitals and two electrons of the binding process[21,24]. To a first approximation, this concept explains satisfactorily and predicts certain chemical and physicochemical properties of cobalt complexes of carbaboranes, particularly the existence of a number of analogies in the chemistry of cobalt complexes of carbaboranes and of

carbaboranes themselves[25]. An example may be provided by the polyhedral expansion and contraction, polyhedral rearrangement, and electrophilic bromination reactions. However, bearing in mind the specific formalism underlying this concept, one must use it with caution in discussing the chemical and physicochemical properties of cobalt complexes of carbaboranes. In the first place we may note that symmetrical complexes of the type $[(B_mC_2N_{n+2})_2Co]^-$, which do not contain the CpCo fragment, also have a number of properties resembling those of carbaboranes and asymmetric cobalt complexes of carbaboranes of the type $CpCoB_nC_2H_{n+2}$. These concern the involvement of the above compounds in the same polyhedral contraction (see Section III), polyhedral rearrangement, and electrophilic bromination (see Section IV) reactions.

Furthermore, the study of the ^{11}B and ^{13}C NMR of halogen-substituted cobalt complexes of carbaboranes $\{[(1,2\text{-}B_9C_2H_{11})_2.Co]^-$, $[(9\text{-}Br\text{-}1,2\text{-}B_9C_2H_{10})_2Co]^-$, and $[(9,12\text{-}Br_2\text{-}1,2\text{-}B_9C_2H_9)_2Co]^-\}$ established that the nature of the change in electron density following the introduction of the halogen is the same for the cobalt complexes of carbaboranes and icosahedral boranes and carbaboranes[26]. The most intense deshielding is observed at boron or carbon atoms occupying the opposite vertices relative to the halogen-substituted boron atoms. The carbon atoms in the complex $[(9,12\text{-}Br_2\text{-}1,2\text{-}B_9C_2H_9)_2Co]^-$ are deshielded to the greatest extent, while the $B_{(5)}$ and $B_{(11)}$ atoms, closest to the substituted $B_{(9)}$ and $B_{(12)}$ atoms, are deshielded to a smaller extent[26]. Furthermore, it has been shown for $3,1,2\text{-}(\eta^5\text{-Cp})CoB_9C_2H_{11}$ by infrared spectroscopy that the coordination of the dicarbollyl ligand to the cobalt atom does not abolish the capacity of the CH group for the formation of a hydrogen bond[27]. Next, a study of the photoelectron spectra of bis(dicarbollyl)cobalt derivatives containing a bridging ligand in the 8- and 8′-positions [−S−S, −S−, −S−$\overset{+}{S}$(Me)−, −S−$\overset{+}{C}$H−S−, −$\overset{+}{S}$(Me)−, and −$\overset{+}{O}$(Me)−] showed that, firstly, within the carbaborane ligand in each derivative there is a uniform distribution of charge density over the boron atoms and, secondly, the presence of a bridging atom more electronegative than boron (S, $\overset{+}{S}$, $\overset{+}{O}$) causes a shift of electron density both from the two carbaborane ligands and from the central cobalt(III) atom[28]. All these findings show that the nature of the bond within the polyhedral ligand apparently does not undergo profound and fundamental changes as a result of coordination; this entails the retention of the properties of carbaboranes in their cobalt complexes. Furthermore, whereas the presence of the negative charge in $[(B_nC_2H_{n+2})_2.Co]^-$ gives rise to certain anomalies, neutral complexes of the type $CpCoB_nC_2H_{n+2}$ are even closer in their properties to the corresponding carbaboranes. The chemical and physicochemical properties of cobalt complexes of carbaboranes therefore in general still depend largely on the structure and properties of the carbaborane fragments involved in the complex.

However, this does not imply that the role of the metal in the carbaborane complexes is insignificant. The possibility, in principle, of the existence of a metal complex of a carbaborane and its stability depend on the nature of the metal atom. In the Fe, Co, Ni series the cobalt atom, which has the stable d^6 electronic state, forms diamagnetic complexes which either have a low molecular charge $\{[(B_nC_2H_{n+2})_2Co]^-\}$ or are altogether uncharged $(CpCoB_nC_2H_{n+2})$. At the same time, as a result of its high molecular charge, the complex $[(1,2\text{-}B_9C_2H_{11})_2Fe^{II}]^{2-}$ is readily oxidised [Fe(II) → Fe(III)] and is converted into the paramagnetic complex $[(1,2\text{-}B_9C_2H_{11})_2Fe^{III}]^-$. Iron ($d^5$ electronic configuration) is an effective oxidant, which to a large extent determines the properties of the paramagnetic complex. (For nickel complexes, see Zakharkin and Kalinin[12].) One may also not that, as a result of coordination, there is a partial redistribution of electron density within the carbaborane ligand in the metal complexes.

The electron-donating influence of the *C*-substituted dianion $(B_9C_2H_{11})^{2-}$ is a combination of the inductive effect (+*I*) and the conjugation effect (+*R*).[29] The direction of the inductive effect in the coordinated dicarbollyl ligand changes (−*I*), while the nature of the conjugation effect remains the same (+*R*).[29,30] The replacement of the dicarbollyl ligand in the complex $[Co(B_9C_2H_{11})_2]^-$ by the cyclopentadienyl ligand enhances the electron-accepting properties of the residual *C*-substituted dicarbollyl group[29]. Comparison of the constants σ_i and σ_R^0, calculated by Taft's method, shows that the $B_9C_2H_{11}CoC_5H_4$ group is a stronger accepter than the $C_5H_5CoB_9C_2H_{10}$ group.

The study of the ^{11}B and ^{13}C NMR of the paramagnetic complexes $CpMB_nC_2H_{n+2}$ [$n = 6$–9, M = Cr(III), Fe(III), Ni(III), or Co(II)] showed that, firstly, there is a redistribution of the unpaired electron density from the non-bonding orbitals of the central metal atom to the molecular orbitals of the carbaborane ligand and, secondly, the unpaired electrons interact not only with atoms linked to the central metal atom, but also with the more remote boron atoms[31]. In cobalt complexes of carbaboranes containing two cobalt atoms one may expect even more profound changes in electron density distribution, particularly in those cases where a Co−Co bond is present in the complex. An increase in the number of cobalt atoms in polyhedral π-complexes should therefore apparently entail changes in properties such that the new compounds will resemble to a decreasing extent their parent compounds (carbaboranes) and the properties will probably approach those of the usual cluster compounds of cobalt. During this transition, one may expect the appearance of compounds of a new type, with unique properties different from those of carbaboranes and clusters.

Theoretically[32,33] it is possible to predict the molecular geometries on the basis of the overall number of valence electrons in the polyhedron. At the same time the structure can be established and the cobalt complexes of carbaboranes identified by comparing the ultraviolet, infrared, NMR and mass spectra as well as the oxidation-reduction potentials. The ultraviolet spectra of cobalt complexes of *closo*-carbaboranes† are known to contain a band in the range 600–650 nm (green and blue complexes), while complexes with a *nido*-structure do not absorb in this region and they are red or brown[35]. Furthermore, the isomers of cobalt complexes of carbaboranes differing in the number of carbon atoms in the open pentagonal surface coordinated to the cobalt atom also exhibit differences in their ultraviolet spectra. In the isomer sequence *a* → *b* → *c* → *d* (Fig. 1 for R = H), the number of carbon atoms diminishes from two to zero and at the same time λ_{max} for the band referred to the *d*–*d* transition undergoes a hypsochromic shift in the ultraviolet spectra of the complexes[6]. Analogous behaviour has been observed in the ultraviolet spectra of the isomers 1,2,4-, 1,2,3-, and $10,2,3\text{-}(\eta^5\text{-Cp})Co(Me_2B_8C_2H_8)$.[36] We may also note that complexes of the type $(CpCo)_2B_nC_2H_{n+2}$ ($n = 6$–8), which differ in the presence or absence of the Co−Co bond, also have characteristic absorption bands in the ultraviolet spectra[37].

The infrared spectra of cobalt complexes of carbaboranes having the general formula $(LCoB_nC_2H_{n+2})^z$ (L = Cp, $z = 0$; L = $B_nC_2H_{n+2}$, $z = -1$) retain all the principal characteristic

† For the nomenclature of the complexes, see Ref. 34 and the reviews by Zakharkin and Kalinin[12] and Grimes[193].

frequencies of the carbaboranes[35,38] and cyclopentadienyl ligands[39] and, on substitution in these ligands, the infrared spectra of the complexes exhibit the same changes as those of the substituted carbaboranes[38] and cyclopentadienylcobalt complexes[39]. The formation of the metal–dicarbollyl bond in $[Co(B_9C_2H_{11})_2]^-$ is characterised by a very intense polarised line in the Raman spectrum at 180–300 cm^{-1}, which has been assigned to the metal–dicarbollyl stretch[40].

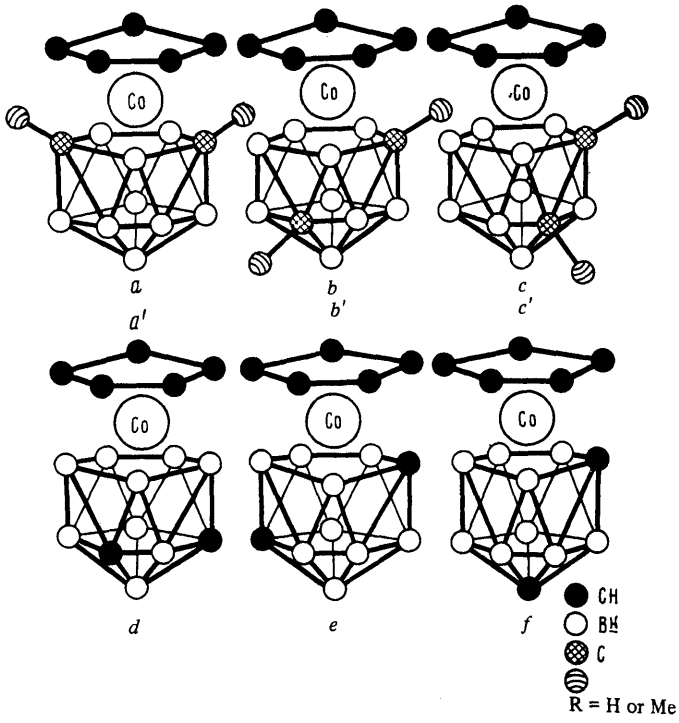


Figure 1. Postulated structures of the isomers (*a*–*f*) formed in the thermal gas-phase rearrangement of 3,1,2-(η^5-Cp)Co.$(1,2\text{-}R_2B_9C_2H_9)$: R = H (*a*–*c*) or CH_3 (*a'*–*c'*).

The use of triple resonance to observe the proton spectra with simultaneous suppression of signals due to ^{11}B and ^1H nuclei permits unambiguous assignments of the resonance lines[41]. Thus parameters of the ^1H [41] and ^{11}B [42–44] NMR spectra such as the chemical shift, the integral intensity, and the spin–spin splitting constant as well as the spin–lattice relaxation times T_1 of the ^{11}B and ^1H nuclei[45] are used successfully for the standard identification of metal complexes of carbaboranes.

Furthermore, substitution in the carbaborane ligand in $CpCo(HCB_9H_9Cr)$ leads to an alteration of the chemical shift of the protons in the Cp ring[46]. With increase of the number of bromine atoms in $CpCoB_9C_2H_{11-n}Br_n$ ($n = 1$–3), the signal of the protons of the Cp ring shifts downfield[47]. (For a description of the influence of the structure of cobalt complexes of carbaboranes on the reduction potential, see Section IV.) However, the most reliable results in the determination of the polyhedral structures were obtained by diffraction methods. X-Ray diffraction analysis of Cs[Co.$(B_9C_2H_{11})_2$] [15] yields the general type of structure of bisdicarbollylcobalt complexes. Figs.2 [48] and 3 [49] illustrate derivatives of the bisdicarbollylcobaltate anion. In both cases substitution takes place at the boron atoms. The cobalt atom in the structure of the anion $[Co(B_7C_2H_9)_2]^-$ (**Fig.4**) is located between the pentagonal B_3C_2 surfaces where the position (6 or 9) of one of the carbon atoms has not been rigorously established[16].

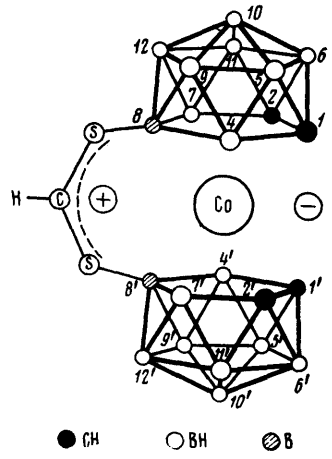


Figure 2. The structure of $[3,3'\text{-}Co(1,2\text{-}B_9C_2H_{10})_2]S_2C^+H$.[48]

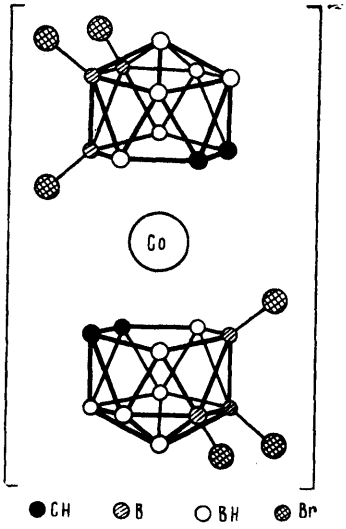


Figure 3. The structure of the $[Co(B_9C_2H_8Br_3)_2]^-$ ion[49].

The carbon atom in the $[3,4\text{-}(\eta^5\text{-}Cp)CoB_7CH_8]^-$ polyhedron (Fig.5) has a low coordination number (5),[50] which agrees with the general postulate, according to which the carbon atom in the polyhedron of the carbaborane in its metal occupies mainly a vertex with a low coordination number[51,52]. The cobalt atom in $(CpCoB_7CH_8)^-$ is coordinated to five boron atoms, where three Co–B distances are 2.15–2.18 Å while two are 1.97 and 1.98 Å.[50]

Figs. 6 and 7 present the structures of two *nido*-complexes 8,6,7-(η^5-Cp)$CoB_7C_2H_{11}$ [53] and (1,2-$B_9C_2H_{11}$-3,11'-Co-9'-C_5H_5N-7',8'-$B_8C_2H_{10}$)$^-$.[54,55] The $CpCoB_7C_2H_{11}$ molecule has a geometry similar to that of decaborane with three heteroatoms (C,C,Co) in the open first surface. Two hydrogen atoms [$H_{(1)}$ and $H_{(2)}$] occupy bridging positions[53]. The carbaborane ligand $B_8C_2H_{10}$ in $(B_9C_2H_{11}CoB_8C_2H_{10}Py)^-$ has an open six-atom surface $C_{(7')}B_{(2')}B_{(6')}B_{(10')}B_{(9')}C_{(8')}$, four atoms of the surface being involved in coordination to the cobalt atom[54,55]. The pyridine fragment is linked to the boron atom. The position of the extra hydrogen has not been established.

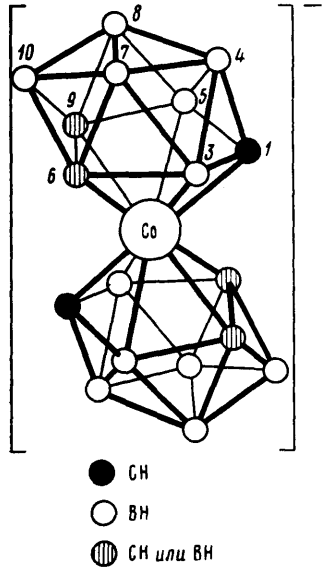


Figure 4. The structure of the $[Co(B_7C_2H_9)_2]^-$ ion[16].

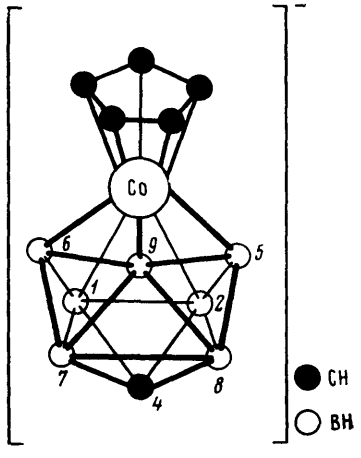


Figure 5. The structure of the $[CpCoB_7CH_8]^-$ ion[50].

The structure of 2,9,1,10-(η^5-CpCo)$_2B_6C_2H_8$ is a distorted square antiprism (Fig. 8), while the 2,3,1,7-(η^5-CpCo)$_2B_8C_2H_{10}$ molecule is a distorted icosahedron (Fig. 9). In both polyhedra the cobalt atoms occupy neighbouring vertices and the Co–Co bond length is 2.489 Å [24,52] and 2.389 Å [56] respectively.

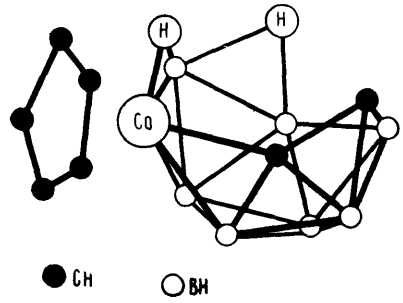


Figure 6. The structure of $CpCoB_7C_2H_{11}$.[53]

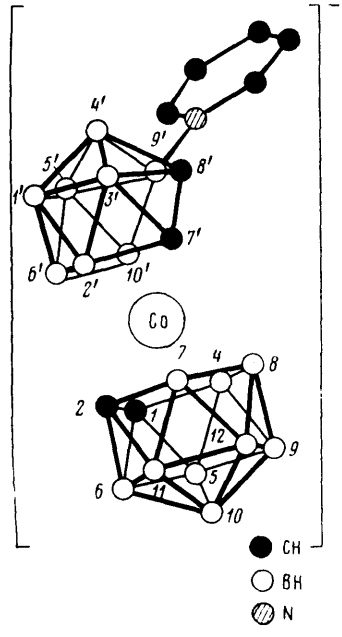


Figure 7. The structure of $[B_9C_2H_{11}Co(B_8C_2H_{10}C_5H_5N)]^-$.[54,55] (The bridging hydrogen atom is not represented.)

The carbaborane ligands in the complex [(η^5-Cp)Co_2.$(B_8C_2H_{10})_2$]$^-$ are non-equivalent and there is no Co–Co bond (Fig. 10). One of the carbaborane ligands is bidentate[44].

Figs. 11 [57,58] and 12 [58,59] illustrate di- and tri-cobalt complexes of carbaboranes, which are derived from the bidentate dicarbacanastide anion $(B_8C_2H_{10})^{4-}$. The Fe–Co bond is present in the (η^5-Cp)CoFe($Me_4B_8C_4H_8$) complex. The molecule has the form of two pentagonal bipyramids joined by the common vertex, which is occupied by the iron atom. The B–H fragment is the vertex of two trigonal pyramids, whose bases consit of the trigonal planes of the two pentagonal

bipyramids. The system is interesting because it contains two electrons less than would be expected according to the number of vertices in the polyhedron[60,63].

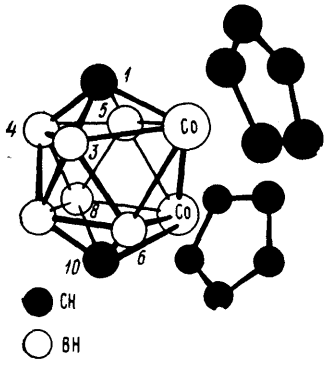


Figure 8. The structure of $(CpCo)_2B_6C_2H_8$.[24,52]

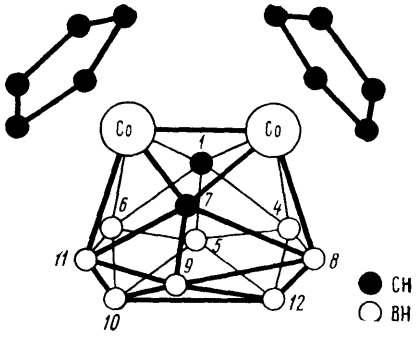


Figure 9. The structure of $(CpCo)_2B_8C_2H_{10}$.[56]

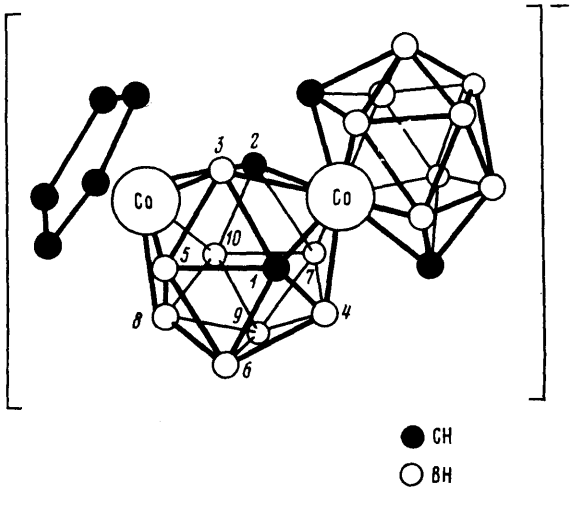


Figure 10. The structure of the $(CpCoB_8C_2H_{10}CoB_8C_2H_{10})^-$ ion[44].

III. SYNTHESIS OF COBALT COMPLEXES OF CARBABORANES

The existing methods for the synthesis of cobalt complexes of carbaboranes can be largely divided into three groups. These include in the first place a series of methods based on the combination of the products of the partial degradation of carbaboranes and (or) their cobalt complexes. The "direct" synthesis, where the starting materials are *nido*- and *arachno*-carbaboranes and cobalt complexes of carbaboranes[20,61,62,64], as well as the polyhedral contraction method, based on the use of cobalt complexes of carbaboranes, should be assigned to this series. Next we may note the polyhedral expansion reaction which includes the reduction of polyhedral *closo*-carbaboranes and (or) cobalt complexes of carbaboranes by sodionaphthalene with subsequent reduction of the resulting anions by $CoCl_2$ and CpNa. These reactions lead to the formation of cobalt complexes of carbaboranes[4,52,65,66] and (or) di- and tri-cobalt carbaborane complexes[67–70] respectively, the new polyhedron containing one vertex more than the initial polyhedron. The third method involves the "direct" synthesis of cobalt complexes of carbaboranes from carbaboranes in the gas phase. We shall examine each method in detail.

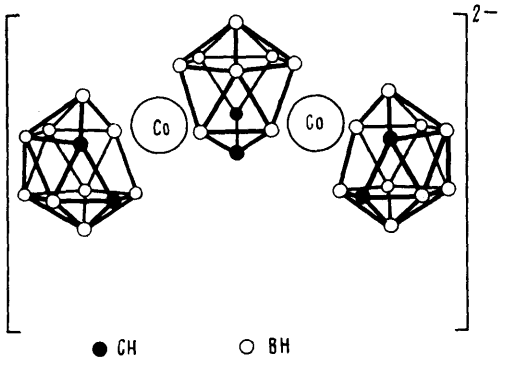


Figure 11. The structure of the $(B_9C_2H_{11}CoB_8C_2H_{10}CoB_9C_2H_{11})^{2-}$ ion[57].

1. The "Direct" Synthesis of Polyhedral Cobalt Complexes of *closo*-Carbaboranes from *nido*- and *arachno*-Carbaboranes

The method can be represented by the following general sequence of reactions:

$$B_{10}C_2H_{12-n}R_n \xrightarrow{Nu} (B_9C_2H_{12-n}R_n)^- \quad , \qquad (1)$$

$$(B_9C_2H_{12-n}R_n)^- \underset{H^+}{\overset{Nu'}{\rightleftarrows}} (B_9C_2H_{11-n}R_n)^{3-} \quad , \qquad (2)$$

$$(B_9C_2H_{11-n}R_n)^{3-} + Co^{2+} \rightarrow [(B_9C_2H_{11-n}R_n)_2Co]^- \quad . \qquad (3)$$

Attack by strong nucleophiles (Nu are alkali metal alkoxides[71,72], ammonia[73], dialkylamines[73], trialkylamines[74], piperidines[75–78], and hydrazines[79–83]) on the electropositive boron atom[38,84,85] leads to the formation of an anion with an open pentagonal surface over which the hydrogen atom is located. Studies of ^{11}B and ^{13}C NMR spectra of the isomers of the dicarba-*nido*-dodecahydroundecaborate(1-) anion showed that the bond between the "extra" hydrogen atom and

the boron atoms is of the bridge type. In the case of $(1,2\text{-}B_9C_2H_{12})^-$ it can be regarded as a three-centre bridge bond or as the product of the dynamic process $B_{(8)}\text{–}H\text{–}B_{(4)} \rightleftharpoons B_{(8)}\text{–}H\text{–}B_{(7)}$. The existence of the $B_{(8)}\text{–}H\text{–}B_{(4)}$ bridge has been postulated in the isomer $(1,7\text{-}B_9C_2H_{12})$.[86] Being an acid ($pK_a = 21.3$,[87,88] R = H), the anion $(B_9C_2H_{12-n}R_n)^-$ readily reacts with nucleophiles (Nu′ = Na,[13] NaH,[13,89] or n-BuLi [90]) with formation of the dianion $(B_9C_2H_{11-n}R_n)^{2-}$. In an aqueous medium NaOH is used as the nucleophile[20,91]. The coordination of the dicarbollide dianions to cobalt ions leads to the formation of the symmetrical polyhedron $[(B_9C_2H_{11-n}R_n)_2Co]^-$, which is an isoelectronic analogue of the cobaltocenium cation. In the presence of the Cp anion, the neutral complex $CpCo.B_9C_2H_{11-n}R_n$ is formed. $[3,1,2\text{-}B_9C_2H_{11}Co(CO)_2]^-$, an analogue of the corresponding Cp derivative of cobalt, has been obtained by treating $Co_2(CO)_8$ with the dicarbollide dianion $(B_9C_2H_{11})^{2-}$.[92]

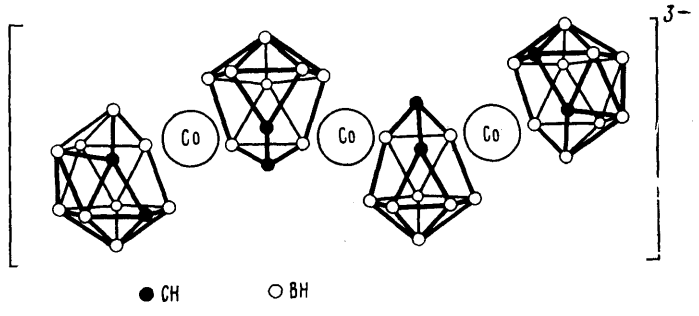


Figure 12. The structure of the $[(B_9C_2H_{11}CoB_8C_2H_{10})_2Co]^{3-}$ ion[59].

Table 1 presents the carbollyl and dicarbollyl sandwich π-complexes of cobalt obtained by the "direct" method. Columns 4 and 5 list respectively the initial carbaborane and the nucleophile (Nu) acting on the former. Next, Table 1 lists the anion formed or its salt (column 6), the reagent reacting with it (column 7), and the polyanion or its salt (column 8) produced by this interaction. Column 9 lists the cobalt compounds reacting with an anion or polyanion to form a π-complex.

The choice of the nucleophile for the first two stages depends on the nature of the carbaborane and the strength of the R–carbaborane bond[38]. The synthesis is carried out in aqueous and alcoholic media or in an absolute complex-forming solvent [tetrahydrofuran (THF), ether, and dimethoxyethane (DME)][20].

The "direct" synthesis under consideration has acquired particular importance when its single-stage version was developed: the anion $(B_9C_2H_{12})^-$ (obtained *in situ* by the alkaline methanolysis of the *o*-carbaborane $B_{10}C_2H_{12}$) $CoCl_2.6H_2O$, and C_5H_6 were added in the presence of an excess of KOH.[64] The yield of $(\eta^5\text{-Cp})CoB_9C_2H_{11}$ was 72%. The authors note[64] that the optimum yield of the asymmetric complex is attained when methanol is used as the solvent. $(\eta^5\text{-Cp})Co.(2,3\text{-}B_8C_2H_{10})$ was obtained similarly[64].

The method of synthesis of the bis(dicarbazapyl)cobaltate ion $[(B_7C_2H_9)_2Co]^-$ [2,2′-*commo*-bisnonahydridodicarba-2-cobalta-*closo*-decaborate (Ed.of Translation)] differs somewhat from that described above[16,61,62]. The initial compound is also a *nido*-carbaborane (Fig.13), which is converted under the influence of sodium hydride into the dianion $(1,3\text{-}B_7C_2H_{11})^{2-}$ (Fig.14). Next, the anion $(1,3\text{-}B_7C_2H_{11})^{2-}$ is made to react with anhydrous $CoCl_2$, which immediately leads to the formation of the polyhedral *closo*-complex $[(B_7C_2H_9)_2Co]^-$. Two moles of hydrogen are evolved in the reaction. The hydrogen is probably formed as a result of the elimination of two bridging hydrogen atoms from the *nido*-carbaborane anion (Fig.14). The structure of the bis(dicarbazapyl)cobaltate anion[16] is illustrated in Fig.4.

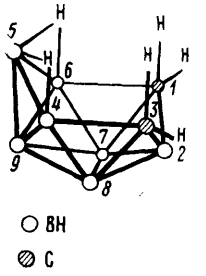


Figure 13. The structure of 1,3-dicarba-*nido*-nonaborane-(13).[38]

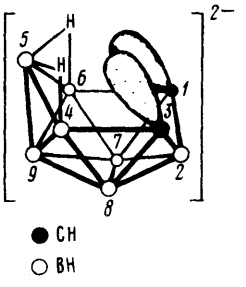


Figure 14. The postulated structure of the 1,3-dicarba-*nido*-undecahydroborate(2-) ion.

2. The "Direct" Synthesis of Polyhedral Dicobalt Complexes of Carbaboranes from Cobalt Complexes of Carbaboranes

It had been established previously that the "direct" synthesis of cobalt complexes of carbaboranes is accompanied in many instances by the formation of di- and tri-cobalt complexes of carbaboranes[58,64,109,110]. The alkaline degradation of $1,2\text{-}B_{10}C_2H_{12}$ led to the isolation of polyhedral cobalt complexes—derivatives of the bifunctional ligand $(B_8C_2H_{10})^{4-}$.[58,109]. The structures of the resulting bimetallic complex $(1,2\text{-}B_9C_2H_{11}\text{-}3,3'\text{-}Co\text{-}1',2'\text{-}B_8C_2H_{10}\text{-}6',3''\text{-}Co\text{-}1'',2''\text{-}B_9C_2H_{11})^{2-}$ (Fig.11) and the trimetallic complex $\{[(3,1,2\text{-}B_9C_2H_{11})Co.(3,6,1,2\text{-}B_8C_2H_{10})]_2Co\}^{3-}$ (Fig.12) were established by X-ray diffraction[57,59]. It has been suggested[58] that the formation

Table 1. Cobalt complexes of carbaboranes obtained by the "direct"method and the reagents used in the synthesis.

	Compound	T.p.	Yield, %	Initial carbaborane	Nucleophile	Anion or its salt	Reagent	Polyanion or its salt	Cobalt cpd.	Refs.
1	$NMe_4[3,1,2\text{-}B_9C_2H_{11})_2Co]$	—	86	$1.2\text{-}B_{10}C_2H_{12}$	MeOH, MeOK	$HNaMe_3(1.2\text{-}B_9C_2H_{12})$	NaOH, H_2O	$(1.2\text{-}B_9C_2H_{11})^{2-}$	$CoCl_2$	91
2	$Cs[3,1,2\text{-}B_9C_2H_{11})_2Co]$	>300	72	$B_{10}C_2H_{12}$	MeOH, MeOK	$HNMe_3(1.2\text{-}B_9C_2H_{12})$	Na or NaH	$Na_2(3,1,2\text{-}B_9C_2H_{11})$	$CoCl_2$	14,20
3	$Cs[(3,1,2\text{-}B_9C_2H_{11})_2Co]$	—	79	—	—	$HNMe_3(1.2\text{-}B_9C_2H_{12})$	40% NaOH in water	$(3,1,2\text{-}B_9C_2H_{11})^{2-}$	$CoCl_2\times\times 6H_2O$	20
4	$Cs[(3,1,7\text{-}B_9C_2H_{11})_2Co]$	>350	80	—	—	$HNMe_3(1.7\text{-}B_9C_2H_{12})$	NaH	$Na_2(1.7\text{-}B_9C_2H_{11})$	$CoCl_2$	20
5	$Cs[(3,1,7\text{-}B_9C_2H_{11})_2Co]$	—	90	—	—	$HNMe_3(1.7\text{-}B_9C_2H_{12})$	50% NaOH in water	$(3,1,7\text{-}B_9C_2H_{11})^{2-}$	$CoCl_2\times\times 6H_2O$	20
6	$NMe_4[(3,1,2\text{-}PhB_9C_2H_{10})_2Co]$	290—293	70	$1.2\text{-}PhB_{10}C_2H_{11}$	MeOH, MeOK	$HNMe_3(3,1,2\text{-}PhB_9C_2H_{11})$	NaH	$Na_2(1.2\text{-}PhB_9C_2H_{10})$	$CoCl_2$	14,20
7	$NMe_4[(3,1,2\text{-}6\text{-}PhB_9C_2H_{10})_2Co]$	275—277	62	$1.2\text{-}3\text{-}PhB_{10}C_2H_{11}$	EtOH, KOH	$HNMe_3[(Ph)B_9C_2H_{11}]$	NaH	$(1.2\text{-}6\text{-}PhB_9C_2H_{10})^{2-}$	$CoCl_2$	93
8	$NMe_4[(3,1,2\text{-}Me_2B_9C_2H_9)_2Co]$	273—275	63	$Me_2B_{10}C_2H_{10}$	MeOH, MeOK	$NHMe_3(1.2\text{-}Me_2B_9C_2H_{10})$	Na or NaH	$Na_2(1.2\text{-}Me_2B_9C_2H_9)$	$CoCl_2$	14,20
9	$NMe_4[(3,1,2\text{-}\mu\text{-}1,2\text{-}(CH_2)_3B_9C_2H_9)_2Co]$	—	46	$(CH_2)_3B_{10}C_2H_{10}$	EtOH, KOH	$K[(CH_2)_3B_9C_2H_{10}]$	n-BuLi	—	$CoCl_2$	94
10	$NMe_4[(3,1,2\text{-}1,2\text{-}(CH=\!=CH_2)_2B_9C_2H_9)_2Co]$	273	51	$1.2\text{-}1.2\text{-}(CH=CH_2)_2B_{10}C_2H_{10}$	EtOH, KOH	$NHMe_3\text{-}1.2\text{-}1.2(CH=\!=CH_2)_2B_9C_2H_{10})$	NaH	$[1.2\text{-}1.2\text{-}(CH=CH_2)_2B_9C_2H_9]^{2-}$	$CoCl_2$	30
11	$AsPh_4[(3,1,2\text{-}1,2\text{-}(3'\text{-cyclo-}C_3H_4)B_9C_2H_9)_2Co]$	203—204	53	$1.2\text{-}1.2\text{-}(3'\text{-cyclo-}C_3H_4)B_{10}C_2H_{10}$	EtOH, KOH	$HNMe_3[1,2\text{-}1,2\text{-}(3'\text{-cyclo-}C_3H_4)B_9C_2H_{10}]$	NaOH	$[1,2\text{-}1,2\text{-}(3'\text{-cyclo-}C_3H_4)B_9C_2H_9]^{2-}$	$CoCl_2$	30
12	$NMe_4[3,1,2\text{-}1,2\text{-}(1,4\text{-dihydro-benzo})B_9C_2H_9]_2Co$	125	30	$1,2\text{-}1,2\text{-}(1,4\text{-dihydro-benzo})B_{10}C_2H_{10}$	KOH	$HNMe_3[1,2\text{-}1,2\text{-}(1.4\text{-dihydrobenzo})B_9C_2H_{10}]$	NaH	$Na_2[1,2\text{-}1,2\text{-}(1,4\text{-dihydro-benzo})B_9C_2H_9]$	$CoCl_2$	95
13	$NMe_4[(3,1,2\text{-}1,2(benzo)B_9C_2H_9)_2Co]$	>300	50	—	—	$[1,2\text{-}1,2(benzo)B_9C_2H_{10}]^-$	NaH	$[3,1,2\text{-}1,2\text{-}(benzo)B_9C_2H_9]^{2-}$	$CoCl_2$	95
14	$B_9C_2H_{11}CoC_5H_5$	247—248	72	$B_{10}C_2H_{12}$	MeOH,	$(B_9C_2H_{12})^-$	Na or NaH	$(B_9C_2H_{11})^{2-}$	$CoCl_2$	14
15	$3,1,2\text{-}B_9C_2H_{11}CoC_5H_5$	246—248	15	—	MeOK	$HNMe_3(3,1,2\text{-}B_9C_2H_{12})$	NaH,Na	$Na_2(3,1,2\text{-}B_9C_2H_{11})$	$CoCl_2$	20
16	$[3,1,2\text{-}1\text{-}(CH_2OH)B_9C_2H_{10}]CoC_5H_5$	208—209	58	—	—	$K[(CH_2OH)B_9C_2H_{11}]$	KOH,	*in situ*	$CoCl_2$	46
17	$[3,1,2\text{-}1\text{-}(CH_2OH)B_9C_2H_{10}]CoC_5H_5$	208—210	13	—	—	$K[(CH_2OH)B_9C_2H_{11}]$	EtOH	$Tl_2[(CH_2OH)B_9C_2H_{10}]$	$CoCl_2$	46
18	$[3,1,2\text{-}1\text{-}(CH_2CN)B_9C_2H_{10}]CoC_5H_5$	233—235	9	—	—	$K[(CH_2CN)B_9C_2H_{11}]$	TlOH	$Tl_2[(CH_2CN)B_9C_2H_{10}]$	$CoCl_2$	46
19	$[3,1,2\text{-}6\text{-}(CH_2=\!=CH)B_9C_2H_{10}]CoC_5H_5$	191—192	60	$3\text{-}CH_2=CHB_{10}C_2H_{11}$	$C_5H_{10}NH$	—	KOH, MeOH	$K(6\text{-}CH_2=CHB_9C_2H_{10})$	$CoCl_2$	96
20	$(3,1,2\text{-}6\text{-}NH_2B_9C_2H_{10})CoC_5H_5$	245—246	80	$3\ NH_2B_{10}C_2H_{11}$	$C_5H_{10}NH$	—	KOH, MeOH	$K(6\text{-}NH_2B_9C_2H_{10})$	$CoCl_2$	96
21	$(3,1,2\text{-}9\text{-}ClB_9C_2H_{10})CoC_5H_5$	193—194	65	$9\text{-}ClB_{10}C_2H_{11}$	KOH, EtOH	—	KOH, MeOH	$K(9\text{-}ClB_9C_2H_{10})$	$CoCl_2$	96
22	$(3,1,2\text{-}9\text{-}IB_9C_2H_{10})CoC_5H_5$	191—192	70	—	—	—	KOH, MeOH	$K(9\text{-}IB_9C_2H_{10})$	$CoCl_2$	96
23	$[3,1,2\text{-}1\text{-}Me\text{-}2\text{-}(COOMe)B_9C_2H_9]CoC_5H_5$	219—220	30	—	—	$K[(Me)(COOMe)B_9C_2H_{10}]$	TlOH	$Tl[(Me)(COOMe)B_9C_2H_9]$	$CoCl_2$	46
24	$[3,1,2\text{-}1\text{-}Me\text{-}2\text{-}(CF=\!=CFCF_3)B_9C_2H_9]CoC_5H_5$	146.5—148.5	3.9	—	—	$K[(Me)(CF=CFCF_3)B_9C_2H_{10}]$	TlOH	$Tl_2[(Me)(CF=\!=CFCF_3)B_9C_2H_9]$	$CoCl_2$	46
25	$NMe_4[3,1,2\text{-}B_9C_2H_{11}Co(CO)_2]$	—	17.6	—	—	$HNMe_3(3,1,2\text{-}B_9C_2H_{12})$	NaH	—	$Co_2(CO)_8$	92
26	$NMe_4[(2,6,7\text{-}B_7C_2H_9)_2Co]$	235	64.5	$B_7C_2H_{13}$	NaH	$Na_2(1,3\text{-}B_7C_2H_{11})$	—	—	$CoCl_2$	61,62
27	$NMe_4[(2,1,6\text{-}B_7C_2H_9)_2Co]$	240	53	$B_7C_2H_{13}$	NaH	$Na_2(1.3\text{-}B_7C_2H_{11})$	—	—	$CoCl_2$	61,62
28	$(2,1,6\text{-}B_7C_2H_9)CoC_5H_5$	158—159	36	$B_7C_2H_{13}$	NaH	$Na_2(1.3\text{-}B_7C_2H_{11})$	—	—	$CoCl_2$	61,62
29	$[(2,3\text{-}Me_2B_4C_2H_4)_2CoH]$ *	—	34	$Me_2B_4C_2H_6$	NaH	$Na(2.3\text{-}Me_2B_4C_2H_5)$	—	—	$CoCl_2$	97,98
30	$(NMe_4)_3[(B_{10}H_{10}CH)_2Co]$	—	—	$B_{10}H_{12}CNMe_3$	Na	$HNMe_3(B_{10}H_{12}CH)$	n-BuLi	—	$CoCl_2$	99,101
31	$Cs_3\cdot H_2O[(B_{10}H_{10}CH)_2Co]$	—	60	$B_{10}H_{12}CNMe_3$	Na	$HNMe_3(B_{10}H_{12}CH)$	50% NaOH in water	—	$CoCl_2\times\times 6H_2O$	99,101
32	$(NMe_4)_3[(B_{10}H_{10}CH)_2Co]$	—	—	$B_{10}H_{12}CNMe_3$	Na	—	—	$Na_3(B_{10}H_{10}CH)$	$CoCl_2$	100
33	$(NMe_4)_3[(B_{10}H_{10}CNH_2Et)_2Co]$	—	—	$B_{10}H_{12}CNH_2Et$	base in water	—	—	—	$CoCl_2\times\times 6H_2O$	100
34	$(NMe_4)_2[(B_{10}H_{10}CNH_2)Co(B_{10}H_{10}CNH_3)]$	—	—	$B_{10}H_{12}CNH_3$	50% NaOH in water	—	—	—	$CoCl_2\times\times 6H_2O$	99,100
35	$NMe_4[(7\text{-}B_{10}H_{10}CH)CoC_5H_5]$	>300	85	—	—	$Cs(B_{10}H_{10}CH_3)$	KOH, EtOH	—	$CoCl_2$	102
36	$B_9H_9CHCoC_5H_5$	—	55	—	—	$NMe_4(6\text{-}B_9CH_{12})$	KOH, EtOH	$(B_9CH_{11})^{2-}$	$CoCl_2\times\times 6H_2O$	103
37	$NMe_4[(1,2\text{-}B_9H_9CHP)_2Co]$	—	13	—	—	$C_5H_{10}NH_2(7,8\text{-}B_9H_{10}CHP)$	NEt_3	—	$CoCl_2$	104
38	$NMe_4[(3,1,7\text{-}B_9H_9CHP)_2Co]$	—	—	$1,7\text{-}B_{10}H_{10}CHP$	$C_5H_{10}NH$	$C_5H_{10}NH_2(1.7\text{-}B_9H_{10}CHP)$	NaH	—	$CoCl_2$	105
39	$NMe_4[3,1,7\text{-}B_9H_9CHP)_2Co]$	—	77	—	—	$HNMe_3(1,7\text{-}B_9H_{10}CHP)$	NMe_3	—	$CoCl_2$	104
40	$(1,2\text{-}B_9H_9CHPMe)_2Co$	276—278	29	$7,8\text{-}B_9H_{10}CHPMe$	NEt_3	—	—	—	$CoCl_2$	104, 105
41	$(1,7\text{-}B_9H_9CHPMe)_2Co$ **	278—279	30	$7,9\text{-}B_9H_{10}CHPMe$	NaH	—	—	—	$CoCl_2$	104, 105
42	$(1,7\text{-}B_9H_9CHPMe)_2Co$ **	232—234	29	$7,9\text{-}B_9H_{10}CHPMe$	NaH	—	—	—	$CoCl_2$	104, 105
43	$(7,8\text{-}B_9H_9CHAs)CoC_5H_5$	250—251	—	$1,2\text{-}B_{10}H_{10}CHAs$	$C_5H_{10}NH$	$C_5H_{10}NH_2(7,8\text{-}B_9H_{10}CHAs)$	NEt_3	—	$CoCl_2$	106
44	$Cs[(B_{10}H_{10}S)_2Co]$	—	—	$B_{10}H_{12}S$	n-BuLi	—	—	—	$CoCl_2$	107, 108
45	$Cs[(B_{10}H_{10}S)_2Co]$	—	—	$B_{10}H_{12}S$	50% NaOH in water	—	—	—	$CoCl_2\times\times 6H_2O$	107, 108
46	$[Co(C_5H_5)_2][(B_{10}H_{10}S)_2Co]$	287—287.5	—	$B_{10}H_{12}S$	n-BuLi	—	—	—	$CoCl_2$	107
47	$(B_{10}H_{10}S)CoC_5H_5$	267.6—268.5	—	$B_{10}H_{12}S$	n-BuLi	—	—	—	$CoCl_2$	107
48	$(B_{10}H_{10}S)Co(PEt_3)_2$	—	—	$B_{10}H_{12}S$	n-BuLi	—	—	—	$CoCl_2\times(PEt_3)_2$	107

*The carbaborane $Me_4B_8C_4H_8$ is also formed as a side product.
**Optically active compound.

of these polyhedral complexes is a result of the partial dehydration of $[(B_9C_2H_{11})_2Co]^-$, formed during the reaction, which gives rise to $[(B_9C_2H_{11})Co(B_8C_2H_{10})]^{3-}$. The interaction of the latter with Co^{2+} and $(B_9C_2H_{11})^{2-}$ results in the

formation of a bimetallic complex, while the reaction of these two anions with Co^{2+} leads to the formation of a trimetallic complex.

Probably the same principle underlies the formation of $3,6,1,2\text{-}(\eta^5\text{-CpCo})_2B_8C_2H_9CH_2OH$ in the alkaline cleavage and 1-hydroxymethyl-o-carbaborane $B_{10}C_2H_{11}CH_2OH$ by treatment with OH^- in absolute alcohol and after subsequent addition of C_5H_6 and $CoCl_2$ in the presence of an excess of KOH; the compound was obtained in 73% yield[111].

Alkaline alcoholysis of cobalt complexes of carbaboranes with subsequent interaction of the resulting anions with M^{2+} (M = Co or Fe) and C_5H_6 is used nowadays as a preparative method for the synthesis of di- and tri-cobalt complexes of carbaboranes[64,70,112].

The reaction of $4,1,8\text{-}(\eta^5\text{-Cp})CoB_{10}C_2H_{12}$ with KOH in EtOH and then with $CoCl_2$ and C_5H_6 yielded $4,5,1,8\text{-}(\eta^5\text{-CpCo})_2B_9C_2H_{11}$. The corresponding dimethyl derivative was obtained analogously from $4,1,8\text{-}(\eta^5\text{-Cp})Co(B_{10}C_2H_{10}\text{-}1,8\text{-}Me_2)$. The compounds were isolated in 43–58% yield[112]. The same method makes it possible to obtain bimetallic carbaborane heterocomplexes by carrying out the reaction in the presence of $FeCl_2$. Thus, $4,5,1,8\text{-}(\eta^5\text{-Cp})_2\text{-}4\text{-Co-}5\text{-Fe-}B_9C_2H_{11}$ and its dimethyl derivative were isolated and characterised[112]. Furthermore, $CpCo(B_9C_2H_{11})FeCp$ was obtained from CpCo.$(6,7\text{-}B_{10}C_2H_{12})$ in EtOH by treatment with KOH and then with an excess of $FeCl_2$ and C_5H_6.[113] The tricobalt carbaborane complex $\{[(\eta^5\text{-Cp})CoB_9C_2H_{11}]_2Co\}^-$ was isolated by treating $4,1,8\text{-}(\eta^5\text{-Cp})CoB_{10}C_2H_{12}$ in ethanol with KOH and by subsequent reaction with $CoCl_2$ in the absence of C_5H_6.[112] The cobalt carbaborane complex $CpCoB_9C_2H_{11}$ is the starting material for the synthesis of $3,6,1,2\text{-}(\eta^5\text{-CpCo})_2B_8C_2H_{10}$. The reaction is carried out in MeOH and the yield is 57%.[64] The synthesis of $[2,11,1\text{-}(\eta^5\text{-CpCo})_2B_9C_2H_{10}]$ by the reaction of Cp_2Co with $(1\text{-}B_9CH_{10})^-$ in the presence of sodium amalgam is of interest[114].

The presence of bridging hydrogen atoms with acid properties in the *nido*-complex $(\eta^5\text{-Cp})CoB_3C_2H_7$ is responsible for its reaction with NaH. Deprotonation gives rise to the anion $(CpCoB_3C_2H_6)^-$, which interacts with $CoCl_2$ and RC_5H_4Na (R = H,[62,102] Me, Et, or $SiMe_3$ [116]) in THF, which gives a moderate yield of the "three-layer" sandwich complex $1\text{-}(\eta^5\text{-Cp})\text{-}7\text{-}(\eta^5\text{-}C_5H_4R)\text{-}1\text{-Co-}7\text{-Co-}2,3\text{-}B_3C_2H_5$.[70,115,116] The *nido,closo*-complex $[(Me_2B_3C_2H_5)Co(Me_2B_4C_2H_4)]^-$ reacts with $CoCl_2$ and NaCp to give a low yield of the neutral complex $(\eta^5\text{-Cp})Co(Me_2B_3C_2H_5)CoH(Me_2B_3C_2H_5)$.[98]

In conclusion we may note that the above method is synthetically simple, can be used on a preparative scale, and as a rule does not give rise to a complex mixture of reaction products. Its disadvantage is a fairly limited set of initial carbaboranes employed.

3. The Polyhedral Contraction Method

The method includes a stage with partial degradation of the cobalt complex of the carbaborane (removal of the BH^{2+} species) and the subsequent oxidation stage. Cobalt complexes of carbaboranes whose molecules contain one vertex more than the initial cobalt carbaborane complex are obtained by this method[110,117,118]. In a general form the reaction is

$$(LCoB_nC_2H_{n+2})^z \xrightarrow[2)\ -2e]{1)\ -BH^{2+}} (LCoB_{n-1}C_2H_{n+1})^z,$$

$$L{=}Cp,\ z{=}0;\ L{=}B_nC_2H_{n+2},\ z = -1.$$

The nucleophiles employed are KOH and EtOH and the oxidants are H_2O_2 and $FeCl_3$. It has been suggested that the polyhedral contraction reaction proceeds via the intermediate formation of *nido*-complexes[35,53]. Indeed, when the *closo*-complex $[3,3\text{-}Co(1,2\text{-}B_9C_2H_{11})_2]^-$ is treated with KOH in an aqueous medium, the product is the *nido*-complex $(1,2\text{-}B_9C_2H_{11}\text{-}3,9'\text{-Co-}7',8'\text{-}B_8C_2H_{11})^-$ in 63% yield. The oxidation of the latter with H_2O_2 in an alkaline medium gives the *closo*-complex $(1,2\text{-}B_9C_2H_{11}\text{-}3,1'\text{-Co-}2',4'\text{-}B_8C_2H_{10})^-$.[35] Furthermore, $CpCoB_8C_2H_{10}$ is converted in the presence of EtOH and $FeCl_3$ into the *nido*-complex $CpCoB_7C_2H_{11}$, which can be dehydrogenated to the *closo*-complex $CpCoB_7C_2H_9$.[53] The study of the intermediates in the polyhedral contraction reaction of $3,1,2\text{-}(\eta^5\text{-Cp})CoB_9C_2H_{11}$ is also consistent with the above hypothesis[35].

The polyhedral contraction of $3,1,2\text{-}(\eta^5\text{-Cp})CoB_9C_2H_{11}$ leads to the formation of the normal reaction product $1,2,4\text{-}(\eta^5\text{-Cp})CoB_8C_2H_{10}$ (63%) and the cobalt carbaborane complex $2,6,7\text{-}(\eta^5\text{-Cp})CoB_7C_2H_9$.[117,118] The initial compound reacts with KOH in an ethylene glycol–ethanol–water mixture and the resulting red solution is then treated with H_2O_2. The hypothesis of the $1,2,4\text{-}(\eta^5\text{-Cp})CoB_8C_2H_{10}$ structure is based on ^1H and ^{11}B NMR data[118] and certain structural analogies[54]. The compound retains the *closo*-geometry of the initial metal carbaborane complex and is its lowest homologue. Under the conditions of the polyhedral contraction reaction, the symmetrical complex $[3,3\text{-}(1,2\text{-}B_9C_2H_{11})_2Co]^-$ forms only the lowest homologues $(1,2\text{-}B_9C_2H_{11}\text{-}3,1'\text{-Co-}2',4'\text{-}B_8C_2H_{10})^-$.[118]

The conversion into the next metal carbaborane complex homologue (B_7) is achieved by refluxing $(1,2\text{-}B_9C_2H_{11}\text{-}3,1'\text{-Co-}2',4'\text{-}B_8C_2H_{10})^-$ in ethanol in the presence of $FeCl_2$.[118] The compound obtained (11% yield) has the structure $(1,2\text{-}B_9C_2H_{11}\text{-}3,2'\text{-Co-}1',6'\text{-}B_7C_2H_9)^-$. If the polyhedral complex $1,2,4\text{-}(\eta^5\text{-Cp})CoB_8C_2H_{10}$ undergoes the polyhedral contraction reaction, the resulting cobalt carbaborane complex CpCo.$.B_7C_2H_{11}$ does not retain the *closo*-geometry of the initial polyhedron[118]. The ^1H NMR spectrum of this compound contains two broad signals to a high field of the tetramethylsilane signal, indicating the presence of non-terminal hydrogen atoms[54,119]. It has therefore been suggested that the resulting complex has the *nido*-structure. The reaction led to the isolation also of a small amount (2%) of $6,7\text{-}(\eta^5\text{-Cp})$.$.CoB_7C_2H_9$—the usual product of the polyhedral contraction reaction. On treatment of $3,1,7\text{-}(\eta^5\text{-Cp})CoB_9C_2H_{11}$ and $1,2,3\text{-}(\eta^5\text{-Cp})CoB_8C_2H_{10}$ with bases, only cobalt hydroxide is formed[118]. The complex is probably decomposed in this case more rapidly than boron is eliminated from the polyhedron of the cobalt complex of the carbaborane. On treatment of $(\eta^5\text{-Cp})CoB_{10}C_2H_{12}$ with an ethanol solution of KOH, the product is (in 60% yield) the polyhedral complex $(\eta^5\text{-Cp})Co.$.$(2\text{-}B_7CH_8)$.[120] If $(\eta^5\text{-Cp})CoB_{10}C_2H_{11}Me$ is used as the starting material, then $(\eta^5\text{-Cp})Co(2\text{-}B_7CH_8)$ and the corresponding *C*-methyl derivative are isolated[120,121].

4. The Polyhedral Expansion Method

(*a*) *The polyhedral expansion of carbaboranes.* In contrast to the first method ("direct" synthesis), which is based on the use of the initial *nido*- and *arachno*-carbaboranes, the polyhedral expansion reaction is based on the comparatively readily available *closo*-carbaboranes $B_nC_2H_{n+2}$ ($n = 4\text{–}10$). Like aromatic benzenoid systems, *closo*-carbaboranes readily combine with two electrons, using for this purpose the nonbonding and the lowest-lying antibonding molecular orbitals. This was demonstrated first for $1,2\text{-}B_{10}C_2H_{12}$:[122]

$$1,2\text{-}B_{10}C_2H_{12} + 2e \rightarrow (1,2\text{-}B_{10}C_2H_{12})^{2-}.$$

As a result of the Jahn–Teller effect or other distortions, the *closo*-carbaborane struture is opened. The dianion

formed exhibits the properties of a complex-forming ligand capable of reacting with the transition metal[3].

The reduction of the carbaborane 1,7-$B_9C_2H_8$#[38] with sodionaphthalene constituted experimental confirmation of the concept of polyhedral expansion[52,123]:

$$1,7\text{-}B_6C_2H_8 + Na \xrightarrow[THF]{C_{10}H_8} Na_2B_6C_2H_8 \quad .$$

When the reduction product is treated with an excess of sodium cyclopentadienide in the presence of an excess of $CoCl_2$, 1,4,5-(η^5-Cp)$CoB_6C_2H_8$ is formed[52,123]. The compound contains one vertex more than the initial $B_6C_2H_8$ and is a typical product of the polyhedral expansion reaction. Another compound obtained in this reaction was the bimetallic complex 2,9,1,10-(η^5-CpCo)$_2B_6C_2H_8$,[52,123] whose structure was established by X-ray diffraction[52] (see Fig.8). This complex is obtained as a result of the polyhedral expansion reaction of a cobalt carbaborane complex—in the present instance of the 1,4,5-(η^5-Cp)$CoB_6C_2H_8$ formed (for further details, see below). We may add that the polyhedral expansion reaction of 1,7-$B_6C_2H_8$, carried out in the absence of CpNa, gives rise to the symmetrical complex $(Ph_4As)^+$(4,5-$B_6C_2H_8$-1,1'-Co-4',5'-$B_6C_2H_8$)$^-$.[52] The carbaborane 4,5-$B_7C_2H_9$ enters into the polyhedral expansion reaction[52]:

$$4,5\text{-}B_7C_2H_9 + 2e \rightarrow (B_7C_2H_9)^{2-}$$
$$(B_7C_2H_9)^{2-} \xrightarrow{Co^{2+};\ Cp^-} 2,3,10\text{-}(\eta^5\text{-Cp})CoB_7C_2H_9 + 4,6\text{-}(\eta^5\text{-Cp})CoB_6C_2H_8 \quad .$$

Under the conditions of the polyhedral expansion reaction, both isomers (1,6- and 1,10-) of the carbaborane $B_8C_2H_{10}$ [38] give rise to symmetrical and asymmetric polyhedral π-complexes of cobalt[52,65]:

$$1,6\text{-}B_8C_2H_{10} \xrightarrow{2e} (B_8C_2H_{10})^{2-} \xrightarrow{Co^{2+};\ Cp^-} 1,2,3\text{-}(\eta^5\text{-Cp})CoB_8C_2H_{10} +$$
$$+ (CpCo)_2B_8C_2H_{10} + [(B_8C_2H_{10})_2Co]^- + 1,6\text{-}(\eta^5\text{-Cp})CoB_7C_2H_9 +$$
$$+ [\eta\text{-}(\sigma\text{-}B_8C_2H_9)B_8C_2H_9]Co(\eta^5\text{-Cp}) \quad .$$

At room temperature the main reaction product (44%) is 1,2,3-(η^5-Cp)$CoB_8C_2H_{10}$. The reaction of the isomer 1,10-$B_8C_2H_{10}$ is also not unambiguous. Together with 1,2,3-(η^5-Cp)$CoB_8C_2H_{10}$ (44%), a large number of side products were isolated: $CpCoB_7C_2H_9$ (4%), $CpCoB_9C_2H_{11}$ (2%), $(CpCo)_2$.$B_8C_2H_{10}$ (two isomers—1 and 0.2%), and $CpCo(B_8C_2H_9$-$B_8C_2H_9)$ (4%). When the polyhedral expansion reaction of the carbaborane 1,6-$B_8C_2H_{10}$ is carried out at −80 °C, mainly three bimetallic complexes are formed, two of which are isomers of $(CpCo)_2B_8C_2H_{10}$ and the third is $[(\eta^5\text{-Cp})Co_2$.$(B_8C_2H_{10})_2]^-$.[44] The amount of the normal polyhedral expansion reaction product, which is 1,2,3-(η^5-Cp)$CoB_8C_2H_{10}$ is greatly reduced compared with the conditions[52] examined above.

Under the conditions of the polyhedral expansion reaction, the carbaborane 2,3-$B_9C_2H_{11}$ gives rise to the two isomers 2,4- and 2,9-(η^5-Cp)$CoB_9C_2H_{11}$.[52] The reaction products were also found to contain the polyhedral π-complexes 2,3-(η^5-Cp)$CoB_8C_2H_{10}$, 1,6- and 3,10-(η^5-Cp)$CoB_7C_2H_9$, and $(CpCo)_2B_8C_2H_{10}$. It has been suggested[74] that the above compounds are formed as a result of the decomposition of the initial carbaborane 2,3-$B_9C_2H_{11}$. The 13-vertex polyhedra (7,9-$B_{10}C_2H_{12}$-13,13'-Co-7',9'-$B_{10}C_2H_{12}$)$^-$ and 13,7,9-(η^5-Cp).$CoB_{10}C_2H_{12}$ (Fig.15c) have been obtained by the reduction of the carbaborane 1,2-$B_{10}C_2H_{12}$ with sodionaphthalene in THF [122,124] followed by the interaction of the resulting dianion with an excess of CpNa and $CoCl_2$;[125,126] the structure of the second compound was determined by X-ray diffraction[127,128].

The side products of the polyhedral expansion reaction of 1,2-$B_{10}C_2H_{12}$ are[125,126] 7,8-(η^5-Cp)$CoB_9C_2H_{11}$ (1%) and the zwitter-ion (η^5-C_2H_5)Co(η^5-$C_5H_4B_9C_2H_{11}$). The latter compound is a cobaltocenium derivative in which the C-substituted anion $(B_9C_2H_{11})^-$ plays the role of a substituent and an anion simultaneously (Fig.16).[129] The "extra" hydrogen atom in the anion (1,2-$B_9C_2H_{11}$)$^-$ is located over the pentagonal surface, is linked to all the atoms of the latter, and is displaced closer to the $B_{(8)}$ atom (Fig.16). The distances of the hydrogen atom from each atom in the surface are smaller than the coresponding van der Waals B–H and C–H radii[129].

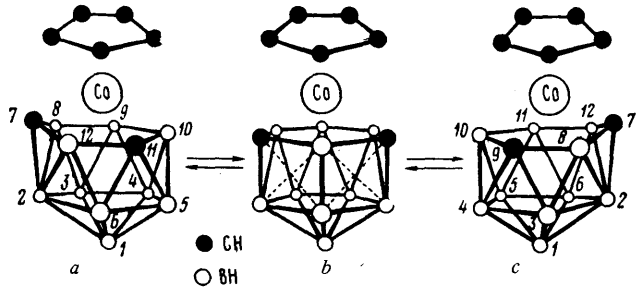


Figure 15. The postulated mechanism of the interaction of the 7,9- and 7,11-enantiomers of (η^5-Cp)$CoB_{10}C_2H_{12}$.

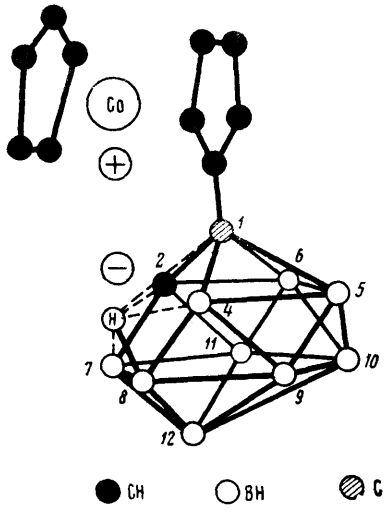


Figure 16. The structure of the zwitter-ion (η^5-Cp)Co(η^5-$C_5H_4B_9C_2H_{11}$) (H is a bridging atom)[129].

The formation of $[(B_{10}H_{10}C_2RR')_2Co]^-$ (R = R' = H or Me; R = H, R' = Me or Ph) from the corresponding dianions $(B_{10}H_{10}C_2RR')^{2-}$ is accompanied by the partial oxidation of the initial dianions to the carbaboranes and of the resulting complexes $[(B_{10}H_{10}C_2RR')_2Co]^-$ to the isomeric B_{10} carbaboranes. The ease of oxidation of the dianions depends on the reduction potential of the carbaborane $B_{10}H_{10}C_2RR'$. The

In previous reviews[3,4] this carbaborane is represented as the 1,6-isomer, which conflicts with the X-ray diffraction study of the *C,C'*-dimethyl analogue[58].

easier the reduction of the carbaborane, the easier the oxidation of its dianion[130]. Thus the dianion $[B_{10}H_{10}C_2HPh]^{2-}$ has been converted under the conditions into the corresponding monoanion $[(B_{10}H_{10}C_2HPh)_2Co]^-$, whereas in the case of $(B_{10}H_{10}C_2Ph_2)^{2-}$ it was possible to isolate only $B_{10}H_{10}C_2Ph_2$.[130] $E_{1/2}$ is known to be −1.95 and −1.14 V respectively for $B_{10}H_{10}C_2HPh$ and $B_{10}H_{10}C_2Ph_2$.

The use of the lowest carbaboranes, particularly $B_5C_2H_7$, under the conditions of the polyhedral expansion reaction, has led to somewhat unexpected results[66]. The formation of twenty compounds, among which $(\eta^5\text{-Cp})CoB_4C_2H_6$ is present in the greatest amount (20–25%), has been observed. Monocobalt carbaborane complexes $(\eta^5\text{-Cp})CoB_nC_2H_{n+2}$ ($n = 5$, 6) and dicobalt carbaborane complexes $(\eta^5\text{-CpCo})_2B_nC_2H_{n+2}$ ($n = 4$, 5, 6), as well as the substituted compounds (η^5-Cp).Co[η^5-(σ-$B_5C_2H_6$)$B_4C_2H_5$] and (η^5-Cp)Co[η^5-(σ-$C_{10}H_7$)$B_4C_2H_5$] have been isolated. The remaining compounds have not been characterised. The product of the polyhedral expansion reaction of 2,4-$B_5C_2H_7$, carried out in the absence of CpNa, is $[Co(2,4\text{-}B_4C_2H_6)_2]^-$ in a very low yield[70].

Under the conditions of the polyhedral expansion reaction, the *nido*-carbaborane 2,3-$B_4C_2H_8$ is largely converted into $(\eta^5\text{-CpCo})_2B_3C_2H_5$ and $(\eta^5\text{-Cp}_6)CoB_3C_2H_5$.[70] The carbaborane 1,6-$B_4C_2H_6$ also does not give rise to the normal polyhedral expansion reaction product and yields 2,4-CpCo.$B_3C_2H_5$CpCoB$_4C_2H_5$-$C_{10}H_7$ and 1,7,2,4-$(CpCo)_2B_3C_2H_5$.[70,115] The latter compound belongs to the new class of "three-layer" sandwich complexes. Under the conditions of the polyhedral expansion reaction, cobalt complexes of carbaboranes have not been obtained at all from the carbaborane 1,5-$B_3C_2H_5$.[70] These findings show that the polyhedral expansion reaction is less typical for the lowest carbaboranes. However, one should note that the change in reaction conditions (time, temperature, etc.) can apparently lead to other results.

(*b*) *The polyhedral expansion reaction of cobalt complexes of carbaboranes.* Like *closo*-carbaboranes, cobalt complexes of carbaboranes are involved in the polyhedral expansion reaction[4]. In a general form, the reaction is as follows:

$$CpCoB_nC_2H_{n+2} \xrightarrow[3)\ [O]]{1)\ 3e;\ 2)\ M'Cl_2;\ CpNa} (Cp)_2CoM'B_nC_2H_{n+2}$$
$$M' = Co \text{ or } Fe.$$

The reduction proceeds formally in two stages: (1) reduction of the metal: Co(III) → Co(II); (2) two-electron reduction of the carbaborane fragment with formation of the anion of the cobalt complex of the *nido*-carbaborane. The subsequent reaction of CpNa with $M'Cl_2$ ($M' = Co$ or Fe) gives a mixture of the di- and tri-cobalt complexes of carbaboranes, which is then oxidised in air. The new compound has one or two vertices more than the initial cobalt carbaborane complex. The reaction time and temperature depend on the initial cobalt carbaborane complex[69].

The first examples of the polyhedral expansion reaction of cobalt carbaborane complexes were examined for the complexes $CpCoB_6C_2H_{10}$ [67] and 2,1,6-$CpCoB_7C_2H_9$.[68] The principal advances in this field have been described by Evans and Hawthorne[69]. Under the conditions of the polyhedral expansion reaction, the complex 2,1,6-$CpCoB_7C_2H_9$ gives rise to a mixture of $(CpCo)_2B_7C_2H_9$ isomers and the trimetallic complex $(CpCo)_3B_7C_2H_9$. The isomers 1,10,2,3-$(CpCo)_2B_7C_2H_9$, 1,8,2,3-$(CpCo)_2B_7C_2H_9$§, and 1,4,2,3-$(CpCo)_2B_7C_2H_9$ were identified by ^1H and ^{11}B NMR. This reaction is accompanied by the polyhedral rearrangement of the initial 2,1,6-$CpCoB_7C_2H_9$, which leads to 3,2,10-CpCo.$B_7C_2H_9$. In addition, 1,9,4,5-$(CpCo)_2B_5C_2H_7$ was detected in the reaction products[69].

The products of the polyhedral expansion reaction of 1,2,3-$CpCoB_6C_2H_{10}$ are 2,3,1,7-$(CpCo)_2B_6C_2H_{10}$ (Fig. 9), whose structure has been established by X-ray diffraction[56], and $[(2,3\text{-}B_6C_2H_{10})_2Co]^-$. Under these conditions, the isomer 1,2,4-$CpCoB_6C_2H_{10}$ gives rise to three compounds, one of which is 3,4,1,2-$(CpCo)_2B_6C_2H_{10}$.[69]

Together with the normal products of the polyhedral expansion reaction of the complex 3,1,2-$CpCoB_9C_2H_{11}$, which consist of the isomers $(CpCo)_2B_9C_2H_{11}$ and [3,3-Co(1,2-$B_9C_2H_{11})_2]^-$, 2,1,7-$CpCoB_9C_2H_{11}$ was also isolated[69].

The isomers 1,14,2,10- and 1,14,2,9-$(CpCo)_2B_{10}C_2H_{12}$ with a 14-vertex polyhedron were obtained under the conditions of the polyhedral expansion reaction of two $CpCoB_{10}C_2H_{12}$ isomers[43]. The reduction of 2,1,6-$CpCoB_7C_2H_9$ and subsequent treatment with an excess of CpNa and $FeCl_2$ lead to a paramagnetic compound, whose reduction with $NaBH_4$ yielded the diamagnetic complex $[CpCo^{III}(B_7C_2H_9)Fe^{III}Cp]$.[113]

The polyhedral expansion reaction of $[CpCoB_7CH_8]^-$ in the presence of $NiBr_2.2C_2H_4(OMe)_2$ leads to the formation of four $[CpCo^{III}(B_7CH_8)Ni^{IV}Cp]$ isomers[131]. However, the only product of the analogous reaction of 2,1-$CpCoB_{10}CH_{11}$ was the naphthalene complex 2,1-$(\eta^6\text{-}C_{10}H_8)CoB_{10}CH_{11}$.[132]

Thus the polyhedral expansion reaction is applicable mainly to the intermediate and higher homologues of carbaboranes and their cobalt complexes. The method makes it possible to obtain a large series of mono-, di-, and tri-cobalt carbaborane complexes as well as dimetallic heterocomplexes of carbaboranes. The possibility of synthesising polymetallic carbaborane complexes by this method is probably problematical. The method is synthetically simple and the initial compounds are readily available, but it often gives rise to a complex mixture of products.

5. The Gas-Phase Synthesis of Cobalt Complexes of Carbaboranes

The direct synthesis of metal complexes of carbaboranes in the gas phase is carried out in a special reactor at an elevated temperature. The initial compounds are the lower carbaborane homologues $B_nC_2H_{n+2}$ ($n = 3$–5) and $CpCo(CO)_2$.[133]

In the presence of $CpCo(CO)_2$ at 230 °C, the carbaborane 1,5-$B_3C_2H_5$ yields $(\eta^5\text{-Cp})CoB_3C_2H_5$ (10%) and two isomers of the dicobalt carbaborane complex: 1,7,2,4- and 1,2,3,5-$(\eta^5\text{-CpCo})_2B_3C_2H_5$. 1,2,4-$(\eta^5\text{-Cp})CoB_4C_2H_6$ (70%) and a small amount (5%) of the eight-vertex polyhedron 3,5,1,7-$(\eta^5\text{-CpCo})_2B_4C_2H_6$ were obtained from the carbaborane 1,6-$B_4C_2H_6$ at 270–280 °C. In the presence of $CpCo(CO)_2$ at 260 °C, a mixture of products, consisting of the cobalt carbaborane complexes $(\eta^5\text{-Cp})CoB_5C_2H_7$ and $(\eta^5\text{-Cp})CoB_4C_2H_6$, two isomers of the dicobalt carbaborane complex $(\eta^5\text{-CpCo})_2B_5C_2H_7$, and two isomers of the tricobalt carbaborane complex $(\eta^5\text{-CpCo})_3B_5C_2H_7$, was obtained from the carbaborane 2,4-$B_5C_2H_7$. The trimetallic carbaborane complex {(η^5-Cp)Co.(2,3-$Me_2B_4C_2H_4$)[$Fe(CO)_3]_2$} is formed when 1,2,3-(η^5-Cp)Co.(2,3-$Me_2B_4C_2H_4$) (structure established by Weiss and Bryan[134]) interacts with an excess of $Fe(CO)_5$ at 125 °C.[135]

Thus the method examined is at present the only preparative procedure for the synthesis of the lowest homologues of cobalt carbaborane complexes. However, under the reaction conditions, the initial carbaborane and its newly formed cobalt complex undergo a polyhedral rearrangement, which leads to a complex mixture of products and hinders their isolation.

§ This is possibly the 1,2,3,8-isomer.

The thermolysis of cobalt complexes of carbaboranes can also be regarded as one of the methods for the synthesis of such complexes. The method is used to synthesise various isomers of cobalt complexes of carbaboranes which cannot be obtained by other methods or for the synthesis of di- and tri-cobalt complexes of carbaboranes from the corresponding monocobalt complexes. The first type of synthesis has already been examined in Section IV. We shall consider separately only the elegant solution of the problem of the synthesis of 1-(η^5-Cp)-7-(η^5-C_5H_4R)-1-Co-7-Co-2,4-$B_3C_2H_5$ from 1-(η^5-Cp)-7-(η^5-C_5H_4R)-1-Co-7-Co-2,3-$B_3C_2H_5$.[116] Whereas the direct reaction of $[(\eta^5\text{-Cp})CoB_3C_2H_6]^-$ with $CoCl_2$ and NaC_5H_4R can be used to synthesise the 1,7,2,3-isomer, in the case of the 1,7,2,4-isomer the polyhedral rearrangement method is the only possible procedure.

Six isomers of the dimetallic carbaborane complex (η^5-$CpCo)_2B_8C_2H_{10}$ were obtained on heating $(\eta^5\text{-Cp})CoB_8C_2H_{10}$ at 235 °C in hexadecane for 7 h; 2,9,1,12-(η^5-$CpCo)_2B_8C_2H_{10}$, in which the cobalt atoms are located in the *para*-positions of the $Co_2B_8C_2H_{10}$ icosahedron, was isolated from the mixture of isomers[136]. The gas-phase thermolysis of the cobalticenium salt $[(\eta^5\text{-Cp})_2Co]^+[Co(B_8C_2H_{10})_2]^-$ at 525 °C and in hexadecane at 270 °C gives rise to five (η^5-$CpCo)_2B_8C_2H_{10}$ isomers[136].

In conclusion one should note that the anionic complexes of carbaboranes are usually isolated as ammonium or alkali metal salts. The synthesis of $[(B_{10}H_{10}S)_2Co]^-[(\eta^5\text{-Cp})_2Co]^+$. where the cobalticenium ion plays the role of the cation, has also been described[107].

IV. THE PROPERTIES OF POLYHEDRAL π-COMPLEXES OF COBALT

1. Intramolecular Rearrangements in the π-Complexes

The absence of symmetry elements from the carbaborane ligand leads to the optical isomerism of the polyhedral π-complexes of cobalt. In particular, the complexes $[(B_9H_9CHP.CH_3)_2Co]^-$,[104] 1,2,4-(η^5-Cp)$CoB_8C_2H_{10}$,[118] and 7,9-(η^5-Cp)$CoB_{10}C_2H_{12}$ (Fig.15*c*)[127] are optically active. The pure enantiomers have not been isolated[104,118,127], but the form of the ^{11}B NMR spectrum of $CpCoB_{10}C_2H_{12}$ at −90 °C indicates unambiguously the presence of two asymmetric 7,9- and 7,11-isomers (Figs.15*a* and 15*c*).[127,128] Below −30 °C, their interconversions can be observed.

The proposed mechanism of the optical rotation of the enantiomers[126] is illustrated in Fig.15. The phenomenon of the polyhedral rearrangement is well known in the carbaborane chemistry[38]. Cobalt complexes of carbaboranes, whose properties are largely determined by the presence of the carbaborane fragment in the molecule, also undergo a polyhedral rearrangement. However, with increase of the number of CoCp fragments in the molecule of the cobalt carbaborane complex, the properties of the latter begin to differ appreciably from those of the carbaborane analogues (see Section I). Indeed, although the occurrence of the isomerisation reaction 2,3,8,1,6-(η^5-$CpCo)_3B_5C_2H_7$ → 2,3,4,1,10-($\eta^5$$CpCo)_3B_5C_2H_7$ has been established in principle (Fig.17), on heating 2,3,8,1,6-(η^5-$CpCo)_3B_5C_2H_7$ mainly decomposes and gives rise to equimolar amounts of 1,8,5,6- and 1,7,5,6-(η^5-$CpCo)_2B_5C_2H_7$.[23] The polyhedral rearrangement of cobalt complexes of carbaboranes was first observed for $Cs[(B_7C_2H_9)_2Co]$ and its asymmetric derivative $CpCoB_7C_2H_9$.[137] The isomers formed are a result of the migration of the carbon atom via the carbaborane fragment. Subsequently it was shown[25,37] that the migration of both the carbon and the cobalt atoms is possible in the isomerisation of cobalt complexes of carbaboranes.

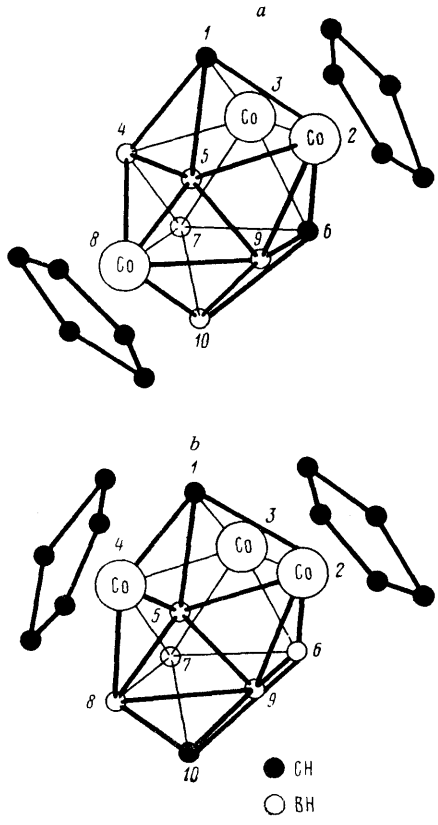


Figure 17. The postulated structures of 2,3,8,1,6-(η^5-$CpCo)_3B_5C_2H_7$ (*a*) and 2,3,4,1,10-(η^5-$CpCo)_3B_5C_2H_7$ (*b*) (one of the Cp ligands is not represented).

(*a*) *Polyhedral rearrangement of cobalt complexes of carbaboranes.* The presence of the cobalt atom in the polyhedron of a cobalt carbaborane complex facilitates the polyhedral rearrangement of the latter compared with the carbaborane itself[22]. Among polyhedral π-complexes the crystal of the 12-atom (η^5-Cp)$CoB_3C_2H_{11}$ polyhedron has the highest energy barrier to the polyhedral rearrangement, which is believed[22] to indicate a high resonance stabilisation of the icosahedron. Non-icosahedral cobalt complexes of carbaboranes of the type (η^5-Cp)$CoB_nC_2H_{n+2}$ ($n = 6$, 7, 8, and 10) have similar activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$, so that it is believed[22] that the polyhedral rearrangements of these complexes have similar mechanisms.

According to an empirical rule governing the polyhedral rearrangement of non-icosahedral systems of the type (η^5-Cp)$CoB_nC_2H_{n+2}$ ($n = 6$, 7, 8, and 10),[22] (1) the coordination number of the cobalt atom, which is high in the polyhedron of the cobalt complex of the carbaborane, does not change in the rearrangement, (2) as a result of the rearrangement there is no mutual approach of the carbon atoms

of the polyhedron, (3) the coordination number of the carbon atom decreases in the course of the rearrangement, and (4) the distance between the carbon and cobalt atom increases. In the latter case the postulates indicated in (2) and (3) must hold. With certain limitations, this rule is applicable also to the lowest homologues of cobalt complexes of carbaboranes ($n = 3$, 4, 5) where partes (2) and (3) mainly hold, while part (4) frequently simply cannot be fulfilled[23].

We shall consider specific examples of the isomerisation of cobalt complexes of carbaboranes. The polyhedral rearrangement of the 3,1,2-(η^5-Cp)$CoB_9C_2H_{11}$ icosahedron[138] and its *C*-alkyl derivatives[139] proceeds in accordance with the empirical rule[22]. In the gas phase (at 400–700 °C) 3,1,2-(η^5-Cp)$CoB_9C_2H_{11}$ gives rise to six new isomers in 87–93% yields (Figs.1*a*–1*f* for R = H). If 3,1,2-(η^5-Cp)Co(1,2-$Me_2B_9C_2H_9$) is sublimed in a hot tube at 400–500 °C, three isomers are formed (Figs.1*a'*–1*c'* for R = Me).[139] At the same time, the rearrangement of 3,1,2-(η^5-Cp)Co[1,2-$(CH_2)_3B_9C_2H_9$] (Fig.18*a*) at 500 °C led to the isolation of only one isomer (Fig.18*b*) in which both carbon atoms are in the *ortho*-positions[139]. The presence of the trimethylene bridge precludes the second part of the empirical rule.

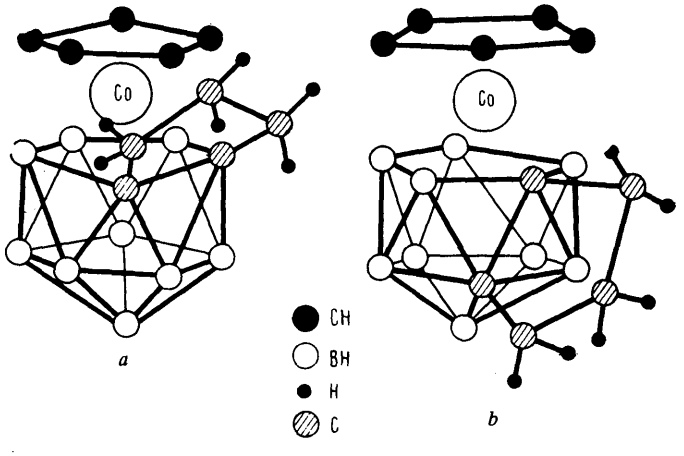


Figure 18. The postulated stuctures of the isomers 3,1,2-(η^5-Cp)Co[1,2-$(CH_2)_3B_9C_2H_9$] (*a*) and 3,1,6-(η^5-Cp)Co[1,6-$(CH_2)_3B_9C_2H_9$] (*b*).

In order to explain the mechanism of the polyhedral rearrangements under consideration, one must assume that the rearrangement follows the *dsd* (*diamond–square–diamond*) scheme proposed by Lipscomb[140] with the simultaneous rotation of the triangular B_2C plane [12,141]. The 4,1,7-(η^5-Cp)$CoB_{10}C_2H_{12}$ non-icosahedral system readily isomerises in solution. On heating at 40 °C, the 4,1,8-isomer is formed, while at 70 °C, the 4,1,13-isomer has been isolated[22]. The identification of the 1,8- and 1,13-isomers has not been confirmed by X-ray diffraction.

Heating of 1,2,4-(η^5-Cp)$CoB_8C_2H_{10}$ [Fig.19 (I, R = H)][32] and its *C*-substituted derivative 1,2,4-(η^5-Cp)Co(2,4-$Me_2B_8C_2H_8$) [Fig.19, (I, R = Me)][36] in solution is also accompanied by a polyhedral rearrangement. In the first case the 1,2,3-isomer [Fig.19, (III, R = H)] was isolated in 94% yield[22]. On heating (2,4-$B_8C_2H_{10}$-1,3'-Co-1',2'-$B_9C_2H_{11}$)$^-$ the only product is also (2,3-$B_8C_2H_{10}$-1,3'-Co-1',2'-$B_9C_2H_{11}$)$^-$.[22] In the case of 1,2,4-(η^5-Cp)Co(2,4-$Me_2B_8C_2H_8$) [Fig.19, (I, R = Me)] a mixture of two isomers is formed[36]. It is believed that in this instance the isomerisation proceeds in steps (1,2,4 → 10,2,3 → 1,2,3) via the intermediate formation of the least stable isomers 10,2,3-(η^5-Cp)Co.(2,3,-$Me_2B_8C_2H_8$)[Fig.19,(II, R = Me)]. The transition 1,2,4-(η^5-Cp)Co(2,4-$Me_2B_8C_2H_8$) → 10,2,3-(η^5-Cp).Co(2,3-$Me_2B_8C_2H_8$)[Fig.19, (I) → (II), R = Me] is accompanied by a decrease of the coordination number of cobalt and an increase of the distance between the carbon atoms in the open B_4C_2 hexagonal surface of the CoB_8C_2 polyhedron. The latter factor promotes the stabilisation of the high positive charge on the cobalt atom by the carbaborane ligand (see Section II). In the course of the further isomerisation (10,2,3 → 1,2,3) [Fig.19, (II) → (III), R = Me] the coordination number of the cobalt atom increases, which agrees with the first part of the empirical rule. However, the fourth part breaks down, since the open hexagonal surface of the 1,2,3-(η^5-Cp)Co(2,3-$Me_2B_8C_2H_8$) isomer now contains two carbon atoms[36]. We may note that mass-spectrometric, ultraviolet spectroscopic, NMR, and oxidation-reduction potential data have been used for the identification of the isomers.

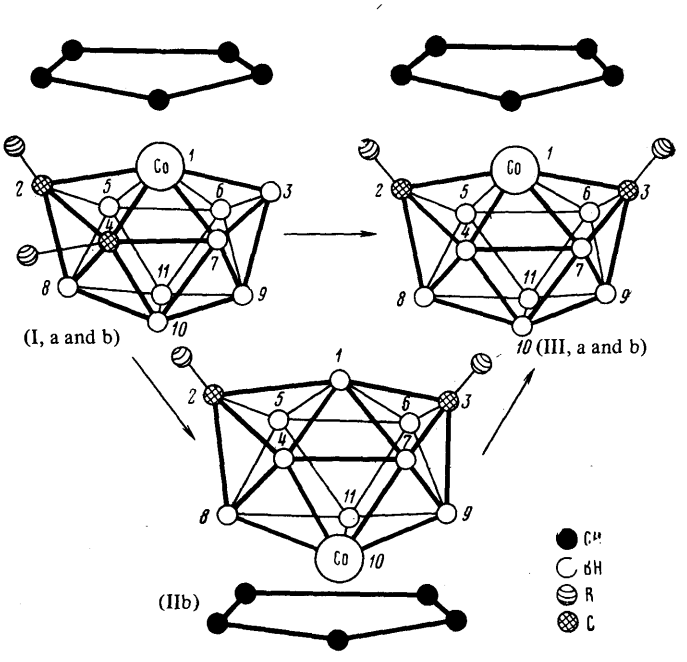


Figure 19. The polyhedral rearrangement of 1,2,4-(η^5-Cp)Co(2,4-$R_2B_8C_2H_8$) (R = H or CH_3).

Five isomers (2,6,9- 2,1,6-, 2,1,7-, 2,1,10-, and 2,3,10-) of the cobalt carbaborane complex (η^5-Cp)$CoB_7C_2H_9$ are known, the complex 2,1,10-(η^5-Cp)$CoB_7C_2H_9$ having the highest thermal stability[22,62]. On heating in solution[22,118] or in the gas phase[62,137], each isomer is converted into the 2,1,10-isomer (Fig.20). The gas-phase rearrangement of the symmetrical complex [(2,1,6-$B_7C_2H_9$)$_2$Co]$^-$$Cs^+$ proceeds analogously[62,137]. The isomerisation of 2,4,5-(η^5-Cp)$CoB_6C_2H_8$ also takes place in conformity with the empirical rule. When the complex is heated in cyclooctane at 150 °C, 2,4,6-(η^5-Cp)$CoB_6C_2H_8$ is

formed[22]. Theoretically[22] the complex 3,1,7-(η^5-Cp)$CoB_5C_2H_7$ (assumed structure) can be converted into the 3,1,8-isomer, since in this case the carbon atom migrates from the open surface of the polyhedron, which decreases the number of Co–C interactions. However, the complex 3,1,7-(η^5-Cp).$CoB_5C_2H_7$, which is stable up to 250 °C, does not isomerise at 340 °C, disproportionating with formation of 2,4-$B_5C_2H_7$, (η^5-CpCo)$_3B_5C_2H_7$, and (η^5-CpCo)$_3B_5C_2H_7$ (traces)[23].

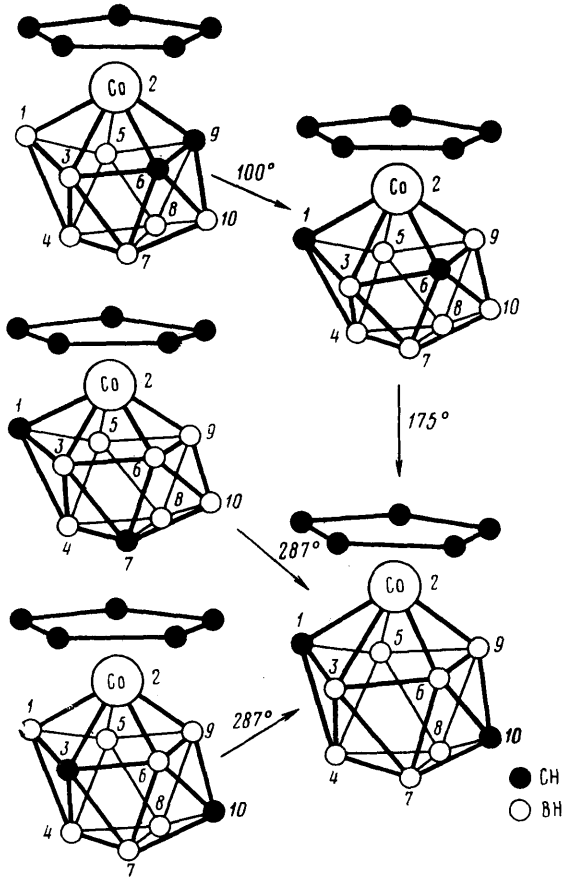


Figure 20. The poyhedral rearrangement of (η^5-Cp)Co.$B_7C_2H_9$.

The polyhedral rearrangement of 1,2,3-(η^5-Cp)$CoB_4C_2H_6$ and its methyl derivative 1,2,3-(η^5-Cp)Co(2-Me$B_4C_2H_5$) (whose structure has been established) takes place in accordance with the empirical rule (the distance between the carbon atoms increases) and leads to the formation of the corresponding 1,2,4-isomers and a small amount of 1,7,2,4-(η^5-CpCo)$_2B_3C_2H_5$.[23]

Among the three possible isomers of the CoB_3C_2 system, only 1,2,4-(η^5-Cp)$CoB_3C_2H_5$ is known, its carbon atoms being located at non-neighbouring vertices[23]. Such carbaboranes and their metal complexes have the highest thermal stabilities. In conformity with these findings, heat treatment of 1,2,4-(η^5-Cp)$CoB_3C_2H_5$ in the gas phase is accompanied solely by the decomposition of the initial compound and the formation of the CoB_4C_2, $Co_2B_3C_2$, and $Co_2B_4C_2$ systems[23].

(b) Polyhedral rearrangement of dicobalt complexes of carbaboranes. The prsence of a second CpCo group in the polyhedron greatly facilitates the isomerisation of the complex. In the course of the rearrangement complexes containing the Co–Co bond are formed as a rule. In these compounds the cobalt and carbon atoms have smaller coordination numbers than in the initial complexes. Furthermore, the initial distances between the carbon atoms can also be retained. Polyhedra with the Co–Co bond are formed at a lower temperature than the final product of the polyhedral rearrangement.

On heating 4,5,1,8-(η^5-CpCo)$_2B_9C_2H_{11}$ at 150 °C in cyclooctane, the isomer 4,5,1,13-(η^5-CpCo)$_2B_9C_2H_{11}$ is formed. In contrast to the initial isomer, in the new isomer both Cp ligands are equivalent. The polyhedral rearrangement of 4,5,1,8-(η^5-CpCo)$_2$(1,8-$Me_2B_9C_2H_9$) proceeds analogously. After the isomerisation, the two Me groups are also equivalent[112]. The hypothesis concerning the structure of the isomer was based on infrared and ultraviolet spectroscopic and NMR data.

The isomers 2,3,1,7-(η^5-CpCo)$_2B_8C_2H_{10}$ [50] and 3,6,1,2-(η^5-CpCo)$_2B_8C_2H_{10}$ [59] (whose structures have been established) isomerise at 250° and 330 °C respectively to 2,4,1,8-(η^5-CpCo)$_2B_8C_2H_{10}$.[25,37] The CpCo fragment and the carbon atom migrate in the former and latter case respectively. The coordination number remains unchanged in the course of the isomerisation.

The 1,4,2,3-(η^5-CpCo)$_2B_7C_2H_9$ polydehdron, containing the Co–Co bond, is formed on isomerisation of 1,6,2,4-(η^5-CpCo)$_2B_7C_2H_9$ and 1,8,2,3-(η^5-CpCo)$_2B_7C_2H_9$. In the course of the 1,6,2,4 → 1,4,2,3 rearrangement the Co–Co bond is retained and the coordination number of the carbon atom decreases. The Co–Co bond appears as a result of the process 1,8,2,3 → 1,4,2,3, Further isomerisation of the 1,4,2,3-isomer gives rise to the 1,10,2,3-(η^5-CpCo)$_2B_7C_2H_9$ polyhedron from which the Co–Co bond disappears. The reaction is accompanied by the formation of (η^5-CpCo)$_3B_7C_2H_9$.[25,37]

The polyhedral rearrangement of 2,6,1,10-(η^5-CpCo)$_2B_6C_2H_8$ (whose structure has been established[24]) gives rise to 2,7,1,10-(η^5-CpCo)$_2B_6C_2H_8$. The compound was identified on the basis of NMR and ultraviolet spectroscopic data. The Co–Co bond disappears as a result of the migration of the CpCo group. The coordination number of cobalt does not change under these conditions[25,37].

The isomerisation 1,8,5,6-(η^5-CpCo)$_2B_5C_2H_7$ → 1,7,5,6-(η^5-CpCo)$_2B_5C_2H_7$ is an exothermic process, i.e. the conversion of the red 1,8,5,6-isomer, in which the cobalt atoms occupy non-neighbouring vertices, into the green 1,7,5,6-isomer, containing the Co–Co bond, is accompanied by the evolution of heat. In addition, it has been shown that at 340 °C equilibrium is established between these isomers[23]. The structure of the isomers has been determined on the basis of a set of spectroscopic data[23] and has been confirmed by X-ray diffraction[142].

Only the single isomer 3,5,1,7-(η^5-CpCo)$_2B_4C_2H_6$ is known for the $Co_2B_4C_2$ system; its structure has been determined by ^1H and ^{11}B NMR. Its conversion into 3,5,2,8-(η^5-CpCo)$_2$.$B_4C_2H_6$ is theoretically possible, since this would entail a decrease of the number of direct Co–C interactions from four to two. However, the isomerisation products were not detected below the decomposition temperature (340 °C).[23]

At 300 °C 1,7,2,3-(η^5-CpCo)$_2B_3C_2H_5$ is converted into 1,7,2,4-(η^5-CpCo)$_2B_3C_2H_5$. There is no Co–Co bond in either compound[102,129]. The structure of the complexes has been established[115,143]. The latter compound does not isomerise up to its decomposition temperature (~400 °C). The rearrangement of the methyl-substituted 1,7,2,3-isomer proceeds similarly. When the isomerisation of 1,7,2,3-(η^5-CpCo)$_2B_3C_2H_5$ was carried out at a lower temperature, the 1,2,4,5- and

1,2,3,5-isomers were also isolated; they both contain the Co–Co bond (the structure was postulated on the basis of ^{11}B NMR data). It has been suggested that the isomerisation of the 1,7,2,3-isomer proceeds in accordance with the scheme 1,7,2,3→1,2,4,5→1,2,3,5→1,7,2,4 (Fig.21). In the first stage the *ortho*-positions of the carbon atoms are retained, but the coordination number of the cobalt atom decreases. The formation of the 1,2,3,5-polyhedron is accompanied by an increase of the distance between the carbon atoms and the migration of the CpCo fragment gives rise to the 1,7,2,4-isomer in which there is no Co–Co interaction and the cobalt atoms have the initial coordination numbers[23].

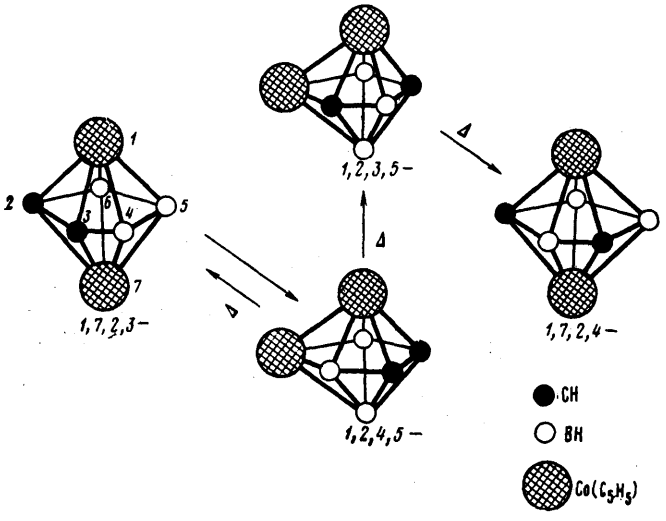


Figure 21. The polyhedral rearrangement of 1,7,2,3-$(\eta^5$-$CpCo)_2B_3C_2H_5$.

corresponding derivatives (V) (Fig.22). Their structure was established by infrared spectroscopy, NMR, and mass spectrometry.

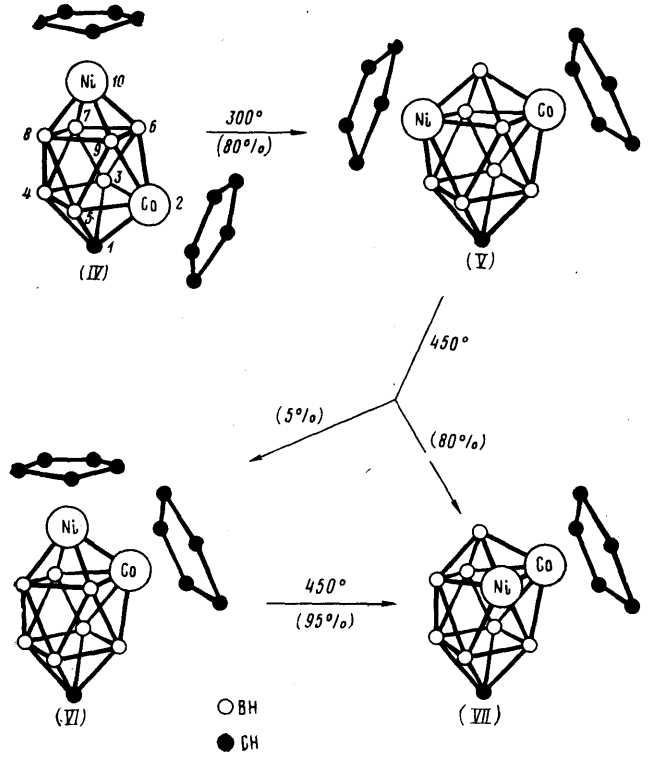


Figure 22. The polyhedral rearrangement of $(\eta^5$-$Cp)^2Co.NiB_7CH_8$ [in (VII) the Cp ligand at the nickel atom is not represented].

Thus the presence of two cobalt atoms in the polyhedron does not by itself introduce fundamental changes into the properties of the complexes, but a new tendency is clearly shown. Firstly, the ability of the polyhedron to undergo a rearrangement depends on the possibility of the formation of complexes with a Co–Co bond in the course of the isomerisation. Secondly, complexes with a Co–Co bond always isomerise. In those cases where compounds with a Co–Co bond were not detected in the course of the polyhedral rearrangement, the reaction was carried out at a high temperature. Possibly the use of milder conditions will permit the isolation of these intermediate complexes.

(c) *Polyhedral rearrangement of bimetallic heterocomplexes of carbaboranes.* It has been suggested that the Co(III)–Fe(III) derivatives, which are electron-deficient systems, decompose under the conditions of the polyhedral rearrangement[21]. Indeed, 4,5,1,8-$(\eta^5$-$Cp)_2CoFeB_9C_2H_{11}$ decomposes on heating and does not give rise to isomerisational products[112]. The bimetallic carbaborane complexes $(\eta^5$-$Cp)_2CoNiB_7CH_8$ readily undergo the polyhedral rearrangement. The isomerisation gives rise to polyhedra with a Co–Ni bond [Fig.22, (IV)–(VII)][132]. The bromo-derivatives (IV) (Fig.22) $(\eta^5$-$Cp)_2CoNiB_7CH_{8-n}Br_n$ ($n=1$, 2) gives rise only to the

The ability of cobalt π-complexes of carbaboranes to isomerise in boiling solvents complicates their analysis and purification.

2. The Oxidation-Reduction Properties of Cobalt Complexes of Carbaboranes

(a) *Electrochemical properties.* The electronic configuration of the cobalt atom in monocobalt complexes of carbaboranes can vary within wide limits ($d^8 \rightarrow d^5$) (Table 2).[91,144] However, complexes containing cobalt in the formal +3 oxidation state (d^6) have been isolated mainly in a chemically pure form. At the same time, oxidation of the yellow-orange diamagnetic compound $[(B_{10}H_{10}CH)_2Co]^{3-}$ gives rise to the black paramagnetic complex $[(B_{10}H_{10}CH)_2Co]^{2-}$, containing cobalt in the d^5 state[99,101].

The cobalt atom has the d^7 electronic configuration in the complex $(B_9C_9CHPCH_3)_2Co$.[104] The existence of the complex $[(B_9C_9CHPCH_3)_2Co]^+$ (d^8) has been demonstrated electrochemically, but it has not been isolated[104]. It followed from the foregoing that, although polyhedral ligands are capable of stabilising the highest and lowest oxidation states of the

cobalt atom, a particular oxidation state of cobalt is preferred for each. The nature of the change in the electrochemical behaviour of cobalt complexes of carbaboranes within a single homologous series is still unknown. However, a clear relation has been established between the reduction potential of the cobalt carbaborane complex and the structure of its isomers. The closer the carbon atom in the polyhedron to the cobalt atom, the easier the reduction of the complex. The isomer containing two carbon atoms in the cobalt coordination plane has the lowest reduction potential compared with other isomers of the given cobalt carbaborane complex (see Nos. 15—17, 21, 22, 23, and 24 in Table 2). This is because the carbon in the polyhedron of the cobalt carbaborane complex is an electron deficient centre and reduces the electron density on the cobalt atom, which facilitates its reduction[99,139]. This property has been used to determine the structures of the isomers of cobalt complexes of carbaboranes[22,36,139].

There exists an analogy between the nature of the influence of substituents on the electrochemical properties of cobalt complexes of carbaboranes and their carbaborane parent compounds[145]. Methyl and phenyl groups at the carbon atom of the dicarbollyl ligand lower the reduction potential of the complex (see Nos. 9, 10, and 11 in Table 2). The presence of three bromine atoms in the polyhedron greatly facilitates the reduction of the complex (No. 12 in Table 2). It is believed that the formal high negative charge of the complex (−3), formed in the $d^6 \rightarrow d^7 \rightarrow d^8$ reduction process, is stabilised as a result of the electron-accepting properties of the bromine atoms[20].

Table 2. The potentials of oxidation-reduction processes (relative to the saturated calomel electrode).

No.	Compound	Method*	$M^{IV}+e \rightarrow M^{III}$ $d^5 \rightarrow d^6$	$M^{III}+e \rightarrow M^{II}$ $d^6 \rightarrow d^7$	$M^{II}+e \rightarrow M^{I}$ $d^7 \rightarrow d^8$	References
1	$NEt_4[(1,2\text{-}B_9C_2H_{11})_2Co]$	P (*c*)	—	−1.36	−2.24	144
2	$NEt_4[(1,2\text{-}B_9C_2H_{11})_2Co]$	P (*d*)	—	−1.37	−2.37	144
3	$Cs[(1,2\text{-}B_9C_2H_{11})_2Co]$	P (*a*)	—	−1.42	—	14,20
4	$Cs[(1,2\text{-}B_9C_2H_{11})_2Co]$	CVA (*b*)	+1.57	−1.46	—	20
5	$[(1,2\text{-}B_9C_2H_{11})_2Co]^-$	CVA (*b*)	+0.70	−1.53	—	58
6	$NEt_4[1,7\text{-}B_9C_2H_{11})_2Co]$	P (*c*)	—	−1.14	−2.52	144
7	$NEt_4[1,7\text{-}B_9C_2H_{11})_2Co]$	P (*d*)	—	−1.21	−2.70	144
8	$Cs[(1,7\text{-}B_9C_2H_{11})_2Co]$	CVA (*b*)	irrevers.	−1.17	—	20
9	$NMe_4[1,2\text{-}Me_2B_9C_2H_9)_2Co]$	P (*a*)	—	−1.16	—	14,20
10	$NMe_4[1,2\text{-}Me_2B_9C_2H_9)_2Co]$	CVA (*b*)	irrevers.	−1.13	—	20
11	$NMe_4[(1,2\text{-}PhB_9C_2H_{10})_2Co]$	P (*a*)	—	−1.28	—	14,20
12	$NMe_4[(1,2\text{-}Br_2B_9C_2H_9)_2Co]$	CVA (*b*)	irrevers.	−0.48	−1.58	20
13	$(1,2\text{-}B_9H_9CHPMe)_2Co$	CVA (*b*)	—	+0.43	−0.78	104
14	$(1,7\text{-}B_9H_9CHPMe)_2Co$ (m.p. = 278—279°)	CVA (*b*)	—	+0,41	−0.74	104
15	$4,1,7\text{-}(\eta^5\text{-Cp})CoB_{10}C_2H_{12}$	CVA (*b*)	—	−0.72	−0.74	22
16	$4,1,8\text{-}(\eta^5\text{-Cp})CoB_{10}C_2H_{12}$	CVA (*b*)	—	−1.15	—	22
17	$4,1,13\text{-}(\eta^5\text{-Cp})CoB_{10}C_2H_{12}$	CVA (*b*)	—	−1.16	—	22
18	$3,1,2\text{-}(\eta^5\text{-Cp})CoB_9C_2H_{11}$	P (*c*)	—	−1.21	−2.11	144
19	$3,1,2\text{-}(\eta^5\text{-Cp})CoB_9C_2H_{11}$	P (*d*)	—	−1.19	−2.21	144
20	$3,1,2\text{-}(\eta^5\text{-Cp})CoB_9C_2H_{11}$	CVA (*b*)	irrevers.	−1.25	—	20
21	$2,1,6\text{-}(\eta^5\text{-Cp})CoB_7C_2H_9$	CVA (*b*)	—	−1.03	—	22
22	$2,1,7\text{-}(\eta^5\text{-Cp})CoB_7C_2H_9$	CVA (*b*)	—	−1.33	—	22
23	$2,4,5\text{-}(\eta^5\text{-Cp})CoB_6C_2H_8$	CVA (*b*)	—	−0.84	—	22
24	$2,4,6\text{-}(\eta^5\text{-Cp})CoB_6C_2H_8$	CVA (*b*)	—	−1.11	—	22
25	$(NMe_4)_2(B_9C_2H_{11}CoB_9C_2H_{10}CoB_9C_2H_{11})$	P (*c*)	—	−1.48	−2.36	144
26	$(NMe_4)_2(B_9C_2H_{11}CoB_9C_2H_{10}CoB_9C_2H_{11})$	P (*d*)	—	−1.49	−2.43	144
27	$(NMe_4)_2(B_9C_2H_{11}CoB_9C_2H_{10}CoB_9C_2H_{11})$	CVA (*b*)	+1.57	−1.46	—	58
28	$(NMe_4)_2[(B_9C_2H_{11}CoB_9C_2H_{10})_2Co]$	CVA (*b*)	+1.07	−1.36	—	58

*P = polarographic method; CVA = cyclic voltamperometric method. The measurements were performed under the following conditions: *a*) in 0.10 M $LiClO_4$ in 50% aqueous acetone as the supporting electrolyte; *b*) in 0.10 M Et_4NClO_4 in acetonitrile as the supporting electrolyte; *c*) in 0.10 M n-Bu_4PF_6 in acetonitrile as the supporting electrolyte; *d*) in 0.15 M n-Bu_4NPF_6 in dimethoxyethane as the supporting electrolyte.

Unsuccessful attempts have been made to carry out the reversible reduction of the complexes $[(B_{10}H_{10}S)_2Co]^-$ [107] and $[(B_9H_9CHP)_2Co]^-$.[104] However, it is not clear whether this is a property of the above π-complexes or is a consequence of the chosen experimental conditions. The reduction of the isomers of $(\eta^5\text{-Cp})Co^{III}(Me_2B_6C_2H_8)$ is a two-stage two-electron process. The first wave corresponds to the Co(III) → Co(II) transition and the second corresponds to the addition of a second electron and the formation of the anion $[CpCo^{II}.(Me_2B_6C_2H_8)]^{2-}$. For the 1,2,4- and 10,2,3-isomers, both stages are reversible: $E_{1/2} = -0.83$ and −1.64 V in the former case and $E_{1/2} = -1.23$ and −1.57 V in the latter. The second stage in the reduction of $1,2,3\text{-}(\eta^5\text{-Cp})Co(2,3\text{-}M_3B_6C_2H_8)$ takes place irreversibly ($E_{1/2} = -0.75$ and −1.66 V).[36]

The complex $2,1\text{-}(\eta^6\text{-}C_{10}H_8)CoB_{10}CH_{11}$, containing the coordinated neutral arene ligand $C_{10}H_8$, is also reduced in two stages. The reversible reduction observed at −0.62 V is attributed to the Co(III) → Co(II) transition. As −1.31 V a quasi-reversible process is observed and is regarded as the reduction of the naphthalene ligand $C_{10}H_8$.[132]

The reduction and oxidation of cobalt complexes of carbaboranes containing two or three metal atoms as a rule proceeds in a reversible one-electron stage (Table 3). The reduction of cluster compounds of transition metals takes place similarly[146]. Probably[112] in this case the high degree of electron delocalisation determines the behaviour of the group of metal atoms within the polyhedron as a single metallic centre.

The reduction potentials of di- and tri-cobalt complexes of carbaboranes also depend on the isomeric structure of the complex. The same relations as those mentioned above for monocobalt complexes of carbaboranes have been observed[112] (see Nos. 2—4, 5, and 6, in Table 3).

Table 3. The reduction and oxidation potentials of di- and tri-metal complexes of carbaboranes.

No.	Compound	Reduction ($E_{p/2}$, V)	Oxidation ($E_{p/2}$, V)	Refs.
1	$1,14,2,10\text{-}(\eta^5\text{-CpCo})_2B_{10}C_2H_{12}$	−1.10	+1.17	43
2	$4,5,1,3\text{-}(\eta^5\text{-CpCo})_2B_9C_2H_{11}$	−0.85	+0.77	112
3	$4,5,1,8\text{-}(\eta^5\text{-CpCo})_2B_9C_2H_{11}$	−0.92	+0.97	112
4	$4,5,1,13\text{-}(\eta^5\text{-CpCo})_2B_9C_2H_{11}$	−1.25	+0.83	112
5	$4,5,1,8\text{-}(\eta^5\text{-CpCo})_2(1,8\text{-}Me_2B_9C_2H_9)$	−0.91	+0.92	112
6	$4,5,1,13\text{-}(\eta^5\text{-CpCo})_2(1,13\text{-}Me_2B_9C_2H_9)$	−1.25	+0.87	112
7	$2,7,1,10\text{-}(\eta^5\text{-CpCo})_2B_9C_2H_8$	−1.50	+1.37	25
8	$\{[(\eta^5\text{-Cp})CoB_9C_2H_{11}]_2Co\}^-$	−0.84	+0.86	112
9	$4,5,1,8\text{-}(\eta^5\text{-Cp})_2\text{-}4Co\text{-}5Fe\text{-}B_9C_2H_{11}$	−0.42	+0.90	112
10	$4,5,1,8\text{-}(\eta^5\text{-Cp})_2\text{-}4Co\text{-}5Fe\text{-}(1,8\text{-}Me_2B_9C_2H_9)$	−0.47	+0.92	112

It is known[112] that the oxidation and reduction of bimetallic heterocomplexes of carbaboranes containing iron and cobalt atoms proceed in a single reversible one-electron stage (Nos. 9 and 10 in Table 3). In this case there is an analogy with the electrochemical behaviour of $(\eta^5\text{-CpCo})_2B_nC_2H_{n+2}$ ($n = 5$ to 10).[43,112] On the other hand, according to cyclic voltamperometric data, the $(\eta^5\text{-Cp})_2CoNiB_7CH_8$ isomers are reduced in a single reversible one-electron stage, while their oxidation is irreversible. The reduction of $(\eta^5\text{-Cp})_2Co^{III}Ni^{IV}.B_7CH_8$ gives rise to a complex containing Co^{III} and Ni^{III}, but it has not been isolated.

(*b*) *The effect of reducing and oxidising agents.* When $[(B_9C_2H_{11})_2Co]^-$ is acted upon by n-BuLi, the product is an analogue of cobaltocene—the complexes $[(B_9C_2H_{11})_2Co]^{2-}$,

which is unstable in air[14]. Paramagnetic complexes of the type $CpCo^{III}(B_nC_2H_{n+2})Fe^{III}Cp$ ($n=7$, 9) are reduced by $NaBH_4$, which yields diamagnetic compounds of the type $[CpCo(B_nC_2H_{n+2})FeCp]^-$.[113]

It has been established that $CpCoB_9C_2H_{11}$ is stable in oxidising media such as in solution of CrO_3 in CH_3COOH, or acetone in the presence of H_2SO_4, or an alkaline solution of $KMnO_4$.[46] At the same time, on treatment with $CuCl_2$ and other oxidants the complexes $[(B_{10}H_{10}C_2RR')_2Co]^-$ are converted quantitatively into *o*-carbaboranes of the type o-$B_{10}H_{10}C_2RR'$ ($R=R'=H$ or Me; $R=H$, $R'=Me$ or Ph).[130]

3. Chemical Properties of Cobalt Complexes of Carbaboranes

There is an analogy between the chemical behaviour of cobalt complexes of carbaboranes and carbaboranes themselves, although under the reaction conditions the cobalt atom or the Cp ligand are not reaction centres (polyhedral expansion reaction, polyhedral rearrangement, bromination, etc.). Reactions of cobalt complexes of carbaboranes are known in which the nature of the products is determined by the presence of the CoCp fragment in the polyhedral molecule. These are metallation, acetylation, and nitration reactions. As far as is allowed by the available structural data, we shall endeavour to compare the chemical properties of cobalt complexes of carbaboranes, carbaboranes, and Cp sandwich complexes of cobalt. Aqueous alkaline solutions of cobaltocenium salts are known to be stable under radiolysis conditions[147]. The complex $[(1,2\text{-}B_9C_2H_{11})_2Co]^-$ is also stable in the water–nitrobenzene system under irradiation from a ^{60}Co γ-source[148]. At the same time the radiolysis of $[(1,2\text{-}B_9C_2H_{11})_2Co]Cs$ in methanol[149] or the nitrobenzene–bromoform mixture[150] leads to the formation of the corresponding bis-(dicarbollyl)cobalt(III) derivative in which the substituent

(>CHOH or –CBr=CBr–) occupies a bridging position

between the two dicarbollyl ligands.

The reaction of $1,2,4\text{-}(\eta^5\text{-Cp})CoB_8C_2H_{10}$ with (*trans*-PhCH=CHPh)$Pt(PEt_3)_2$ in toluene at 20 °C leads to $1\text{-}(\eta^5\text{-Cp})Co\text{-}8\text{-}(PEt_3)_2Pt\text{-}2,7\text{-}B_8C_2H_{10}$ (Fig.23), which is regarded as a compound resulting from the inclusion of the $(Et_3P)_2Pt$ fragment in the carbaborane ring[151]. Another bimetallic carbaborane heterocomplex $(C_8H_{12})NiC_2B_8H_{10}CoCp$ is formed when $1,2,4\text{-}(\eta^5\text{-Cp})CoB_8C_2H_{10}$ is treated with $(1,5\text{-}C_8H_{12})_2Ni$.[151] We may note that the carbaborane $2,3\text{-}Me_2\text{-}2,3\text{-}B_9C_2H_9$ also reacts with the analogous zerovalent nickel and platinum complexes to form *closo*-carbaborane complexes of nickel and platinum[151].

In aqueous THF solution in the presence of acid the complex $(C,C'\text{-}Me_2B_4C_2H_2)_2CoH$ is almost quantitatively converted into $(Me_2B_3C_2H_5)CoH(Me_2B_4C_2H_4)$.[98] The latter compound contains two B–H–B fragments and a Co–H fragment. NMR studies failed to demonstrate the occurrence of exchange between B–H–B and Co–H, although the authors[98] do not rule out the possibility of such an exchange at a very low rate. It is of interest that, under the influence of NaH or KOH, $[(Me_2B_3C_2H_5).Co(Me_2B_4C_2H_4)]^-$ is obtained from $(Me_2B_3C_2H_5)CoH(Me_2B_4C_2H_4)$, the proton being split off from the cobalt atom, while the B–H–B fragments are retained. We may note that this process is reversible[98].

The symmetric and asymmetric *closo*-complexes having the general formula $[(2,4\text{-}B_8C_2H_{10})CoL]^{z-}$ ($L=1,2\text{-}B_9C_2H_{11}$, $z=-1$; $L=Cp$, $z=0$) are converted into complexes with the *nido*-structure of the type $[(B_8C_2H_{10}.Nu)CoL]^z$ ($Nu=$pyridine, piperidine, or ethanol) on interaction with Lewis bases[35, 53,117,118] The structure of $(1,2\text{-}B_9C_2H_{11}\text{-}3,11'\text{-}Co\text{-}9'\text{-}C_5H_5N\text{-}7',8'\text{-}B_8C_2H_{10})^-$ has been established by NMR [35,117] and X-ray diffraction[54,55] (Fig. 7).

It is believed[35] that the structure of the $CoB_8C_2H_{10}.Nu$ fragment in the *nido*-complexes $(\eta^5\text{-Cp})CoB_8C_2H_{10}.Nu$ ($Nu=C_5H_5N$ or $C_5H_{10}NH$), obtained by treating $1,2,4\text{-}(\eta^5\text{-Cp}).CoB_8C_2H_{10}$ with pyridine or piperidine, is analogous to that discussed above. However, there is no unanimous view concerning the structure of $(\eta^5\text{-Cp})CoB_8C_2H_{10}.EtOH$.[53,118]

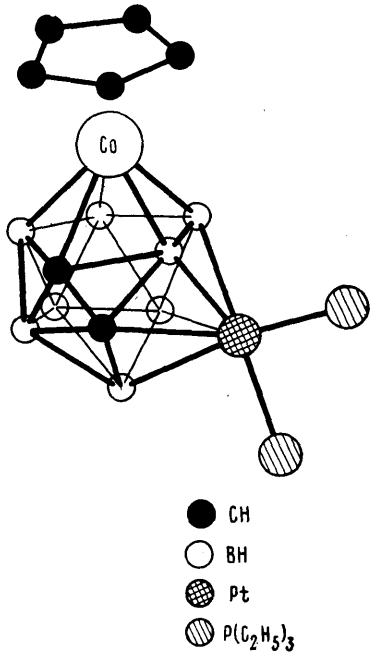


Figure 23. The structure of $1\text{-}(\eta^5\text{-Cp})Co\text{-}8\text{-}(PEt_3)_2Pt\text{-}2,7\text{-}B_8C_2H_{10}$.[151]

The hydrogen atoms attached to the boron atoms in $3,1,2\text{-}(\eta^5\text{-Cp})CoB_9C_2H_{11}$ and $1,2,4\text{-}(\eta^5\text{-Cp})CoB_8C_2H_{10}$ are exchanged for deuterium in the presence of $(PPh_3)_3RuHCl$. The exchange apparently proceeds via a stage involving the oxidative addition of the terminal BH bond of the complex to the catalyst[152].

The moderate acidity of the hydrogen atom in the C–H bond of the carbaborane $B_{10}C_2H_{12}$ is responsible for the ready formation of the *C*-lithio-derivative in the reaction of the carbaborane with n-BuLi. The reaction of the carbaborane with RMgBr proceeds similarly[38]. The reaction of organometallic compounds (RLi, RMgBr) with an isoelectronic analogue of the complex $CpCoB_9C_2H_{11}$—the cobalticenium cation—gives rise to the products of addition to the Cp ring, i.e. $CpCoC_5H_5R$. There has been only one mention of the formation of the substituted cobalticenium $[RC_5H_4CoCp]^+$ in this reaction, but hitherto this finding has not been confirmed experimentally[153]. We shall now turn to cobalt complexes of carbaboranes. The reaction n-BuLi with $1,2,4\text{-}(\eta^5\text{-Cp})CoB_8C_2H_{10}$ in ether leads to the alkylation of the complex in the Cp ligand and the formation of $1,2,4\text{-}(\eta^5\text{-}C_5H_4Bu).CoB_8C_2H_{10}$.[35] RLi ($R=$n-Bu or C≡CPh) [154] and ArMgBr ($Ar=Ph$, *m*-FC_6H_4, or *p*-FC_6H_4) [155] in THF also react with $3,1,2\text{-}(\eta^5\text{-Cp})CoB_9C_2H_{11}$. The reaction of $3,6,1,2\text{-}(\eta^5\text{-CpCo})_2$.

$.B_8C_2H_{10}$ with RLi (R = Bu or Ph) in THF leads to the substitution of the hydrogen atom in one of the Cp ligands by an R-group with formation of 3-(η^5-CpCo)-6-(η^5-C_5H_4RCo)-1,2-$B_8C_2H_{10}$ (R = Bu or Ph).[156]

It is believed[35,154-156] that the reduction process Co(III) → Co(II) takes place in the course of the reaction and the radical $C_4H_9^{\cdot}$ is formed, which leads to the alkylation of the Cp ring. On the other hand, on treatment of 3,1,2-(η^5-Cp).$CoB_9C_2H_{11}$ with BuLi (molar ratio 1:1) in ether, the main product is the *C*-lithio-derivative 3,1,2-(η^5-Cp)Co(1-$LiB_9C_2H_{10}$). For a reactant ratio of 2:1, the product is 3,1,2-(η^5-Cp)Co(1,2-$Li_2B_9C_2H_9$). The compounds have been isolated in the form of carboxylic acids. 3,1,2-(η^5-C_5H_4Bu)$CoB_9C_2H_{11}$ is formed in a small amount as a side product[154].

Instances of the electrophilic substitution of hydrogen atoms in the polyhedral ligand of a cobalt carbaborane complex are known. Substitution takes place at the boron atoms most remote from the carbon atoms, which results in an enhancement of their electron density[157,158]. When $[(1,2\text{-}B_9C_2H_{11})_2Co]^-$ is treated with an excess of bromine in glacial acetic acid, the bromo-derivative $[(8,9,12\text{-}Br_3\text{-}1,2\text{-}B_9C_2H_8)_2.Co]^-$, illustrated in Fig.3, is formed[20]. Its structure was established by X-ray diffraction[49]. The asymmetric complex 3,1,2-(η^5-Cp)$CoB_9C_2H_{11}$ is also brominated under analogous conditions[47]. It has been established that the bromination of 3,1,2-(η^5-Cp)$CoB_9C_2H_{11}$ with bromine in CH_2Cl_2 in the presence of $AlCl_3$ takes place in steps. Depending on the amount of bromine, mono-, di-, or tri-bromo-derivatives of 3,1,2-(η^5-Cp)$CoB_9C_2H_{11}$ are formed. The authors suggest[47] that initially substitution takes place at the boron atom in the 8-position and then successively in the 9- and 12-positions. 3,1,2-(η^5-Cp)Co(1-$MeB_9C_2H_{10-n}Br_n$) (n = 1, 2) has been obtained similarly[47]. On bromination of the complex CpCo(1,6-$B_7C_2H_9$),[62] substitution takes place also at the boron atom[159]. On treatment with an excess of bromine in CCl_4, CpCo.$(B_7C_2H_7Br_2)$ is formed.

Bimetallic carbaborane heterocomplexes, particularly isomers IV and V of the complex $(\eta^5\text{-Cp})_2CoNiB_7CH_8$, are also brominated successfully (Fig.22). Bromination is achieved with one or two moles of bromine in CCl_4, which yields respectively mono- and di-bromo-derivatives[132]. In all the instances examined, there is no substitution in the Cp ligand. We may note that cobaltocene is oxidised by bromine to the cobalticenium ion[160].

Thus cobalt complexes of carbaboranes behave analogously to carbaboranes under the conditions of electrophilic bromination[38]. In addition, bromination of the π-complexes takes place also in glacial acetic acid, while carbaboranes are inert under these conditions.

Another electrophilic substitution reaction, the Friedel–Crafts acetylation, also leads to the formation of B-substituted complexes only.

Acetylation of (η^5-Cp)Co(1,6-$B_7C_2H_9$) gives a 72% yield of (η^5-Cp)Co(8-$CH_3CO\text{-}B_7C_2H_8$). The acetyl derivative readily gives rise to the corresponding 2,4-dinitrophenylhydrazone, but is not converted into the corresponding carbinol in the presence of $LiAlH_4$.[159] The complex (η^5-Cp)Co(1,10-$B_7C_2H_9$) is inert under the conditions corresponding to the acylation of the 1,6-isomer. This is apparently a consequence of a more symmetrical distribution of electron density in the ligand of the 1,10-isomer.

The acetylation of 3,1,2-(η^5-Cp)$CoB_9C_2H_{11}$ does not proceed as smoothly as in the case of (η^5-Cp)Co(1,6-$B_7C_2H_9$).[161] The reaction is carried out in an atmosphere of nitrogen by treatment with CH_3COCl and $AlCl_3$. As in bromination, substitution takes place at the $B_{(8)}$ atom, which is most remote from the electron-deficient carbon atoms and therefore has the highest electron density. The structure of 3,1,2-(η^5-Cp)Co(8-$CH_3COB_9C_2H_{10}$) has been established by X-ray diffraction[161]. However, 3,1,2-(η^5-Cp)Co(8-$CH_3COB_9C_2H_{10}$) is formed in a small amount and is not the only reaction product. At the same time, 3,1,2-(η^5-Cp)Co(8-$RB_9C_2H_{10}$), where R = Cl, OH, or $OCOCH_3$, have been isolated[161]. Acetylation of 3,1,2-(η^5-Cp)Co(1-$PhB_9C_2H_{10}$) with a mixture of CH_3COCl and $AlCl_3$ in dichloroethane at 45–55 °C leads only to the oxidation of the B–H bond and the formation of the B-hydroxy-derivative[162]. We may note that, among the known cyclopentadienyl π-complexes of cobalt, acetylation is undergone only by (η^5-Cp)Co(η^4-C_4H_4), with substitution at a carbon atom of the C_4H_4 ligand (yield approximately 10%).[163]

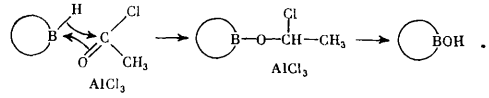
When 3,1,2-(η^5-Cp)$CoB_9C_2H_{11}$ is refluxed in benzene with an excess of $AlCl_3$, the B-substituted derivative 3,1,2-(η^5-Cp)Co(8-$ClB_9C_2H_{10}$) is formed[161].

The B–H bond in 3,1,2-(η^5-Cp)$CoB_9C_2H_{11}$ is oxidised more readily than in the *o*-carbaborane. The oxidation takes place under the influence of CrO_3 in $(CH_3CO)_2O$ or CH_3COOH in the presence of H_2SO_4 [162] and of the nitrating mixture ($HNO_3:H_2SO_4 = 1:3$) [162] and also in Friedel–Crafts acetylation[161,162]. In the first case the *B*-acetoxy and *B*,*B*-diacetoxy-derivatives are formed together with 3,2,1-(η^5-Cp)Co(8-$HOB_9C_2H_{10}$).[162] The reaction with the nitrating mixture gives the nitrate 3,2,1-(η^5-Cp)Co(8-$O_2NOB_9C_2H_{10}$).[162]

The nitration of 3,2,1-(η^5-C_5H_4Ph)$CoB_9C_2H_{11}$ and 3,2,1-(η^5-Cp)Co(1-$PhB_9C_2H_{10}$) gives two series of compounds. On the one hand, the *para*-nitro-derivatives 3,2,1-(η^5-$C_5H_4C_6H_4NO_2$-*p*)$CoB_9C_2H_{11}$ and 3,2,1-(η^5-Cp)Co(1-*p*-$NO_2C_6H_4B_9C_2H_{10}$) are formed, and, on the other, the products are the corresponding $B_{(8)}$ derivatives 3,2,1-(η^5-$C_5H_4C_6H_4NO_2$-*p*)Co(8-$O_2NOB_9C_2H_{10}$) and 3,2,1-(η^5-Cp)Co(1-*p*-$NO_2C_6H_4$-8-$O_2NOB_9C_2H_9$).[162] It is believed that the *B*-hydroxy-derivative is formed initially and is then converted into the nitrate.

The formation of the *B*-hydroxy- and *B*-acetoxy-derivatives 3,2,1-(η^5-Cp)Co(8-$RB_9C_2H_{10}$) (R = OH or $OCOCH_3$ from 3,2,1-(η^5-Cp)$CoB_9C_2H_{11}$ under the conditions of the acetylation reaction (treatment with $CH_3COCl + AlCl_3$) is fairly unexpected[161,162], since the $CH_3COCl + AlCl_3$ mixture does not have very pronounced oxidising properties. Furthermore, the reaction of CH_3COCl and $AlCl_3$ with 3,2,1-(η^5-Cp)Co(1-$PhB_9C_2H_{10}$) in dichloroethane also led to the formation of the *B*-hydroxy-derivative 3,2,1-(η^5-Cp)Co(1-Ph-8-$HOB_9C_2H_9$) instead of the expected acetylation in the benzene ring[162]. 3,2,1-(η^5-Cp)Co(1-Me-8-$HOB_9C_2H_9$) has been obtained similarly[162].

It is believed that the formation of the *B*-hydroxy-derivatives must be regarded as a hydride shift reaction:



This hypothesis agrees well with the idea that there is enhanced electron density at the $B_{(8)}$ atom and with known experimental facts (the formation of $B_{(8)}$ derivatives alone).

The enhanced hydride mobility of the hydrogen atoms linked to boron atoms facilitates the hydrogen–halogen exchange in reactions of alkyl halides with 3,1,2-(η^5-Cp)$CoB_9C_2H_{11}$ compared with the carbaboranes $B_{10}C_2H_{12}$. On treatment of 3,1,2-(η^5-Cp)$CoB_9C_2H_{11}$ with RX (R = Me, Et, or iso-Br; X = I or Br), both alkylation and exchange halogenation in the carbaborane ring takes place. The reaction leads to the formation of the *B*-alkyl-*B*-halogeno-derivatives $CpCoB_9C_2H_{11}$:[164]

$$3,1,2\text{-}(\eta^5\text{-Cp})\,CoB_9C_2H_{11} + RX \xrightarrow[20^\circ]{AlCl_3} (\eta^5\text{-Cp})\,CoB_9C_2H_{11-n-m}R_nX_m \quad n = 3, 4;\ m = 1, 2.$$

There exists another series of reactions of dicarbollylcobalt complexes in which substitution takes place only at the $B_{(8)}$ atom. All these reactions are carried out in the presence of acids. On treatment of $[3,3\text{-}Co(1,2\text{-}B_9C_2H_{11})_2]^-$ with diethyl sulphide in a strongly acid medium, a neutral compound is formed[165]:

$$[3,3\text{-Co}(1,2\text{-}B_9C_2H_{11})_2]^- + HCl + Et_2S \rightarrow 1,2\text{-}B_9C_2H_{11}\text{-}3,3'\text{-Co-}8'\text{-}SEt_2\text{-}1',2'\text{-}B_9C_2H_{10} + H_2.$$

Treatment of $[3,3\text{-Co-}(1,2\text{-}B_9C_2H_{11})_2]^-$ with carbon disulphide in the presence of $AlCl_3$ and HCl yields the compounds $\{[3,3\text{-Co-}(1,2\text{-}B_9C_2H_{10})_2]^-S_2C^+H\}$, in which two dicarbollyl groups are linked by the $[SC^+(H)S]$ bridge[166]. The 1,7-isomer reacts similarly[166]; the structure of the resulting compound is illustrated in Fig. 2.[48,167]

The electron-deficient carbon atom in the complexes formed is stabilised by the free electron pair of the sulphur atom. The compound in which the $[OC^+(CH_3)O]$ fragment is a bridge between dicarbollyl groups has been isolated by treating $[3,3\text{-Co}(1,2\text{-}B_9C_2H_{11})_2]^-$ with the CH_3COOH–$(CH_3CO)_2O$ mixture in the presence of catalytic amounts of $HClO_4$.[147] It has been suggested[165] that a protonated complex is formed in the course of the reaction and is then subjected to nucleophilic attack by a neutral molecule (Et_2S or CS_2), which results in the formation of the corresponding $B_{(8)}$ derivative and evolution of molecular hydrogen[165,166]. The protonated complex hypothesis agrees satisfactorily with the hypothesis of the hydride properties of the hydrogen at the boron atom in the 8-position[162].

The carbonium centres in the complexes $\{[(1,2\text{-}B_9C_2H_{10})_2Co]^-.O_2C\overset{+}{C}H_3\}$ and $\{[(1,2\text{-}B_9C_2H_{10})_2Co]^-S_2\overset{+}{C}H\}$ are inert towards protic solvents. This is probably a consequence of the partial delocalisation of the positive charges of the neighbouring heteroatoms and the proximity of the negative charge. The interaction with $NaBH_4$ is rapid and gives a good yield[166]:

$$\{[(1,2\text{-}B_9C_2H_{10})_2Co]^-S_2C^+H\} + NaBH_4 \rightarrow [(1,2\text{-}B_9C_2H_{10})_2CoS_2CH_2]^-.$$

The hydrolysis of $\{[(1,2\text{-}B_9C_2H_{10})_2Co]^-O_2C^+CH_3\}$ and the analogous sulphur-containing derivatives leads to the formation of a diol and a dithiol respectively[166]. Furthermore, the corresponding thiolothioformyl derivative was isolated in the hydrolysis of $\{[(1,2\text{-}B_9C_2H_{10})_2Co]^-S_2C^+H\}$.[166]

The reaction of $[3,3\text{-Co}(1,2\text{-}B_9C_2H_{11})_2]^-$ with S_2Cl_2 in CH_2Cl_2 leads to $[8,8\text{-}S(B_9C_2H_{10})_2Co]^-$ after alkaline methanolysis[168]. This reaction has no analogies in the chemistry of carbaboranes. The sulphur atom in the complex is highly reactive and is readily alkylated with formation of 8,8-RS.$.(B_9C_2H_{10})_2Co$, R = alkyl[168].

In the presence of diazonium salts $[(7,8\text{-}B_9C_2H_{11})_2Co]^-$ gives rise to the complex $RC_6H_4N_2.[(7,8\text{-}B_9C_2H_{11})Co]$. On heating, this compound is converted into the *B*-substituted derivative in which the phenylene unit occupies a bridging position between the two dicarbollyl groups[169].

The reaction of the dicarbollyl complex 3,2,1-(η^5-Cp).$.CoB_9C_2H_{11}$ with $PhBCl_2$ is interesting[170]: there is a complete analogy with the chemical behaviour of cobaltocene. In both cases the addition of the Ph(Cl)B fragment to the Cp ligand is accompanied by the heterolysis of the B–Cl bond and a ring expansion reaction, which leads to the formation of a six-electron borinate ion involved in a π-type coordination[153]:

$$3,2,1\text{-}(\eta^5\text{-Cp})CoB_9C_2H_{11} + PhBCl_2 \rightarrow 3,2,1\text{-}(\eta^6\text{-}C_6H_5B\text{—Ph})CoB_9C_2H_{11}.$$

3,2,1-(η^5-Cp)$CoB_9C_2H_{11}$ is initially reduced with sodionaphthalene in THF, whereupon, after the addition of an excess of $PhBCl_2$ and exposure of the reaction product to air, a derivative of the borinate ion is obtained in 17% yield[170]. When $CpCoB_9H_9CHCCH(OH)R$ is treated with $LiAlH_4$ and H_2AlCl, the CHOH group is reduced and $CpCoB_9H_9CHCCH_2R$ is formed[171].

The oxidation of 3,1,2-(η^5-Cp)$CoB_9H_9CHCCH_2OH$ with chromium trioxide in acetone in the presence of H_2SO_4 yields 3,1,2-(η^5-Cp)$CoB_9H_9CHCCHO$. The oxidation of the CH_2OH group to CHO then takes place more readily than the oxidation of the aldehyde group to the carboxy-group[46]. Under the influence of CrO_3 in an acid medium, the complex $(\eta^5\text{-CpCo})_2.$ $.B_8H_8CHCCH_2OH$ yields the corresponding aldehyde. Further oxidation of $(\eta^5\text{-CpCo})_2B_8H_8CH_8CCHO$ is difficult apparently owing to pronounced steric hindrance[111].

The aldehyde and ketone groups in 3,1,2-(η^5-Cp)Co.$.B_9H_9CHCR$ (R = CHO [46] or $COCH_3$ [161]) form the corresponding hydrazones on reaction with 2,4-dinitrophenylhydrazine. On treatment of 3,1,2-(η^5-Cp)$CoB_9H_9CHCCHO$ with C_2H_5ONa or t-C_4H_9ONa, the CHO group is split off with formation of $CpCoB_9H_9C_2H_2$, while the reactions with Grignard reagents take place stereoselectively and leads to diastereoisomeric secondary alcohols[171]. The Clemmensen reduction of 3,1,2-(η^5-Cp)$CoB_9H_9CHCCOCH_3$ gives rise to an ethyl-substituted complex[161]. The carboxylic acid 3,1,2-(η^5-Cp)$CoB_9H_9CHC.$ $.COOH$ ($pK_a = 3.54$) is converted into the methyl ester by treatment with diazomethane or into the acid chloride by reaction with PCl_5.[46] The acid chloride 3,1,2-(η^5-Cp)Co.$.B_9C_9CHCCOCl$ does not hydrolyse and undergoes very slowly the Friedel–Crafts reaction with benzene. The passivity of the COCl group is also regarded as a consequence of steric factors[46]. Treatment of the *B*-hydroxy-derivative 3,1,2-(η^5-Cp)Co(8-$HOB_9C_2H_{10}$) with acetic anhydride or CH_3COCl leads to the corresponding *B*-acetoxy-derivative 3,1,2-(η^5-Cp)Co(8-$CH_3OCOB_9C_2H_{10}$).[161,162] The amino- (pK_a = 6.04) and vinyl groups in 3,1,2-(η^5-Cp)Co(6-$RB_9C_2H_{10}$), where $R = NH_2$ or $CH=CH_2$, exhibit a reduced reactivity compared with the corresponding carbaborane derivatives[96]. The nitro-derivatives 3,1,2-(η^5-Cp)$CoB_9H_9CHCC_6H_4NO_2$ and 3,1,2-(η^5-$C_5H_4C_6H_4NO_2)CoB_9C_2H_{11}$ are reduced to the corresponding substituted anilines on treatment with tin and HCl in an alcoholic solution[162].

Thus it follows from the examples presented that the chemical behaviour of the functional groups in the polyhedral ligand in a cobalt carbaborane complex differs little from the usual chemical reactions of these groups.

In conclusion of the discussion of the chemical properties of cobalt complexes of carbaboranes, we may mention that the properties of the complex [(η^5-Cp)Co(7-$B_{10}CH_{11}$)]$^-$ differ significantly from those of the compounds considered here. The complex is chemically inert and is stable for 90 h at 100 °C in KOH and EtOH solutions. It does not undergo polyhedral expansion and contraction reactions. The anion [(η^5-Cp)Co(7-$B_{10}CH_{11}$)]$^-$ is not converted into a neutral complex containing Co(IV) on treatment with oxidants ($KMnO_4$, $FeCl_3$, or the Ce^{4+} ion).[102]

V. POLYHEDRAL COBALT COMPLEXES OF *NIDO*-CARBABORANES

The *nido*-complexes of cobalt are obtained by the polyhedral contraction reaction[35,118] (see Section III) or by treating with nucleophiles (pyridine, piperidine, and ethanol) *closo*-complexes of the type $[(B_8C_2H_{10}CoL)]^z$, where L = 1,2-$B_9C_2H_{11}$ with $z = -1$ or L = Cp with $z = 0$ [35,53,117,118] (for further details, see Section IV).

When polyhedral cobalt *nido*-carbaborane complexes $[(B_8C_2H_{10}NC_5H_5)CoL]^z$ [35,117] or $CpCoB_7C_2H_{11}$ (Fig. 6) are oxidised[118] with iron(III) chloride, a non-terminal hydrogen atom is split off and the closed system of the cobalt *closo*-carbaborane complex is formed:

$$[(7,8\text{-}B_8C_2H_{10}\cdot NC_5H_5)CoL]^z \xrightarrow{FeCl_3} [(2,4\text{-}B_8C_2H_9NC_5H_5)CoL]^{z+1}$$
$$L = C_5H_5,\ z = 0;\ L = 1,2\text{-}B_9C_2H_{11},\ z = -1$$
$$CpCoB_7C_2H_{11} \xrightarrow{FeCl_3} CpCo(6,7\text{-}B_7C_2H_9).$$

The $[1,2,4\text{-}(\eta^5\text{-Cp})Co(7\text{-}C_6H_5NB_8C_2H_9)]^+$ formed is precipitated by PF_6 anions. The compound is decomposed in polar solvents[35]. A more stable neutral *closo*-complex $(\eta^5\text{-Cp}).CoB_8C_2H_9C_5H_{10}$ is obtained in 34% yield by oxidising $(\eta^5\text{-Cp}).CoB_8C_2H_{10}.NHC_5H_{10}$ and iron(III) chloride and by subsequent treatment with K_2CO_3.[35]

Like the anion $(B_9C_2H_{12})^-$, the cobalt *nido*-carbaborane complex $(1,2\text{-}B_9C_2H_{11}\text{-}3,9'\text{-}Co\text{-}7',8'\text{-}B_8C_2H_{11})^-$ is protonated in the presence of HCl and converted into the complex $(1,2\text{-}B_9C_2H_{11}\text{-}3,9'\text{-}Co\text{-}7',8'\text{-}B_8C_2H_{12})^-$ having the *nido*-structure[35]. The oxidation of the latter with hydrogen peroxide in an alkaline medium gives rise to $(1,2\text{-}B_9C_2H_{11}\text{-}3,1'\text{-}Co\text{-}2',4'\text{-}B_8C_2H_{11})^-$ (yield 75%).[35]

The main product of the reaction between $(\eta^5\text{-Cp})CoB_8C_2H_{10}$ (VIII) and EtOH in the presence of $FeCl_3$ is $2,1,10\text{-}(\eta^5\text{-Cp})Co.B_7C_2H_9$ (IX). It has been suggested[53] that the reaction proceeds via the intermediate formation of the *nido*-complex $8,6,7\text{-}(\eta^5\text{-Cp})CoB_7C_2H_{11}$ (X), which is converted into $3,2,1\text{-}(\eta^5\text{-Cp})CoB_7C_2H_9$ (XI) after dehydrogenation. The thermal rearrangement of the latter gives the final *closo*-complex (XI).[53]

On refluxing in cyclooctane (at approximately 150 °C) complexes with the *nido*-structure can also be converted into cobalt complexes of *closo*-carbaboranes[53,118]:

$$CpCoB_7C_2H_{11} \xrightarrow{\Delta} CpCo(1,10\text{-}B_7C_2H_9)$$

$$(1,2\text{-}B_9C_2H_{11}\text{-}3,9'\text{-}Co\text{-}7',8'\text{-}B_8C_2H_{12})^- \xrightarrow{\Delta} (1,2\text{-}B_9C_2H_{11}\text{-}3,1'\text{-}Co\text{-}2',3'\text{-}B_8C_2H_{10})^-.$$

Thus cobalt complexes of *nido*-carbaboranes usually have the properties of carbaboranes with the *nido*-structure[38].

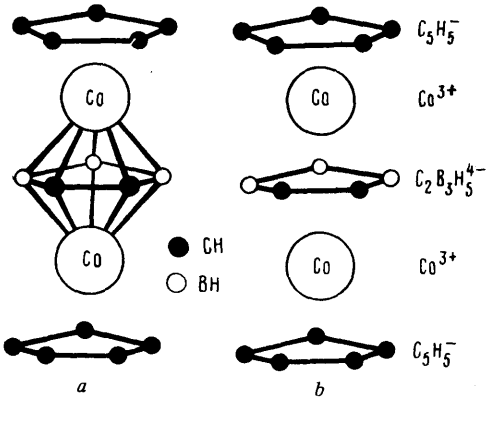


Figure 24. Schematic illustration of two different descriptions of the type of bond in the "three-layer" sandwich compound $(\eta^5\text{-CpCo})_2B_3C_2H_5$.

VI. CARBABORANE-CONTAINING THREE-LAYER SANDWICH STRUCTURES

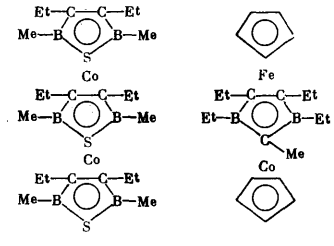
The complex $(\eta^5\text{-CpCo})_2B_3C_2H_5$ is the lowest homologue among the known polyhedral dicobalt complexes of carbaboranes having the general formula $(\eta^5\text{-CpCo})_2B_nC_2H_{n+2}$ ($n = 3$–10). The compound exists in the form of four isomers, two of which [1,7,2,3- and 1,7,2,4-$(\eta^5\text{-CpCo})_2B_3C_2H_5$] contain cobalt atoms in the *para*-position with respect to the carbaborane fragment (Fig.24). In the non-Soviet literature compounds of this type are referred to as "triple-decker sandwich structures"; we shall refer to them as three-layer sandwich structures. There exist two equivalent but different qualitative descriptions of the type of binding in these compounds[116,143]. They can be regarded as dicobalt complexes of carbaboranes existing as a result of strong and highly localised covalent interactions (Fig.24*a*). Here the central $Co_2B_3C_2$ fragment contains 16 valence electrons, in agreement with the empirical rule[21,172]. The other alternative description of the binding is based on the formal subdivision of the molecule into three planar ring systems ($C_5H_5^-$, $B_3C_2H_5^{4-}$, and $C_5H_5^-$) and two Co^{3+} ions (Fig.24*b*).

The structures of $1,7,2,3\text{-}(\eta^5\text{-CpCo})_2(3\text{-}MeB_3C_2H_4)$ [115] and $1,7,2,4\text{-}(\eta^5\text{-CpCo})_2(2\text{-}MeB_3C_2H_4)$ have been determined[143]. All the three rings in the complexes are planar but not parallel. The C–C distances in the carbaborane ligand in the 1,7,2,3- and 1,7,2,4-isomers are 1.44 and 1.52 Å respectively.

The results of the study of the ^1H and ^{11}N NMR of the two isomers show that the electron density in the $B_3C_2H_5$ ligand of the 1,7,2,4-isomer is delocalised over the ring, while in the 1,7,2,3-isomer it is localised mainly at the C–C bond[116]. The presence of substituents in the $B_3C_2H_5$ ligand alters the positions of the chemical shifts for all three rings. Substitution of the Cp ring influences mainly the electron density in the central $B_3C_2H_5$ ligand[116]. The red complex $1,7,2,3\text{-}(CpCo)_2B_3C_2H_5$ absorbs in the ultraviolet at 776 nm, while the green complex $1,7,2,4\text{-}(CpCo)_2B_3C_2H_5$ absorbs in the region of 555 μm.[116] The thermal stability of the 1,7,2,3-isomer is lowest. At 200 °C it is converted into the 1,2,3,5-, 1,2,4,5-, and 1,7,2,4-isomers[23]. The isomers of $(CpCo)_2B_3C_2H_5$ are diamagnetic, resistant to oxidation in the solid state, and do not react with water[115,143].

The isomer $1,7,2,4\text{-}(CpCo)_2B_3C_2H_5$ has been obtained by oxidising the products of the reaction of CpNa and an excess of $CoCl_2$ with the carbaborane $1,6\text{-}B_4C_2H_6$ subjected to preliminary treatment with sodionaphthalene[70,115]. Another isomer and its C-substituted derivatives have been obtained by the reaction of $(RB_4C_2H_6)^-$ with CpNa and $CoCl_2$ followed by oxidation (R = H, Me,[70,115] Ph, or $SiMe_3$ [116]). The 1,7,2,3-isomer or its Cp-substituted derivative $CpCoB_3C_2H_5Co(C_5H_4R)$ (R = H, Me, Et, or $SiMe_3$) has been obtained by the reaction of $[(\eta^5\text{-Cp})CoB_3C_2H_6]^-$ with an excess of $CoCl_2$ and RC_5H_4Na in THF.[70,115,116] The three-layer sandwich structure $1,7,2,3\text{-}(\eta^5\text{-CpCo})_2(\mu\text{-}2,3\text{-}1,3\text{-}C_3H_4B_3C_2H_3)$ is also known[173]. The reaction of $CpCo(CO)_2$ with $(C,C'\text{-}Me_2B_4C_2H_4)_2CoH$ in THF on irradiation or on refluxing in the absence of irradiation yields $1,2,4,5\text{-}(\eta^5\text{-CpCo})_2(Me_2B_3C_2H_3)$ and $(\eta^5\text{-Cp})Co.(Me_2B_3C_2H_3)CoH(Me_2B_3C_2H_5)Co(\eta^5\text{-Cp})$,[98] while the reaction of $CpCo(CO)_2$ with $(Me_2B_4C_2H_4)_2FeH_2$ results in the formation of $1,7,2,3\text{-}(\eta^5\text{-Cp})Co(Me_2B_3C_2H_3)Fe(CO)_3$.[63] In the reactions considered three-layer sandwich structures are formed in low yields (≤5%) and are mixed with other cobalt complexes of carbaboranes[70,98,115,173]. The compounds are isolated by chromatographic methods on silicone gel. The interaction of $Co_2(CO)_8$ with thiaborolene gives rise to the formation of a three-layer sandwich structure (XII) in which the thiadiborolene ligand plays the role of both a μ-ligand and an η-ligand[174]. The Lewis acid 1,3-diborolene reacts with $Co_2(CO)_8$ to form $[\eta\text{-}R_4(Me)B_2C_3]Co(CO)_2$.[175] The interaction of 1,3-diborolene with $CpCo(CO)_2$ in the presence of $[CpFe(CO)_2]_2$ gives rise to the formation of compound (XIII).[175] Compounds (XII) and (XIII) have high thermal stability and are resistent

to oxidation:



(XII) (XIII)

VII. COBALT σ-COMPLEXES OF CARBABORANES

As a result of the marked electron-deficient properties $B_{10}C_2H_{12}$, the σ-complex $\{[(B_{10}C_2H_{10})_2]_2Co\}^{2-}$ does not contain the usual stabilising ligands (CO or PR_3). A cobalt complex is formed when 2,2′-ligand dilithiobiscarbaborane is treated with anhydrous $CoCl_2$.[176,177]

The coordination sphere of the cobalt atom consists of four Co–Co σ-bonds and the Co–H–B bridge bond. In the carbaborane icosahedra there is a tetrahedral arrangement around the cobalt atom[178]. Under the influence of oxidants and reductants, the cobalt in $\{[(B_{10}C_2H_{10})_2]_2Co\}^-$ readily undergoes a change in its formal oxidation state from +3 to +1.[176,177] The complex $(HC_2B_{10}C_2H_{11})Co_2(CO)_6$, obtained from $Co_2(CO)_8$ and $HC{\equiv}CB_{10}C_2H_{11}$, is also known[179]. It does not contain a direct cobalt-carbaborane σ-bond, but is an interesting example of carbaborane-containing acetylenic cobalt complexes[180].

VIII. COBALT-CONTAINING BORANES

Like the cobalt complexes of carbaboranes, the known cobalt complexes of boranes can be regarded as borane derivatives in the polyhedra of which the BH vertex has been replaced by the CpCo group. Fig.25 illustrates the molecular structure of 2-(η^5-cyclopentadienyl)-2-cobalt-*nido*-η^3-pentaborane(9).[181] The cobalt atom is located between the Cp and B_4H_8 fragments, the latter behaving as a three-electron-donating ligand in relation to cobalt[181]. The complex (η^5-Cp).Co(5-B_9H_{13}), the dicobalt borane complex 1,2-(η^5-CpCo)$_2B_4H_6$, and its substituted derivatives 1,2-(η^5-CpCo)$_2$-(3-cyclo-$C_5H_9B_4H_{15}$), 1,2-(η^5-CpCo)$_2$(4-cyclo-$C_5H_9B_4H_5$), and (η^5-Cp.Co)$_2$(σ-4-$C_5H_9B_4H_5$) are also known[173].

The crystal and molecular structures of (η^5-Cp)Co(5-B_9H_{13}) have been determined by X-ray diffraction[182]. The complex has the *nido*-structure and contains four bridge bonds, among which three are of the B–H type and one is of the B–H–Co type. The B_4 surface of the borane ligand is almost parallel to the plane of the Cp-ring.

The above compounds are resistant to the action of air and water. The complex 2-(η^5-Cp)CoB_4H_8 undergoes a polyhedral rearrangement at 200 °C, the cobalt atom migrating to the 1-position[173]. A mixture of complexes has been obtained by adding an excess of $CoCl_2$ and CpNa in THF to a solution of $Na^+[B_5H_8]^-$ at −196 °C; it was then separated by thin-layer chromatography and silica gel. (CpCo)$_2$(3-cyclo-$C_5H_9B_4H_5$) and (CpCo)$_2$(4-cyclo-$C_5H_9B_4H_5$) are apparently formed when the Cp anion is hydrogenated by the hydroborate anion $(B_5H_8)^-$.[173,183] Apart from the compounds enumerated above, (η^5-CpCo)$_3B_3H_5$, (η^5-CpCo)$_3B_4H_4$, and (η^5-CpCo)$_4B_4H_4$ were later isolated in lower yields from the products of the reaction of $Na^+[B_5H_8]^-$ with $CoCl_2$ and CpNa.[173,184] The crystal and molecular structures of 1,2,3-(η^5-CpCo)$_3B_3H_5$ and 1,2,3-(η^5-CpCo)$_3B_4H_4$ gave been determined by X-ray diffraction[185]. Under the conditions of the gas-phase method, not only the complexes described above[183,184] but also clusters containing five boron atoms, (η^5-CpCo)$_3B_5H_5$ and (η^5-CpCo)$_3B_5H_4C_5H_5$,[186] have been obtained from pentaborane(9), cyclopentadiene, and cobalt.

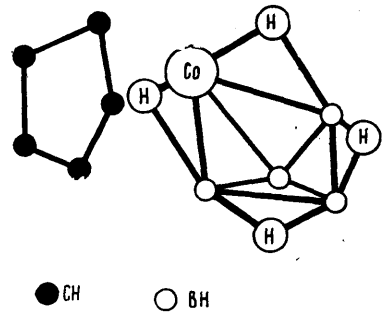


Figure 25. The structure of 2-(η^5-cyclopentadienyl)-2-cobalta-*nido*-pentaborane(9).[181]

The symmetrical cobalt borane complex $[(B_{10}H_{12})_2Co]^{2-}$ is formed when the labile $Zn(B_{10}H_{12}).(C_4H_8O)_2$ [187] is acted upon by anhydrous $CoCl_2$ in acetone[188]. The salt $[N(CH_3)_4]_2.[(B_{10}H_{12})_2Co]$ is sparingly soluble in water, is more soluble in alcohol, and is very readily soluble in acetonitrile, acetone, and DMF.

The interaction of $Co_2(CO)_8$ with $NaB_{10}H_{13}$ [188] or $Na_2(B_{18}H_{20})$ [189,190] in THF yielded carbonyl derivatives of cobalt borane complexes $[N(CH_3)_4][(B_{10}H_{12})Co(CO)_3]$ (yield 55%) and $[N(CH_3)_4][(B_{18}H_{20})Co(CO)_3]$ (yield 20%) respectively. The complex $[N(CH_3)_4]_2[Co(B_{10}H_{12})_2]$ catalyses the condensation of nitriles with acetylenes, which leads to the formation of alkylpyridines[191]. The cobalt-containing derivatives of phosphadecaborane (η^5-Cp)Co(7-$B_{10}H_{10}$PR) and [(η^5-Cp)Co(7-$B_{10}H_{10}$P)]$^-$ (R = Me, Et, n-Pr, or Ph) have been obtained in 15–35% yield by the reaction of 7-$B_{10}H_{12}$PR with $CoCl_2$ and C_5H_6 in the presence of an excess of KOH in anhydrous EtOH. The alkylation of [(η^5-Cp)Co(7-$B_{10}H_{10}$P)]$^-$ with RI (R = Me, Et, or n-Pr) gives a high yield of (η^5-Cp)Co(7-$B_{10}H_{10}$PR). A hypothesis concerning their structure was put forward on the basis of ^{11}B and ^1H NMR and ultraviolet spectroscopic data[192].

During the preparation of this review for the press, a while series of communications devoted to the development of theoretical ideas about the structure and nature of the bonds in metal carbaborane complexes as well as new methods of synthesis and new compounds were published. A review[193] discusses the nature of the bonds in metal complexes of carbaboranes, their structure, and nomenclature, as well as general problems of the synthesis of such complexes. It includes tabes with data on known complexes; the methods of synthesis of principal metal carbaborane complexes are described. Another review[194] discusses advances in the chemistry of metal carbaborane complexes during the last ten years. These reviews[193,194] include exhaustive information about studies on the chemistry of metal complexes of carbaboranes published up to 1974 inclusive. The bibliography for 1950–1976, reflecting the results of electrochemical research into transition metal complexes, including cobalt complexes of carbaboranes, is presented in another review[195].

The topology of the bonds in polyhedral boranes, carbaboranes, and metal complexes of carbaboranes is discussed from the standpoint of graph theory in a paper by King and Rouvray[196]. Wade's empirical rule[196,197] is used widely in the study of the principal characteristics of various types of rearrangements in carbaboranes and their metal complexes[198] and in the discussion of the structures of cobalt complexes of carbaboranes[199–203]. The *closo*-complexes 1,8,2,3-(η^5-Cp)$_2$-1-Fe-8-Co-$B_7C_2H_9$ [199] and (η^5-CpCo)$_4B_4H_4$,[200] whose structures have been determined by X-ray diffraction, contain fewer electrons than would be expected from Wade's rule. It is believed[204] that such electron deficiency leads either to partial filling of the *d* orbitals of the transition metal or to the formation of the so-called M–M "extra bond" and the consequent distortion of the geometry of the polyhedron (see, for example, Stanko et al.[199]). The presence of five 12-vertex clusters, containing twenty eight electrons and having both *nido*- and *closo*-structures, also constitutes a deviation from Wade's rule[201,202,205]. The causes of these deviations are also discussed by Nishimura[206].

The structures of the zwitter-ions 5-[(η^5-Cp)Co(η^5-C_5H_4)-2,3-$Me_2B_4C_2H_3$]Co(2,3-$Me_2B_3C_2H_5$) [209] and (η^5-Cp)Co(η^5-C_5H_4)-$Me_4B_8C_4H_8$,[210] the mixed cluster 2,3,10-(η^5-Cp)$_2$-2-Ni-3-Co-B_7CH_8,[211] the cluster (η^5-CpCo)$_2$($Me_4B_6C_4H_6$),[203] the isostructural analogue of one of the isomers of the corresponding unsubstituted complex[205], the pentasubstituted compound 8,1,2,3,7-(η^5-Cp)Co(12-C_2H_5O-1,2,3,7-$Me_4B_7C_4H_6$),[201] the polyhedron (NMe_4)[(η^5-CpCo)$_2B_9CH_{10}$],[209] the three-layer sandwich compound 1,7,2,3-(η^5-CpCo)$_2$[(μ-2,3)-1,3-$C_3H_4B_3C_2H_3$], whose planar bicyclic ligand $(B_3C_5H_7)^{4-}$ is isoelectronic with the pentalenide anion $(C_8H_7)^-$,[210] and the metal *closo*-carbaborane complex 1,2-(η^5-CpCo)$_2B_4H_6$, in which the Co–Co distance amounts to 2.577 Å and is a maximum for compounds of this kind[211], have been determined by X-ray diffraction.

The gas-phase reaction is used widely for the direct synthesis of cobalt complexes of boranes and carbaboranes. 1-(η^5-Cp)CoB_5H_9 and 2-(η^5-Cp)CoB_9H_{13},[212] (η^5-Cp)Co(Me_2-$SnB_4C_2H_4$),[213] 1,7,2,5-(η^5-CpCo)$_2$(2,5-Me_2-$B_5C_2H_5$), and others[214] have been obtained. In the last instance[214] the synthesis was carried out without the preliminary formation of the carbaborane ligand, metallic cobalt or $CpCo(CO)_2$, pentaborane(9), and but-2-yne may be used as the starting materials. $CpCo(CO)_2$ is being used with increasing fequency as the starting material. The reaction is carried out under ultraviolet irradiation[205] or with heating[218]. The isomeric compounds (η^5-Cp)Co($Me_4B_6C_4H_6$) and (η^5-Cp)Co($Me_4B_7C_4H_7$) [205] as well as the isomeric compounds 2-[1,3,5-(2',4'-$B_5C_2H_6$)-1,8,5,6-(η^5-CpCo)$_2B_5C_2H_6$] [218] have been obtained in this way.

The method based on the use of the products of the partial degradation of polyhedral carbaboranes and boranes under the influence of nucleophiles continues to be developed[219]. The π-complex [1,2-(η^5-Cp)CoB_9CH_{10}]$^-$ [220] and new cobalt heteroborane complexes containing arsenic[221,222], antimony[222], selenium, and tellurium[223] have also been obtained by this method. ($Me_2B_4C_2H_4$)$_2FeH_2$ [204] and 2-(η^5-Cp)CoB_4H_8 [224] have been used as starting materials.

The range of applications of the polyhedral expansion reaction has been increased. The reaction has been carried out for $Me_4B_8C_4H_8$ [205] and the nickel borane complex [*nido*-(η^5-Cp)$NiB_{10}H_{12}$]$^-$.[225]

The oxidative coupling reaction, examined previously[98], has been studied in relation to new examples. The synthesis of (η^5-Cp)Co[(R)(Me_4)$B_7C_4H_6$] (R = H [205] or C_2H_5O [204]) has been achieved by the interaction of [($Me_2B_4C_2H_4$)CoH.($Me_2B_3C_2H_3$)]$^-$ [205] or ($Me_2B_4C_2H_4$)$_2FeH_2$ [204] with $CoCl_2$ in the presence of a cyclopentadienylating agent. The complex (η^5-Cp)$CoB_7C_4H_{11}$ and three isomers of the complex (η^5-CpCo)$_2B_6C_4H_{10}$ are formed on treating *closo*-1,2,3-(η^5-Cp)$CoB_4C_2H_6$ or *nido*-1,2,3-(η^5-CpCo)$B_3C_2H_7$ with a KOH solution in ethanol.

The tetramethyl derivative (η^5-CpCo)$_2$($Me_4B_6C_4H_6$), which is a structural analogue of one of the isomers of the complex (η^5-CpCo)$_2B_6C_4H_{10}$, was obtained as the only reaction product under analogous conditions from the corresponding C,C'-dimethyl-substituted cobalt complexes of carbaboranes[205]. The mechanism of the reaction and the causes responsible for it have been discussed[202,205].

The chemistry of the dicarbollylcobalt complex has been enriched by new reactions. When 3,1,2-(η^5-Cp)$CoB_9C_2H_{11}$ reacts with sulphur in benzene in the presence of $AlCl_3$, a mixture of mercapto-isomers 3,1,2-(η^5-Cp)Co(n-HS-$B_9C_2H_{10}$), where n = 8 or 9, is formed. The symmetrical complex gives rise to the S-bridged compound Cs[Co(3,1,2-$B_9C_2H_{10}$)$_2$-8,8'-S] under these conditions. In the absence of sulphur the final reaction product is the complex Cs[Co(3,1,2-$B_9C_2H_{10}$)$_2$-8,8'-(1,2-C_6H_4)] with the phenylene unit in the bridge position[221]. The substitution of the hydrogen at the boron atom in the 8-position, which has enhanced electron density, and the formation of complexes with substituents in the bridge position have been observed also in the reaction of [Co.($B_9C_2H_{11}$)$_2$]$^-$ with $NaNO_2$, RCHO (R = H or Me), SeO_2, or Te in H_2SO_4. Nitrogen-, selenium-, and tellurium-containing complexes are readily alkylated by treatment with Me_2SO_4, forming [Co($B_9C_2H_{10}$)$_2$-8,8'-X], where X = NHMe, NMe_2, Se^+Me, or Te^+Me.[222] The oxidation-reduction properties of "thre-layer" sandwich compounds of the type ($CpCo)_2B_3C_2H_5$ have been investigated by electrochemical methods[228].

Like boranes, cobalt complexes 2-(η^5-Cp)CoB_4H_8 are deprotonated by sodium hydride and interact with acetylene. In the latter case the product is a carbaborane system, in particular 1,2,3-(η^5-Cp)$CoB_5C_2H_7$. The reaction with higher alkynes RC≡CR' gives rise to "addition products" of the type $CpCoB_4H_8.RC_2R'$, which are regarded as intermediates[219]. Ultraviolet irradiation of 2-(η^5-Cp)CoB_4H_8 in the presence of $Fe(CO)_5$ gives rise to the mixed cluster 1,2,3-(η^5-Cp)$_2Co_2$.$(CO)_4FeB_3H_3$.[219]

Liquid chromatography has been used successfully for the separation and identification of cobalt π-complexes of carbaboranes[223].

REFERENCES

1. M.F.Hawthorne, Acc.Chem.Res., **1**, 281 (1968).
2. L.J.Todd, Adv.Organometal.Chem., **8**, 87 (1970).
3. M.F.Hawthorne and G.B.Dunks, Science, **178**, 462 (1972).
4. M.F.Hawthorne, Pure Appl.Chem., **33**, 478 (1973).
5. L.J.Todd, Pure Appl.Chem., **30**, 587 (1972).
6. M.F.Hawthorne, Pure Appl.Chem., **29**, 547 (1972).
7. D.S.Matteson, J.Organometal.Chem., **41**, 13 (1972).
8. R.N.Grimes, Pure Appl.Chem., **39**, 455 (1974).
9. M.F.Hawthorne, J.Organometal.Chem., **100**, 97 (1975).
10. T.E.Paxson, K.P.Gallahan, E.L.Hoel, and M.F.Hawthorne, Proc.I.Japan—USA, 1975, p.1, Organotransition—Met.Chem.
11. T.Onak, Organometal.Chem., **5**, 67 (1976), A Special Periodical Report, A Review of the Literature Published during 1975, The Chemical Society, Burlington House, London.
12. L.I.Zakharkin and V.N.Kalinin, Uspekhi Khim., **43**, 1207 (1974) [Russ.Chem.Rev., No.7 (1974)].
13. M.F.Hawthorne, D.C.Young, and P.A.Wegner, J.Amer.Chem.Soc., **87**, 1818 (1965).

14. M.F.Hawthorne and T.D.Andrews, Chem.Comm., 443 (1965).
15. A.Zalkin, T.E.Hopkins, and D.H.Templeton, Inorg. Chem., 6, 1911 (1967).
16. D.St.Clair, A.Zalkin, and D.H.Templeton, Inorg. Chem., 11, 377 (1972).
17. C.B.Harris, Inorg.Chem., 7, 1517 (1968).
18. I.Pavlik and E.Maxova, "Proceedings of the IIIrd Conference on Coordination Chemistry, Bratislava, 1971", p.247; Chem.Abs., 77, 40 808 (1972).
19. L.L.Lohr, Jr. and W.N.Lipscomb, J.Chem.Phys., 35, 1329 (1961).
20. M.F.Hawthorne, D.C.Young, T.D.Andrews, D.V.Howe, R.L.Pilling, A.D.Pitts, M.Reintjes, L.F.Warren, Jr., and P.A.Wegner, J.Amer.Chem.Soc., 90, 879 (1968).
21. C.J.Jones, W.J.Evans, and M.F.Hawthorne, Chem. Comm., 543 (1973).
22. D.F.Dustin, W.J.Evans, C.J.Jones, R.J.Wiersema, H.Gong, S.Chan, and M.F.Hawthorne, J.Amer.Chem. Soc., 96, 3085 (1974).
23. V.R.Miller and R.N.Grimes, J.Amer.Chem.Soc., 97, 4213 (1975).
24. E.L.Hoel, C.E.Strouse, and M.F.Hawthorne, Inorg. Chem., 13, 1388 (1974).
25. W.J.Evans, C.J.Jones, B.Stibr, R.A.Grey, and M.F.Hawthorne, J.Amer.Chem.Soc., 96, 7405 (1974).
26. A.R.Siedle et al., Inorg.Chem., 13, 2321 (1974).
27. L.E.Vinogradova, L.A.Leites, R.Kh.Bikkineev, V.V.Kobak, and L.I.Zakharkin, Izv.Akad.Nauk, SSSR, Ser.Khim., 2641 (1976).
28. H.Binder et al., Z.anorg.Chem., 433, 26 (1977).
29. R.C.Adler and M.F.Hawthorne, J.Amer.Chem.Soc., 92, 6174 (1970).
30. D.A.T.Young, P.E.Paxson, and M.F.Hawthorne, Inorg.Chem., 10, 786 (1971).
31. R.J.Wiersema and M.F.Hawthorne, J.Amer.Chem.Soc., 96, 761 (1974).
32. D.M.P.Mingos and M.I.Forsyth, J.Chem.Soc., Dalton Trans., 610 (1977).
33. R.E.Williams, Adv.Inorg.Chem.Radiochem., 18, 67 (1976).
34. "Nomenclature of Boron Compounds", Inorg.Chem., 7, 1945 (1968).
35. C.J.Jones, J.N.Francis, and M.F.Hawthorne, J.Amer. Chem.Soc., 95, 7633 (1973).
36. G,D.Mercer, M.Tribo, and F.R.Scholer, Inorg.Chem., 14, 764 (1975).
37. W.J.Evans et al., J.Organometal.Chem., 60, C27 (1973).
38. R.N.Grimes, "Carboranes", Acad.Press, New York–London, 1970.
39. V.T.Aleksanyan and B.V.Lokshin, "Stroenie Molekul i Khimicheskaya Svyaz'" (Molecular Structure and the Chemical Bond), Vol.5, "Kolebatel'nye Spektry π-Kompleksov Perekhodnykh Metallov" (Vibrational Spectra of Transition Metal π-Complexes), Izd.VINITI, Moscow, 1976, p.51.
40. L.A.Leites and L.E.Vinogradova, "Tezisy Dokladov, I-aya Vsesoyuznaya Konferentsiya po Metallorganicheskoi Khimii" (The First All-Union Conference on Organometallic Chemistry. Abstracts of Reports), 1979, p.184.
41. V.R.Miller and R.N.Grimes, Inorg.Chem., 16, 15 (1977).
42. A.R.Siedle, G.M.Bodner, and L.J.Todd, J.Organometal.Chem., 33, 137 (1971).
43. W.J.Evans and M.F.Hawthorne, Chem.Comm., 38 (1974).
44. G.Evrard, J.A.Ricci, and I.Bernal, Chem.Comm., 234 (1974).
45. R.Weiss and R.N.Grimes, J.Amer.Chem.Soc., 99, 1036 (1977).
46. L.I.Zakharkin and R.Kh.Bikkineev, Zhur.Obshch. Khim., 44, 2473 (1974).
47. L.I.Zakharkin and R.Kh.Bikkineev, Izv.Akad.Nauk SSSR, Ser.Khim., 2377 (1974).
48. M.R.Churchill and K.Gold, Inorg.Chem., 10, 1928 (1971).
49. B.G.de Boer, A.Zalkin, and D.H.Templeton, Inorg. Chem., 7, 2288 (1968).
50. K.P.Callaghan, Inorg.Chem., 13, 1393 (1974).
51. R.E.Williams, Progr.Boron.Chem., 2, 37 (1970).
52. W.J.Evans, C.B.Dunks, and M.F.Hawthorne, J.Amer. Chem.Soc., 95, 4565 (1973).
53. K.P.Callahan et al., Inorg.Chem., 13, 2842 (1974).
54. M.R.Churchill and K.Gold, Chem.Comm., 901 (1972).
55. M.R.Churchill and K.Gold, Inorg.Chem., 12, 1157 (1973).
56. K.P.Callahan, C.E.Strouse, A.L.Sims, and M.F.Hawthorne, Inorg.Chem., 13, 1397 (1974).
57. D.St.Clair, A.Zalkin, and D.H.Templeton, Inorg. Chem., 8, 2080 (1969).
58. J.N.Francis and M.F.Hawthorne, Inorg.Chem., 10, 863 (1971).
59. M.R.Churchill and A.H.Reis, J.Amer.Chem.Soc., 92, 4993 (1970).
60. W.M.Maxwell, E.Sinn, and R.N.Grimes, J.Amer.Chem. Soc., 98, 3490 (1976).
61. M.F.Hawthorne and T.A.George, J.Amer.Chem.Soc., 89, 7114 (1967).
62. T.A.George and M.F.Hawthorne, J.Amer.Chem.Soc., 91, 5475 (1969).
63. W.M.Maxwell, V.R.Miller, and R.N.Grimes, Inorg. Chem., 15, 1343 (1976).
64. J.Plesek, B.Stibr, and S.Hermanek, Synt.Inorg.Metal. Org.Chem., 3, 291 (1973).
65. W.I.Evans and M.F.Hawthorne, J.Amer.Chem.Soc., 93, 3063 (1971).
66. V.P.Miller and R.N.Grimes, J.Amer.Chem.Soc., 95, 2830 (1973).
67. W.I.Evans and M.F.Hawthorne, Chem.Comm., 611 (1972).
68. W.J.Evans and M.F.Hawthorne, Chem.Comm., 706 (1973).
69. W.J.Evans and M.F.Hawthorne, Inorg.Chem., 13, 869 (1974).
70. R.N.Grimes et al., Inorg.Chem., 13, 1138 (1974).
71. R.A.Wiesboeck and M.F.Hawthorne, J.Amer.Chem.Soc., 86, 1642 (1964).
72. L.I.Zakharkin and V.N.Kalinin, Izv.Akad.Nauk SSSR, Ser.Khim., 462 (1967).
73. L.I.Zakharkin and A.V.Grebennikov, Izv.Akad.Nauk SSSR, Ser.Khim., 2019 (1966).
74. T.Yoshizaki, M.Shiro, Y.Nakagawa, and H.Watanabe, Inorg.Chem., 8, 698 (1969).
75. L.I.Zakharkin and V.N.Kalinin, Dokl.Akad.Nauk SSSR, 163, 110 (1965).
76. L.I.Zakharkin and V.N.Kalinin, Tetrahedron Letters, 407 (1965).
77. L.I.Zakharkin and V.N.Kalinin, Izv.Akad.Nauk SSSR, Ser.Khim., 579 (1965).
78. M.F.Hawthorne, P.A.Wegner, and R.C.Stafford, Inorg. Chem., 4, 1675 (1965).
79. D.Grafstein, J.Bobenki, J.Dvorak, H.F.Smith, N.N.Schwartz, M.S.Cohen, and M.M.Fein, Inorg. Chem., 2, 1120 (1963).
80. L.I.Zakharkin and V.N.Kalinin, Dokl.Akad.Nauk SSSR, 164, 477 (1965).

81. L.I.Zakharkin and V.N.Kalinin, Zhur.Obshch.Khim., **35**, 1691 (1965).
82. V.I.Stanko and V.A.Brattsev, Zhur.Obshch.Khim., **37**, 515 (1967).
83. V.I.Stanko and V.A.Brattsev, Zhur.Obshch.Khim., **38**, 662 (1968).
84. W.N.Lipscomb, "Boron Hydrides", W.A.Benjamin, New York, 1963.
85. M.F.Hawthorne, D.E.Young, P.M.Garrett, D.A.Owen, S.G.Schwerin, F.N.Tebbe, and P.A.Wegner, J.Amer. Chem.Soc., **90**, 862 (1968).
86. D.V.Howe et al., Inorg.Chem., **10**, 2516 (1971).
87. L.I.Kruglyak, E.S.Petrov, V.N.Kalinin, L.I.Zakharkin, and A.I.Shatenshtein, Izv.Akad.Nauk SSSR, Ser.Khim., 471 (1972).
88. L.I.Kruglyak, E.S.Petrov, V.N.Kalinin, E.G.Rys, L.I.Zakharkin, and A.I.Shatenshtein, Zhur.Obshch. Khim., **42**, 2670 (1972).
89. L.I.Zakharkin, E.I.Kukulina, and L.S.Podvisotskaya, Izv.Akad.Nauk SSSR, Ser.Khim., 1866 (1966).
90. J.S.Roscoe, S.Kongpricha, and S.Papetti, Inorg.Chem., **9**, 1561 (1970).
91. L.F.Warren, Jr. and M.F.Hawthorne, J.Amer.Chem. Soc., **89**, 470 (1967).
92. M.F.Hawthorne and H.W.Ruhle, Inorg.Chem., **8**, 176 (1969).
93. M.F.Hawthorne and P.A.Wegner, J.Amer.Chem.Soc., **90**, 896 (1968).
94. T.E.Paxson, M.K.Kaloustian, G.M.Tom, R.J.Wiersema, and M.F.Hawthorne, J.Amer.Chem.Soc., 94, 4882 (1972).
95. D.S.Matteson and R.E.Grunzinger, Inorg.Chem., **13**, 671 (1974).
96. L.I.Zakharkin, V.N.Kalinin, and E.G.Rys, Zhur. Obshch.Khim., **47**, 841 (1977).
97. W.M.Maxwell, V.R.Miller, and R.N.Grimes, J.Amer. Chem.Soc., **96**, 7116 (1974).
98. W.M.Maxwell, V.R.Miller, and R.N.Grimes, J.Amer. Chem.Soc., **98**, 4818 (1976).
99. W.H.Knoth, Inorg.Chem., **10**, 598 (1971).
100. D.E.Hyatt, J.L.Little, J.T.Moran, F.R.Scholer, and L.J.Todd, J.Amer.Chem.Soc., **89**, 3342 (1967).
101. W.H.Knoth, J.Amer.Chem.Soc., **89**, 3342 (1967).
102. R.R.Reitz, D.F.Dustin, and M.F.Hawthorne, Inorg. Chem., **13**, 1580 (1974).
103. J.Dolansky, K.Base, and B.Stibr, Chem.Ind., 853 (1976).
104. J.L.Little, P.S.Welcker, N.J.Loy, and L.J.Todd, Inorg.Chem., **9**, 63 (1970).
105. L.J.Todd et al., J.Amer.Chem.Soc., **90**, 4489 (1968).
106. L.J.Todd et al., Inorg.Chem., **9**, 2175 (1970).
107. W.R.Hertler, F.Klanberg, and E.L.Muetterties, Inorg. Chem., **6**, 1696 (1967).
108. W.R.Hertler, US P.3 508 885 (1970); Chem.Abs., **73**, 5553 (1970).
109. J.N.Francis and M.F.Hawthorne, J.Amer.Chem.Soc., **90**, 1663 (1968).
110. C.J.Jones and M.F.Hawthorne, Inorg.Chem., **12**, 608 (1973).
111. L.I.Zakharkin, V.V.Kobak, A.I.Kovredov, and R.Kh.Bikkineev, Izv.Akad.Nauk SSSR, Ser.Khim., 921 (1974).
112. D.F.Dustin and M.F.Hawthorne, J.Amer.Chem.Soc., **96**, 3462 (1974).
113. D.F.Dustin, W.Y.Evans, and M.F.Hawthorne, Chem. Comm., 805 (1973).
114. C.G.Salentine, C.E.Strouse, and M.F.Hawthorne, Inorg.Chem., **15**, 1832 (1976).
115. D.C.Beer, V.R.Miller, L.G.Sneddon, R.N.Grimes, M.Mathew, and G.J.Palenik, J.Amer.Chem.Soc., **95**, 3046 (1973).
116. R.Weiss and R.N.Grimes, J.Organometal.Chem., **113**, 29 (1976).
117. C.J.Jones, J.N.Francis, and M.F.Hawthorne, Chem. Comm., 900 (1972).
118. C.J.Jones, J.N.Francis, and M.F.Hawthorne, J.Amer. Chem.Soc., **94**, 8391 (1972).
119. D.A.Young, R.I.Wiersema, M.F.Hawthorne, R.R.Smeath, J.L.Little, A.R.Burke, and L.J.Todd, Chem.Comm., 693 (1970).
120. D.F.Dustin and M.F.Hawthorne, Chem.Comm., 1329 (1972).
121. D.F.Dustin and M.F.Hawthorne, Inorg.Chem., **12**, 1380 (1973).
122. D.Grafstein and J.Dravak, Inorg.Chem., 2, 1128 (1963).
123. G.B.Dunks and M.F.Hawthorne, J.Amer.Chem.Soc., **92**, 7213 (1970).
124. L.I.Zakharkin, V.N.Kalinin, and L.S.Podvisotskaya, Izv.Akad.Nauk SSSR, Ser.Khim., 2310 (1967).
125. G.B.Dunks, M.M.McKown, and M.F.Hawthorne, J.Amer.Chem.Soc., **93**, 2541 (1971).
126. D.F.Dustin, G.B.Dunks, and M.F.Hawthorne, J.Amer.Chem.Soc., **95**. 1109 (1973).
127. M.R.Churchill and B.D.de Boer, Chem.Comm., 1326 (1972).
128. M.R.Churchill and B.G.de Boer, Inorg.Chem., **13**, 1411 (1974).
129. M.R.Churchill and B.G.de Boer, J.Amer.Chem.Soc., **96**, 6310 (1974).
130. L.I.Zakharkin, V.N.Kalinin, and N.P.Levina, Zhur. Obshch.Khim., **44**, 2478 (1974).
131. C.G.Salentine and M.F.Hawthorne, Chem.Comm., 560 (1973).
132. C.G.Salentine and M.F.Hawthorne, J.Amer.Chem.Soc., **97**, 6382 (1975).
133. V.R.Miller, L.G.Sneddon, D.C.Beer, and R.N.Grimes, J.Amer.Chem.Soc., **96**, 3090 (1974).
134. R.Weiss and R.F.Bryan, Acta Cryst., **33**, 589 (1977).
135. W.M.Maxwell and R.N.Grimes, Chem.Comm., 943 (1975).
136. W.J.Evans and M.F.Hawthorne, J.Amer.Chem.Soc., **96**, 301 (1974).
137. T.A.George and M.F.Hawthorne, J.Amer.Chem.Soc., **90**, 1661 (1968).
138. M.K.Kaloustian, R.J.Wiersema, and M.F.Hawthorne, J.Amer.Chem.Soc., **93**, 4912 (1971).
139. M.K.Kaloustian, R.J.Wiersema, and M.F.Hawthorne, J.Amer.Chem.Soc., **94**, 6679 (1972).
140. W.N.Lipscomb, Science, 153, 373 (1966).
141. E.L.Muetterties and W.H.Knoth, "Polyhedral Barenes", Marcel Dekker, New York, 1968.
142. R.N.Grimes, A.Zalkin, and W.T.Robinson, Inorg. Chem., **15**, 2274 (1976).
143. W.T.Robinson and R.N.Grimes, Inorg.Chem., **14**, 3056 (1975).
144. W.E.Geliger and D.E.Smith, Chem.Comm., 8 (1971).
145. A.P.Snyakin, Candidate's Thesis, Institute of Organo-elemental Compounds, USSR Academy of Sciences, Moscow, 1971.
146. L.I.Denisovich and S.P.Gubin, Uspekhi Khim., **46**, 50 (1977) [Russ.Chem.Rev., No.1 (1977)].
147. N.N.Rukhlyada, E.V.Leonova, N.S.Kochetkova, and N.V.Bychkov, "Tezisy Dokladov, I-aya Vsesoyuznaya Konferentsiya po Metallorganicheskoi Khimii" (The First All-Union Conference on Organometallic Chemistry. Abstracts of Reports), 1979, p.200.

148. J.Rais and J.Teply, Radiochem.Radional.Letters Czech., Bratislava, **22**, 119 (1975).
149. L.Matel and R.Cech, Radiochem.Radional.Letters Czech., Bratislava, **28**, 67 (1977).
150. L.Matel, R.Cech, F.Macasek, S.Hermanek, and J.Plesek, Radiochem.Radional.Letters Czech., Bratislava, **29**, 317 (1977).
151. M.Green et al., J.Chem.Soc., Dalton Trans., 179 (1975).
152. E.L.Hoel and M.F.Hawthorne, J.Amer.Chem.Soc., **96**, 4676 (1974).
153. A.N.Nesmeyanov (Editor), "Metody Elementoorganicheskoi Khimii, Kobal't, Nikel', Platinovye Metally" (Methods of Organometallic Chemistry. Cobalt, Nickel, and Platinum Metals), Izd.Nauka, Moscow, 1978, pp.38, 39.
154. L.I.Zakharkin and R.Kh.Bikkineev, Izv.Akad.Nauk SSSR, Ser.Khim., 2128 (1974).
155. L.I.Zakharkin and R.Kh.Bikkineev, Zhur.Obshch. Khim., **45**, 476 (1975).
156. L.I.Zakharkin, A.I.Kovredov, and V.V.Kobak, Zhur. Obshch.Khim., **46**, 1661 (1976).
157. W.N.Lipscomb, "Boron Hydrides", W.A.Bajamin, New York, 1966, p.68.
158. G.B.Dunks and M.F.Hawthorne, Inorg.Chem., **9**, 893 (1970).
159. B.M.Graybill and M.F.Hawthorne, Inorg.Chem., **8**, 1799 (1969).
160. A.N.Nesmeyanov, R.B.Materikova, I.R.Lyatifov, T.Kh.Kurbanov, E.V.Leonova, and N.S.Kochetkova, J.Organometal.Chem., **136**, C55 (1977).
161. T.Totani, H.Nakai, M.Shiro, and T.Nakagana, J.Chem.Soc., Dalton Trans., 1938 (1975).
162. L.I.Zakharkin and R.Kh.Bikkineev, Izv.Akad.Nauk SSSR, Ser.Khim., 1338 (1976).
163. A.N.Nesmeynov (Editor), "Metody Elementoorganicheskoi Khimii, Kobal't, Nikel', Platinovy Metally" (Methods of Organometallic Chemistry. Cobalt, Nickel, and Platinum Metals), Izd.Nauka, Moscow, 1978, p.22.
164. L.I.Zakharkin, I.V.Pisareva, and R.Kh.Bikkineev, Izv.Akad.Nauk SSSR, Ser.Khim., 641 (1977).
165. M.F.Hawthorne, L.F.Warren, K.P.Callahan, and N.F.Travers, J.Amer.Chem.Soc., **93**, 2407 (1971).
166. J.N.Francis and M.F.Hawthorne, Inorg.Chem., **10**, 594 (1971).
167. M.R.Churchill et al., J.Amer.Chem.Soc., **91**, 1222 (1969).
168. J.Plešek, S.Hermanek, and L.Janoušek, Chem.Ind. (London), 108 (1974).
169. J.N.Francis, C.J.Jones, and M.F.Hawthorne, J.Amer. Chem.Soc., **94**, 4878 (1972).
170. R.N.Leyden and M.F.Hawthorne, Inorg.Chem., **14**, 2018 (1975).
171. L.I.Zakharkin, R.Kh.Bikkineev, and N.V.Grandberg, Izv.Akad.Nauk SSSR, Ser.Khim., 1582 (1977).
172. K.Wade, Chem.Brit., 11, 177 (1975).
173. V.R.Miller, R.Weiss, and R.N.Grimes, J.Amer.Chem. Soc., **99**, 5646 (1977).
174. W.Siebert and W.Rothermel, Angew.Chem.Int.Ed., **16**, 333 (1977).
175. W.Siebert and U.Bochmann, Angew.Chem.Int.Ed., **16**, 857 (1977).
176. D.A.Owen and M.F.Hawthorne, J.Amer.Chem.Soc., **92**, 3194 (1970).
177. D.A.Owen and M.F.Hawthorne, J.Amer.Chem.Soc., **93**, 873 (1971).
178. R.A.Love and R.Ban, J.Amer.Chem.Soc., **94**, 8274 (1972).
179. K.P.Callahan and M.F.Hawthorne, J.Amer.Chem.Soc., **95**, 4574 (1973).
180. A.N.Nesmeyanov (Editor), "Metody Elementoorganicheskoi Khimii, Kobal't, Nikel', Platinovye Metally" (Methods of Organometallic Chemistry. Cobalt, Nickel, and Platinum Metals), Izd.Nauka, Moscow, 1978, p.65.
181. L.G.Sneddon and D.Voet, Chem.Comm., 118 (1976).
182. J.R.Pipal and R.N.Grimes, Inorg.Chem., **16**, 3251 (1977).
183. V.R.Miller and R.N.Grimes, J.Amer.Chem.Soc., **95**, 5078 (1973).
184. V.R.Miller and R.N.Grimes, J.Amer.Chem.Soc., **98**, 1600 (1976).
185. J.R.Pipal and R.N.Grimes, Inorg.Chem., **16**, 3255 (1977).
186. L.W.Hall, G.J.Zimmerman, and L.G.Sneddon, Chem. Comm., 45 (1977).
187. N.N.Greenwood and N.F.Trawes, Inorg.Nuclear Chem. Letters, **2**, 169 (1966).
188. F.Klamberg, P.A.Wegner, G.W.Parschall, and E.L.Muetterties, Inorg.Chem., **7**, 2072 (1968).
189. R.L.Smeath, J.L.Little, A.R.Burke, and L.J.Todd, Chem.Comm., 693 (1970).
190. R.L.Smeath and L.J.Todd, Inorg.Chem., 12, 44 (1973).
191. R.A.Clement, US P.3 829 429 (1974); Chem.Abs., **81**, 135 962 (1974).
192. J.L.Little, Inorg.Chem., **15**, 114 (1976).
193. R.N.Grimes, Organometallic Reactions and Syntheses, **6**, 63 (1977).
194. K.P.Callahan and M.F.Hawthorne, Adv.Organometal. Chem., **14**, 145 (1976).
195. D.de Moutauzon et al., Electrochim.Acta, **23**, 1247 (1979).
196. R.B.King and D.H.Rouvray, J.Amer.Chem.Soc., **88**, 7834 (1977).
197. K.Wade, Adv.Inorg.Chem.Radiochim., **18**, 1 (1976).
198. R.W.Rudolph, Acc.Chem.Res., **9**, 446 (1976).
199. V.I.Stanko, V.N.Brattsev, and S.P.Knyazev, Uspekhi Khim., **48**, 241 (1979) [Russ.Chem.Rev., No.2 (1979)].
200. K.P.Callahan et al., Inorg.Chem., 17, 1658 (1978).
201. J.R.Pipal and R.N.Grimes, Inorg.Chem., **18**, 257 (1979).
202. J.R.Pipal and R.N.Grimes, J.Amer.Chem.Soc., **100**, 3083 (1978).
203. J.R.Pipal and R.N.Grimes, Inorg.Chem., **18**, 1936 (1979).
204. W.M.Maxwell, K.-S.Wong, and R.N.Grimes, Inorg.Chem., **16**, 3094 (1977).
205. W.M.Maxwell and R.N.Grimes, Inorg.Chem., **18**, 2174 (1979).
206. E.K.Nishimura, Chem.Comm., 858 (1978).
207. K.-S.Wong et al., J.Amer.Chem.Soc., **100**, 5045 (1978).
208. W.N.Lipscomb, Inorg.Chem., **18**, 901 (1979).
209. J.R.Pipal, W.M.Maxwell, and R.N.Grimes, Inorg.Chem., **17**, 1447 (1978).
210. R.N.Grimes, J.R.Pipal, and E.Sinn, J.Amer.Chem.Soc., **101**, 4172 (1979).
211. G.E.Hardy, K.P.Callahan, and M.Hawthorne, Inorg. Chem., **17**, 1662 (1978).
212. V.Subrtova, Acta Cryst., **33B**, 3843 (1977).
213. J.R.Pipal and R.N.Grimes, Inorg.Chem., **17**, 10 (1978).
214. J.R.Pipal and R.N.Grimes, Inorg.Chem., **18**, 252 (1979).
215. R.Wilczynski and L.G.Sheddon, Inorg.Chem., **18**, 864 (1979).
216. K.-S.Wong and R.N.Grimes, Inorg.Chem., **16**. 2053 (1977).

217. G.J.Zimmerman et al., J.Organometal.Chem., **154**, C29 (1978).
218. J.S.Plotkin and L.G.Sneddon, Inorg.Chem., **18**, 2165 (1976).
219. J.Plesek, B.Stibr, and S.Hermanek, Czech.P.175 600 (1978); Chem.Abs., **91**, 5357 (1979).
220. B.Stibr, K.Base, J.Plesek, S.Hermanek, J.Dalansky, and L.Janousek, Pure Appl.Chem., **49**, 803 (1977).
221. J.L.Little and S.S.Pao, Inorg.Chem., **17**, 584 (1978).
222. J.L.Little, Inorg.Chem., **18**, 1598 (1979).
223. J.L.Little, G.D.Friesen, and L.J.Todd, Inorg.Chem., **16**, 869 (1977).
224. R.Weiss, J.R.Bowser, and R.N.Grimes, Inorg.Chem., **17**, 1522 (1978).
225. R.N.Leyden et al., J.Amer.Chem.Soc., **100**, 3758 (1978).
226. J.Plesek and S.Hermanek, Coll.Czech.Chem.Comm., **43**, 1325 (1978).
227. J.Plesek, S.Hermanek, K.Base, L.J.Todd, and W.F.Wright, Coll.Czech.Chem.Comm., **41**, 3509 (1976).
228. D.E.Brennau and W.E.Geiger, J.Amer.Chem.Soc., **101**, 3399 (1979).
229. Z.Plzak, J.Plesek, and B.Stibr, J.Chromatog., **168**, 280 (1979).

Institute of Organoelemental
Compounds, USSR Academy
of Sciences, Moscow

Translated from *Uspekhi Khimii*, **49**, 327-361 (1980) U.D.C. 541.14,541.65,535.37

Theoretical Foundations of the Classification of Molecules by Luminescence Spectra

V.G.Plotnikov

The relationship between the luminescence spectra and the structure of aromatic molecules is discussed theoretically. Various semi-empirical methods of calculating the electronic states of polyatomic molecules are briefly described. The orbitals involved in the electronic transitions and states and the effect of molecular structure and other factors on the energy of the states are considered. The spin-orbit interaction of molecular states is discussed, and radiative transitions in molecules are examined in relation to the nature of the molecule. Modern views on the nature of the conversion processes are outlined, and the variation of their rate with the type of transition and with the energy spectrum and structure of the molecule is analysed. Molecules are classified into five types according to their luminescence spectra, and a justification of this classification is given.
The bibliography includes 154 references.

CONTENTS

I.	Introduction	172
II.	The adiabatic approximation	173
III.	Types of molecular orbital, electronic transition, and electronic state	174
IV.	Effect of structure on the position of the lower electronically excited states of molecules	176
V.	Spin-orbit interaction in electronic states of molecules	178
VI.	Radiative transitions in aromatic molecules	179
VII.	Non-radiative conversion processes	181
VIII.	Classification of molecules by luminescence spectra	185

I. INTRODUCTION

Many problems in photochemistry, radiation chemistry, the chemistry of organic phosphors and scintillators, chemiluminescence, and photobiology are difficult (or impossible) to solve without a knowledge of the relationship between the luminescence-spectral properties of molecular systems and their structure. This is because of the widespread use of luminescence as a method of investigation in those fields of science, and also because the light emission process (luminescence) is one of the most important paths for the dissociation of electronically excited molecules, and must be included in the overall scheme of possible reaction mechanisms.

The study of the luminescence spectra of molecules as a function of molecular structure is a fundamental aspect of molecular spectroscopy: it is one part of the more general problem of the relationship between properties and structure in molecules, first formulated and investigated by Butlerov. The practical importance of this problem was suddenly magnified by the increasing use of organic molecules (especially aromatic molecules, including dyes) in laser technology[1]. A rational search for compounds offering good generation properties (i.e. efficient phosphors and scintillators) presupposes an understanding of the dependence of the luminescence properties on the structural parameters of the molecules.

In the last 5–10 years important advances have been made towards the solution of this problem as a result of the widespread application of theoretical ideas on the structure of molecules and on the nature of their electronic states to the large number of experimental results stimulated by the discovery of the Shpol'skii effect. The experimental aspects of this work have been discussed[2,3] and reviewed[4], but the theoretical side has not yet been reviewed in detail. This article aims to fill this gap. The discussion will be limited mainly to aromatic and hetero-aromatic molecules (all of which will be termed aromatic in the interest of brevity) in the condensed phase. These are the systems of greatest practical interest, both because of their widespread application in different fields of technology and because of the multiplicity of their luminescence properties. The vast majority of the published work, both experimental and theoretical, relates to molecules of this type.

Our decision to confine the discussion to the condensed phase stems not only from the overwhelmingly greater practical importance of condensed systems. No less relevant is the fact that the fast ($\lesssim 10^{-11}$ s) vibrational relaxation processes which are possible in the condensed phase introduce a considerable simplification of the theoretical treatment, since both radiative and non-radiative processes normally take place from an electronically excited state in vibrational equilibrium. This is not always true in the case of luminescence from vapours at low pressures[5,6], and the theoretical treatment of this case is less well developed than its experimental study[7]. Discussions of molecules in the condensed phase are usually confined to the low-temperature region, where the vibrational energy of the molecules (active vibrations, see Section VII) would be greater than the thermal energy. Under these conditions the problem is simplified still further, because the initial state of the radiative and conversion processes is the zeroth vibrational state of the excited energy level.

Throughout most of the discussion we shall assume that the molecules are photochemically stable, as is the case in practice for most aromatic compounds in rigid solvents[8]. Only in the concluding section will the effect of possible photochemical reactions be considered (briefly). Most of the formulae use a system of atomic units in which the charge and mass of the electron and Planck's constant $\hbar$ are taken to be unity.

II. THE ADIABATIC APPROXIMATION

The Hamiltonian of a molecular system can be expressed as the sum of the electronic kinetic energy operator T_r, the nuclear kinetic energy operator T_R, terms describing the interactions of electrons ($U(r, r')$), nuclei ($U(R, R')$), and electrons and nuclei ($U(r, R)$), and the spin–orbit interaction operator H_{so}:

$$H = T_r + U(r, r') + U(r, R) + T_R + U(R, R') + H_{so}, \quad (1)$$

where r denotes the set of electron coordinates $\{r_i\}$ and R the set of nuclear coordinates $\{R_q\}$. The eigenfunctions of the Hamiltonian (1) cannot be found in the general case, and we must resort to approximate methods.

In molecules which contain no heavy atoms the effect of spin–orbit interaction on the position of the electronic states is not very important. Therefore in the first stage of our discussion we can ignore the operator H_{so}, but we shall allow for it (by using perturbation theory) in the subsequent treatment (see Sections VI and VII). The eigenfunction ($H - H_{so}$) of the Hamiltonian can be chosen to be also the eigenfunction of the operator of the square of the total electronic spin moment of the molecule ($\hat{S}^2$) and of the operator of one of its projections ($\hat{S}_z$). The states described by these wave functions are called pure spin states and can be classified in terms of the quantum numbers S and S_z. In most molecules the ground state is a singlet ($S = 0$, $S_z = 0$). Excited states can be either singlet or triplet ($S = 1$, $S_z = 0, \pm 1$). Under the influence of spin–orbit and spin–spin interaction and of an external magnetic field the triplet state splits into three sublevels corresponding to the three possible values of S_z.

The second approximation, known as the adiabatic or Born–Oppenheimer approximation[9–14], relies on the fact that the mass of the nuclei is several orders of magnitude greater than the mass of the electrons, and therefore the velocity of the electrons is much greater than that of the nuclei. The full wave function of the system in the adiabatic approximation is expressed as the product $\Phi_j(r, R)\Omega_j^n(R)$. The electronic part of the wave function $\Phi_j(r, R)$, which is parametrically dependent on the coordinates of the nuclei, is determined by a wave equation with fixed values of R:

$$[T_r + U(r, r') + U(r, R) + U(R, R') - E_j(R)]\,\Phi_j(r, R) = 0, \quad (2)$$

where $E_j(R)$ is the electronic energy of the system for fixed values of the nuclear coordinates. The subscript j denotes the set of electronic quantum numbers; $E_j(R)$ defines the potential energy surface of the electronic state of the system (energy level). The wave function describing the motion of the nuclei, $\Omega_j^n(R)$, is found from the equation

$$[T_R + E_j(R) + \langle \Phi_j(r, R) | T_R | \Phi_j(r, R) \rangle - W_{jn}]\,\Omega_j^n(R) = 0, \quad (3)$$

where the index n denotes the set of vibrational quantum numbers and W_{jn} is the vibronic energy of the system. The term $\langle \Phi_j(r, R) | T_R | \Phi_j(r, R) \rangle$, in which the angle brackets indicate integration with respect to the coordinates of the electrons, is usually small.

The states described by the wave function $\Phi_j(r, R)\Omega_j^n(R)$ are called adiabatic pure spin states. We shall also use the symbol $|j\{n\}\rangle$ for these states. The methods of evaluating the wave functions $\Phi_j(r, R)$ are described in Section III. The problem of evaluating the wave functions $\Omega_j^n(R)$ reduces to solving the classical problem of small vibrations in a system of particles[11]. The potential surface is determined from the condition of correspondence between calculated and experimental vibration frequencies. The Morse potential is commonly used[12] when allowance for the anharmonicity of the vibrations is needed.

Let us briefly examine the conditions under which the adiabatic approximation is valid†. We shall define the non-adiabaticity operator $\hat{V}$ through its effect on the adiabatic wave functions:

$$\hat{V}(\Phi_j\Omega_j^n) = \Omega_j^n T_R \Phi_j - \sum_q M_q^{-1} \frac{\partial \Phi_j}{\partial R_q} \cdot \frac{\partial \Omega_j^n}{\partial R_q}, \quad (4)$$

where M_q is the mass of the nucleus q, and the operator T_R takes the form

$$T_R = \frac{1}{2} \sum_q M_q^{-1} \frac{\partial^2}{\partial R_q^2}. \quad (5)$$

A detailed analysis[9,10,13] has shown that the adiabatic approximation is valid when the $\langle j\{n\}|\hat{V}|j'\{n'\}\rangle$ matrix elements with $j \neq j'$ are small compared to the difference in energy between the corresponding states. A sufficient condition is low molecular vibration frequencies (as compared to the electronic transition energies[10,13]). Similarly, the approximation in which the operator H_{so} is ignored is valid if the $\langle j\{n\}|H_{so}|j'\{n'\}\rangle$ matrix elements are small in comparison to the energy of the transitions. In molecules which do not contain heavy atoms these matric elements are usually smaller than ~100 cm^{-1} (see Section V). Both conditions are easily met by the lower vibrational levels of the ground state of most molecules. On the other hand in electronically excited states neither of these criteria applies, and as a result we have long-lived after-effects. Nevertheless, for the non-trivial reasons discussed in Section VII, we are forced to use adiabatic pure spin functions in any discussion of the luminescence, photochemical, and other spectral properties of molecules.

The most widely used (and often quite satisfactory) model is the "coarse" adiabatic approximation, which ignores the dependence of Φ_j on the coordinates of the nuclei and assumes equilibrium values of R_0 (for a given electronic state) in the expression for Φ_j.[14] The expressions for the H_{so} and $\hat{V}$ matrix operators become

$$\langle j\{n\}|\hat{V}|j'\{n'\}\rangle = \langle \Omega_j^n | \Omega_{j'}^{n'} \rangle \langle \Phi_j^0 | T_R | \Phi_{j'}^0 \rangle - \sum_q M_q^{-1} \left\langle \Omega_j^n \left| \frac{\partial}{\partial R_q} \right| \Omega_{j'}^{n'} \right\rangle \left\langle \Phi_j^0 \left| \frac{\partial}{\partial R_q} \right| \Phi_{j'}^0 \right\rangle, \quad (6)$$

$$\langle j\{n\}|H_{so}|j'\{n'\}\rangle = \langle \Phi_j^0 | H_{so} | \Phi_{j'}^0 | \rangle \langle \Omega_j^n | \Omega_{j'}^{n'} \rangle; \quad (7)$$

where the differentials with respect to nuclear coordinates, the Φ_j^0 and $\Phi_{j'}^0$ wave functions, and the H_{so} operator are taken for equilibrium geometry. This approximation is also known as the Condon approximation. The Franck–Condon factors $\langle \Omega_j^n | \Omega_{j'}^{n'} \rangle$ do not vanish, in general, for $n \neq n'$. The following formula is also useful for calculating (from Eqn.(2)) the matrix elements of the operator $\hat{V}$:

$$\left\langle \Phi_j \left| \frac{\partial}{\partial R_q} \right| \Phi_{j'} \right\rangle = \left\langle \Phi_j \left| \frac{\partial U(r, R)}{\partial R_q} \right| \Phi_{j'} \right\rangle [E_{j'}(R) - E_j(R)]^{-1}. \quad (8)$$

When allowance for the variation of Φ_j with R is unavoidable (for example, when the matric elements vanish in the Condon approximation) we use the Herzberg–Teller expansion[15] in which the dependence of the electronic wave functions on the nuclear coordinates is allowed for by an expansion with respect to electronic wave functions of the different electronic states (with an equilibrium configuration), using coefficients depending on the deviation (δR_q) of the coordinate R_q from its equilibrium value:

$$\Phi_j(r, R) = \Phi_j^0 + \sum_q \sum_{j' \neq j} a_{j'j}^q \delta R_q \Phi_{j'}^0. \quad (9)$$

†The terminology used in recent publications often fails to distinguish between the adiabatic approximation and the approximation in which the H_{so} operator also is ignored.

Under conditions for which the first-order perturbation theory is applicable the quantity $a^q_{j'j}$ is given by

$$a^q_{j'j} = \left\langle \Phi^0_{j'} \left| \left(\frac{\partial U(r, R)}{\partial R_q} \right)_{R=R_0} \right| \Phi^0_j \right\rangle [E_j(R_0) - E_{j'}(R_0)]. \quad (10)$$

III. TYPES OF MOLECULAR ORBITAL, ELECTRONIC TRANSITION, AND ELECTRONIC STATE

The molecular orbital (MO) method is the most widely used and effective approach to the study of the electronic structure of molecules, but the localised orbital (LO) method is also commonly used to describe the spectroscopic characteristics of molecules. The former method can be used to describe directly the one-electron properties of molecules (e.g. in photo-electron spectroscopy). The latter method often offers a fairly clear interpretation of the nature and properties of electronically excited states of molecules. In their most developed form (allowing for configurational interaction) the two methods give the same results for identical sets of basic functions.

The MO method is discussed extensively in the literature[16-20], and therefore we shall limit our own discussion to a few general remarks. In the simplest case the electronic wave function of the system (Φ_j) is expressed as a Slater determinant, assembled from one-electron spin orbitals in which the spatial part is an expansion with respect to fixed basic functions

$$\psi_i = \sum_\nu \chi_\nu c_{\nu i}. \quad (11)$$

In the case of a singlet ground state the equations for the coefficients $c_{\nu i}$ and for the orbital energies ε_i have the form[16]

$$\sum_{\nu'} (F_{\nu\nu'} - \varepsilon_i S_{\nu\nu'}) c_{\nu' i} = 0, \quad (12)$$

where $F_{\nu\nu'}$ are the matrix elements of the Hartree–Fock operator F, and $S_{\nu\nu'} = \langle \chi_\nu | \chi_{\nu'} \rangle$ are the overlap integrals of the basic function. The system (12) is solved by an iterative method.

In calculations for complex polyatomic systems the functions χ_ν are usually represented by Slater atomic orbitals, which for the atoms of the first two periods can be written

$$\begin{gathered} 1s = (\xi^3/\pi)^{1/2} e^{-\xi r}, \quad 2s = (\xi^5/3\pi)^{1/2} r e^{-\xi r}, \\ 2p_x = (\xi^5/\pi)^{1/2} e^{-\xi r} x, \quad 2p_y = (\xi^5/\pi)^{1/2} e^{-\xi r} y, \\ 2p_z = (\xi^5/\pi)^{1/2} e^{-\xi r} z, \end{gathered} \quad (13)$$

where ξ are the Slater parameters[9]. The functions (13) are defined in a system of Cartesian coordinates with its origin at the nucleus of the appropriate atom.

In planar molecules (which include most aromatic and hetero-aromatic molecules) we can distinguish two types of molecular orbital: π and σ. If the z axis of the coordinate system is chosen at right angles to the plane of the molecule the π orbitals will contain only p_z functions in their expansion, whereas the σ orbitals will contain (in general) p_x, p_y, and s atomic functions.

Semi-empirical methods of studying π-electron systems rely on the principle of zero differential overlap[17-20]. The expressions for the $F_{\nu\nu'}$ matrix elements in this approximation (the Pariser–Parr–Pople or PPP approximation) are

$$\begin{gathered} F_{\nu\nu} = H_{\nu\nu} + N_\nu \gamma_{\nu\nu} - \frac{1}{2} p_{\nu\nu} \gamma_{\nu\nu} + \sum_{\nu'} (p_{\nu'\nu'} - N_{\nu'}) \gamma_{\nu\nu'}, \\ F_{\nu\nu'} = H_{\nu\nu'} - \frac{1}{2} p_{\nu\nu'} \gamma_{\nu\nu'}. \end{gathered} \quad (14)$$

In these expressions $H_{\nu\nu} = -I_\nu$ if the ν atom contributes one electron to the π system ($N_\nu = 1$), and $H_{\nu\nu} = -I_\nu - \gamma_{\nu\nu}$ if $N_\nu = 2$; I_ν is the ionisation potential of the p electrons of the ν atom; $\gamma_{\nu\nu}$ and $\gamma_{\nu\nu'}$ are the one-centre and the two-centre Coulomb integrals of the electronic interaction respectively; $p_{\nu\nu}$ is the electron density on the ν atom; $p_{\nu\nu'}$ is the bond order of the ν and ν' atoms; $H_{\nu\nu'} = \beta_{\nu\nu'}$ is the resonance integral. The integrals $\gamma_{\nu\nu}$, $\gamma_{\nu\nu'}$, and $\beta_{\nu\nu'}$ are determined empirically[17-20]. In spite of the large number of different ways of defining the quantities $\gamma_{\nu\nu}$, $\gamma_{\nu\nu'}$, and $\beta_{\nu\nu'}$ most of the results discussed below are independent of the method of parametrisation. Of course, in studies of specific classes of molecules the integrals must be defined uniquely#.

Various semi-empirical methods of calculating the electronic structure of molecules in the valence approximation have been proposed. In molecules containing hetero-atoms whose valence is lower than the number of electrons in the valence shell we can distinguish some σ orbitals for which the coefficients of the expansion are large only on the hetero-atom or on several equivalent hetero-atoms in the molecule. These orbitals (whose energy is greater than ~−10 eV) are doubly occupied in the electronic ground state and correspond to the antibonding orbitals of the LO method (n orbitals). Assuming full localisation of the n orbitals on the hetero-atom (as in the LO method, see below), the energy ε_n for these orbitals is determined only by the diagonal matrix element $\langle n|F|n\rangle$, where $|n\rangle$ denotes the atomic wave functions of the n electrons. If the number of π electrons of a hetero-atom with n electrons is one, the energy ε_n is given by the expression[21-23]

$$\varepsilon_n = -I_n - \sum_\nu (p_{\nu\nu} - N_\nu) \gamma_{\nu n} - \frac{1}{2} p^\pi_n \varkappa, \quad (15)$$

where I_n is the ionisation potential of the unshared pair of the hetero-atom in the valence state, $\gamma_{\nu n}$ are the integrals of the Coulomb interaction of the n electrons with the $p\pi$ electrons of the ν atom, p^π_n is the density of π electrons on the hetero-atom with n electrons, and $\varkappa$ is the one-centre exchange interaction integral of the n and $p\pi$ electrons.

The parameters which appear in Eqn.(15) can be evaluated semi-empirically[20-24]. In carbonyl, nitro, and thiocarbonyl compounds the n electrons of the O (or S) atoms are described by a p atomic orbital whose axis of symmetry is perpendicular to the bond between the carbon atom and the hetero-atom. In aza-heterocyclic compounds the wave function of the n orbitals takes the form of an sp^2 hybrid orbital. In compounds containing several equivalent pairs of n electrons (for example, in nitro compounds) the wave function of the n electrons should be expressed, strictly speaking, as a linear combination of the orbitals of the individual atoms even in the localised model: this leads to some change in the energy values and to splitting of the energy levels of the excited states[24]. This splitting is usually small, but it can be important in the interpretation of the luminescence spectra of molecules[4].

Another method frequently used for qualitative conclusions at present is the Hückel method, in which the parameters are the matrix elements of the Hartree–Fock operator $F_{\nu\nu} = \alpha_\nu$ and $F_{\nu\nu'} = \beta_{\nu\nu'}$.[18,20]

The π and σ orbitals can be bonding or antibonding: in the latter case they are denoted as π^* and σ^*. In the electronic ground state the bonding orbitals and the n orbitals are doubly occupied by electrons (see Fig.1). Knowing ε_i and $c_{\nu i}$ we can calculate the energy of the ground state

---

#Typical values are $\gamma_{\nu\nu} \cong 10$ eV, $\gamma_{\nu\nu'} \leqslant 5$–$7$ eV, $\beta_{\nu\nu} \leqslant 2$ eV, and $\varkappa \cong 1$ eV (see also formula (15)).[17-20,23,24]

(Φ_0) by the formula

$$E_0 = 2\sum_i \varepsilon_i - \sum_{i,i'} (2J_{ii'} - A_{ii'}), \qquad (16)$$

where the summation extends only over the occupied orbitals, $J_{ii'}$ is the Coulomb interaction integral, and $A_{ii'}$ is the exchange interaction integral of the electrons on the i and i' MO.

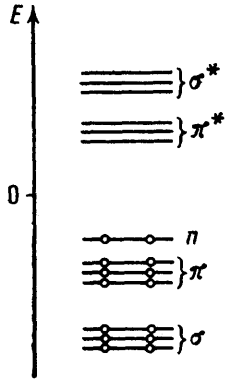


Figure 1. Relative position of one-electron levels in molecules.

In complex molecules the wave functions of the excited states and their energies are usually defined as follows. Using π^* and σ^* virtual orbitals we construct the $|i \to k>$ excited configurations, corresponding to the transition of an electron from the i orbital (filled in the ground state) to the vacant k orbital. These configurations can be singlet (S) or triplet (T), and their energies are given by the formulae

$$^S E_{ik} = \varepsilon_k - \varepsilon_i - J_{ik} + 2A_{ik}, \qquad (17)$$

$$^T E_{ik} = \varepsilon_k - \varepsilon_i - J_{ik}, \qquad (18)$$

where the integrals J_{ik} and A_{ik} have the same significance as in Eqn.(16). The wave function of the excited state is assembled as a superposition of excited configurations with coefficients given by the variational principle. We note that since $A_{ik} > 0$ the energies of the triplet configurations (and of the triplet states) are lower than the energies of the corresponding singlets. The parameters used in the calculation of $F_{\nu\nu'}$ are also used to evaluate the integrals J_{ik} and A_{ik}. In the Hückel method the energy of a transition is equal to the difference between the corresponding orbital energies§.

Thus, the following types of electronic transition are possible in aromatic molecules: $\pi \to \pi^*$, $n \to \pi^*$, $\sigma \to \sigma^*$, $n \to \sigma^*$, $\pi \to \sigma^*$, and $\sigma \to \pi^*$, as well as the following electronic states: $S_{\pi\pi^*}$, $T_{\pi\pi^*}$, $S_{n\pi^*}$, $T_{n\pi^*}$, $S_{\pi\sigma^*}$, $T_{\pi\sigma^*}$, $S_{\sigma\sigma^*}$, $T_{\sigma\sigma^*}$, etc. We should remember that these designations apply only in the absence of quasi-degeneracy of the states.

The designations of the $\pi\pi^*$ states are unnecessarily general, because they contain no detailed information on the nature of the electronic transition. Yet it is experimentally well established[4,25-27] that the luminescence spectra of π-electron molecules are strongly influenced by the presence of electron-donor (OH, NH_2, OCH_3, Hal, etc.) or electron-acceptor (BH_2) substituents. Hence we must distinguish different types of $\pi\pi^*$ state while retaining as far as possible the generality of the designation. This is most conveniently (and most clearly) done in the language of the LO method[28].

Let us examine the most characteristic features of the LO method by considering aromatic molecules containing electron-donor substituents. In addition to the σ (and n) electrons the hetero-atoms of the donor substituents (O, N, Hal) have an unshared pair of electrons which can take part in π-conjugation (unlike the n-electrons). The orbitals of these electrons are conventionally designated by the index l.[25]

In the zeroth approximation we can ignore the interaction of the electrons in the aromatic part of the molecule with the l-electrons of the substituent. The configuration which contributes most to the ground state is obtained from the doubly occupied π orbitals and the atomic l orbital. In addition to this configuration we can construct other configurations corresponding to the excitation of π electrons and configurations with an electronic transition from an l orbital to a π^* orbital. The latter configurations (involving charge transfer) can be designated $l\pi^*$ (or la_π configurations in Kasha's nomenclature[25]). These make some contribution to the wave function of the ground state. The wave functions of the excited states are constructed by superimposing $\pi\pi^*$ and $l\pi^*$ configurations. In molecules containing relatively few π-electrons these configurations have comparable weight[29]. Electronically excited states in molecules with l-electrons have therefore been designated[29] as $\pi l, \pi^*$. The only difference between the $\pi l, \pi^*$ states of planar molecules and $\pi\pi^*$ states is a substantial redistribution of the electron density during the transition from the S_0 to the $\pi l, \pi^*$ state. Nevertheless the difference in the corresponding luminescence spectra is very marked (see below). The designation is widely used at present, though it is somewhat artificial, since as the number of π-electrons increases the contribution of $l\pi^*$ configurations to the excited states decreases and the $\pi l, \pi^*$ states are continuously transformed into $\pi\pi^*$ states[29].

The situation is very similar in the case of molecules containing atoms (or electron-acceptor groups) with low-lying empty atomic orbitals (ν orbitals). The charge-transfer configurations are now those in which an electron has been transferred from a π orbital to a ν orbital: $\pi\nu$ configurations, which can interact with the $\pi\pi^*$ configurations of the aromatic part of the molecule. Therefore we have suggested[30] the designation $\pi,\nu\pi^*$ for the $\pi\pi^*$ excited states in the special case of boron-aromatic molecules. This designation has not yet been extended to include compounds with electron-acceptor groups (H–C=O, NO_2, etc.), in which the vacant π^* orbitals of the groups act as ν orbitals. We therefore retain the conventional designation $\pi\pi^*$ of these states. In molecules containing l and ν orbitals the excited states can, of course, be termed $\pi l, \nu\pi^*$. In the case of molecules with n-electrons and ν-orbitals we can use the designation $n,\nu\pi^*$ for the $n\pi^*$ states. We should stress that the LO method is often applied to aromatic molecules which do not contain l and ν orbitals, but consist of weakly bound fragments. In this case the π and π^* orbitals of the fragments play the role of localised orbitals.

As stated above, the concept of n-electrons localised on a hetero-atom is more characteristic of the LO than of the MO method. Indeed, calculations by the MO method show some delocalisation (often substantial) of the n-electrons on the σ-orbitals[31-34]. Experimental data[35], mainly on vibronic spectra (see Section VI), indicate a large degree of localisa-

§ The exchange interaction A_{ik} of the electrons should not be confused with the exchange interaction of the Heitler–London theory, which in most cases (in the S-state) leads to bonding and therefore has a negative sign.

tion of n-electrons and $n \rightarrow \pi^*$ transitions. The slight inconsistency between MO results and experiment can be avoided by allowing for the interaction of the $\sigma\pi^*$ configurations, which leads to marked localisation of the excitation. It follows that in order to calculate the energy of $n\pi^*$ states allowing for the interaction of the $n\pi^*$ configurations but not of the $\sigma\pi^*$ configurations we must use a localised model of the n-electrons with partial allowance for electron correlations.

Only very brief mention of non-planar molecules can be made here. If the deviation from planarity is small, and the energies of the π orbitals are significantly different from those of the σ orbitals, the unavoidable mixing of the π and σ orbitals is also not very great[36]. This mixing has little effect on the position of the lower electronically excited states of the molecules, and therefore on the probability of singlet–singlet optical transitions. However one of the parameters of the electronic structure of molecules is very sensitive to deviations from planarity: the spin–orbital interaction (see Section V). We must therefore allow for this effect when considering $S-T$ conversion and the properties of triplet states. Throughout this paper the lower excited states of this type of molecule will be interpreted as $\pi\pi^*$, πl, π^*, etc.

IV. EFFECT OF STRUCTURE ON THE POSITION OF THE LOWER ELECTRONICALLY EXCITED STATES IN MOLECULES

Calculations of the energies of $\pi\pi^*$ states are described in many recent publications[17,18,20–24,37–41]. In spite of the variety of the methods used, two important conclusions can be drawn from these measurements. 1) The energy of the $\pi\pi^*$ states decreases as the length of the chain of conjugated bonds in the molecule increases, the magnitude of this effect increasing with the conjugation energy. 2) The difference in energy between the lower $S_{\pi\pi^*}$ and the lower $T_{\pi\pi^*}$ states is relatively high ($\geq$1 eV or 10^4 cm^{-1}, see below)[21–24,29,37–41]. The first of these conclusions can be obtained by the simple Hückel method. Thus, for a polyene chain containing $N\pi$-electrons (where N is even) the energy of the long-wave transition (between the $(N/2)$ and $(N/2)+1$ orbitals) is given by the expression[28]

$$E_{\pi\pi^*} = 4|\beta| \sin \frac{\pi}{2(N+1)}, \qquad (19)$$

where β is the resonance integral. We can see from this equation that the energy of the transition decreases as N increases, and vanishes in the limit of $N \rightarrow \infty$. However formula (19) is not applicable at high values of N, since experimental values of $E_{\pi\pi^*}$ tend towards a finite limit. It has been shown[42] that allowance for electron correlation makes the asymptotic value of $E_{\pi\pi^*}$ finite at high values of N. The energies of $\pi\pi^*$ states in aromatic molecules span the range 5–1 eV. The general rules describing the change in the energy of $\pi\pi^*$ states with the size and the topology of the conjugated bond system in aromatic hydrocarbons are discussed in Refs.4 and 41.

The second conclusion, which is fully consistent with experiment, stems from the presence of large (~10 eV) $\gamma_{\nu\nu}$ one-centre Coulomb integrals in the expression for the exchange integral A_{ik} of Eqn.(17): the coefficients in front of $\gamma_{\nu\nu}$ are not small, since the π and π^* orbitals are not spatially separated.

The energy of the $n\pi^*$ states depends on several characteristics of the molecules, the most important of which are the nature of the atom with n-electrons, the length and topology of the chain of conjugated bonds, and the presence of electron-donor substituents (l-orbitals) in the system.

According to formula (15) the energy of the $n\pi^*$ states decreases as the ionisation potential of the atom with n-electrons decreases. It follows, for example, that the energy of the $n\pi^*$ states should decrease on going from the carbonyl to the analogous thiocarbonyl compounds. This conclusion is confirmed by the experimental $S_{\pi\pi^*}$ energies[4] of the $S_{\pi\pi^*}$ states for benzophenone (~3.3 eV) and thiobenzophenone (1.8 eV) molecules.

Let us discuss the dependence of the energy of the $n\pi^*$ states on the length of the conjugated chain. The simplest treatment, based on the Hückel method, leads to the conclusion that the energy of the $n\pi^*$ states should decrease with increase in the length of the chain of conjugated bonds. Thus, if we assume that the energy of the n-orbital ε_n is independent of the length of the conjugated chain (a valid assumption, since the ionisation potential for the n-electrons is only weakly affected by the number of π-electrons[43]) we can express the energy of the $n \rightarrow \pi^*$ transition as $E_{n\pi^*} = \varepsilon_{\pi^*} - \varepsilon_n$, where ε_{π^*} is the energy of the lower vacant π-orbital. For a polyene molecule with a substituent containing n-electrons (e.g. O=CH–(CH=CH)$_{(N/2)-1}$–H) we have $\varepsilon_{\pi^*} = \alpha + 2\beta \cos[j\pi/(N+1)]$ with $j = (N/2)+1$ if we ignore the effect of the hetero-atom on the π-system[28]. Therefore[44]

$$E_{n\pi^*} = 2\beta \cos \frac{(N+2)\pi}{2(N+1)} + \alpha - \varepsilon_n = \Delta I_n + 2|\beta| \sin \frac{\pi}{2(N+1)}, \qquad (20)$$

where ΔI_n is a parameter of the same order of magnitude as the difference in ionisation potential between the p-electrons of the C atom and the n-electrons. It follows from (19) and (20) that the energy of the $n\pi^*$ states increases more slowly than the energy of the $\pi\pi^*$ states (by a factor of two, on average) when N increases. Since for small N the energy of the $n\pi^*$ states is lower than that of the $\pi\pi^*$ states[4,41] the levels should become inverted as N increases. This result[44] was one of the basic propositions used to construct a systematic classification of the molecules.

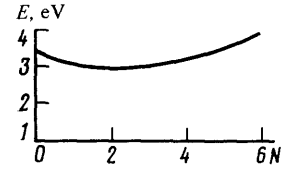


Figure 2. Energy of the $S_{n\pi^*}$ states of H–(CH=CH)$_N$–HC=O molecules as a function of N.

A stricter analysis[23], allowing for electron interaction and configurational interaction, confirmed this conclusion but revealed additional complications. It is clear from formulae (17) and (18) that the energy of the transition is determined by two terms, since the quantity A_{ik} is small for $n\pi^*$ states (see below). The first term, $\varepsilon_{\pi^*} - \varepsilon_n$, varies with N as described by formula (20). The Coulomb interaction integral $J_{n\pi^*}$ also decreases as N increases, since the π-electrons are becoming more delocalised. These two terms appear in the expressions with different signs, and therefore different variants of the change in the $n \rightarrow \pi^*$ transition energy with N are possible: the energy can decrease, remain unchanged, or increase as N increases. All these possibilities are realised in the polyene ketone molecules (Fig.2) with different values of N. The conclusion that the $n\pi^*$ and $\pi\pi^*$ states can become inverted as N increases remains valid, but the value of N for which inversion takes place is defined more exactly.

The singlet–triplet splitting of the $n\pi^*$ states is much smaller than the splitting of the $\pi\pi^*$ states. This is because the expression for the $A_{n\pi^*}$ exchange integral contains only the κ exchange integrals, the largest of which (one-centre integral) is ~1 eV. Furthermore the spatial separation of the n- and π-electrons makes $A_{n\pi^*}$ smaller than $A_{\pi\pi^*}$. Calculations[22–24,45–52], supported by experiment[4,41], give values between 0.2 and 0.5 eV for the $S-T$ splitting of the $n\pi^*$ states.

Calculated values of the energies of the $S_{\pi\pi^*}$, $T_{\pi\pi^*}$, $S_{n\pi^*}$, and $T_{n\pi^*}$ states for $H-(CH=CH)_N-CH=O$ molecules[23] are shown in Fig.3. We can distinguish five different variants (or types) of relative position of the electronic states. Similar results have been obtained for aromatic ketones (Fig.4), and also (both theoretically[23,24,52] and experimentally[2–4]) for aza-aromatic and nitro compounds, quinones, and thioketones. All these results indicate the existence of five different types of relative position of $n\pi^*$ and $\pi\pi^*$ S and T state. Classification of molecules into five types according to the relative position of these energy states was suggested for the first time[53] in 1966.

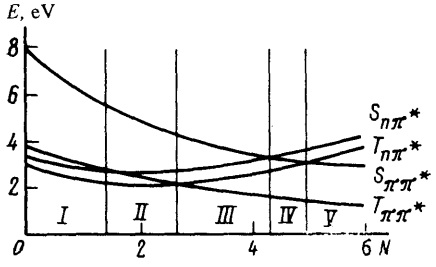


Figure 3. Five types of relative position of the electronic states of $H-(CH=CH)_N-HC=O$ molecules.

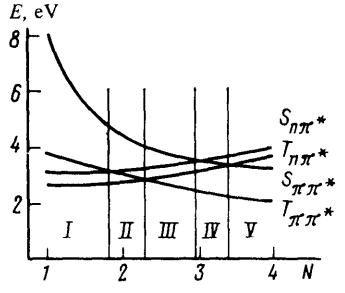


Figure 4. Relative position of the electronic states of $Ph-(CH=CH)_N-HCO$ molecules.

The change in relative position of the $n\pi^*$ and $\pi\pi^*$ states caused by electron-donor substituents is due to the change in energy of both the $n\pi^*$ and $\pi\pi^*$ states attending the transformation of the latter into $\pi l, \pi^*$ states. Many theoretical studies of the position of the $\pi l, \pi^*$ states with respect to the $\pi\pi^*$ states of the unsubstituted hydrocarbons have been published[24,28,29,52,54]: the conclusion in every case is that the introduction of l-orbitals into a system of π-conjugated bonds decreases the energy of the lower $\pi\pi^*$ (or, more accurately, $\pi l, \pi^*$) states. This effect is most marked when the ionisation potential of the l-electrons is low and the chain of conjugated bonds is short[29,52]. The influence of the substituent decreases as the length of the conjugated chain of the hydrocarbon part of the molecule increases. This is a consequence of the lack of a sharp boundary between $\pi\pi^*$ and $\pi l, \pi^*$ states (in contrast to the $\pi\pi^*$ and $n\pi^*$ states).

An important spectroscopic property of the $\pi l, \pi^*$ states is their relatively low $S-T$ interval (0.7–0.8 eV [25–29]), which is lower than that of the $\pi\pi^*$ states of aromatic hydrocarbons though it is greater than that of $n\pi^*$ states. This lowering is due to the contribution of $l\pi^*$ configurations to the wave functions of the excited states and to the spatial separation of the l and π orbitals, which lowers the value of A_{ik} in Eqn.(17).[29,54,55] All these statements apply also to the $\pi, \nu\pi^*$ states[30].

The introduction of electron-donor groups into the molecule increases the energy of the $n\pi^*$ states. The simplest explanation of this effect[46,56] postulates an increase in the energy level of the π^* orbital on introducing l-orbitals into a π-conjugation system. Calculations by the PPP method[24] indicate a substantial contribution to the increase in energy of the $n\pi^*$ states from the change in Coulomb interaction of the electrons. The electronic states of the nitrobenzene molecule and its amino derivatives, calculated[24] by that method, are shown in Fig.5: it is clear that the introduction of l-electrons does indeed raise the energy of the $n\pi^*$ states, the magnitude of the effect depending on the position of the substituent. Many examples of the effect of electron-donor substituents on the relative position of the $n\pi^*$ and $\pi\pi^*$ (or $\pi l, \pi^*$) states are given in Ref.4. Substituents with ν-orbitals should lower the energy of the $n\pi^*$ states[52], but this effect has not been adequately studied.

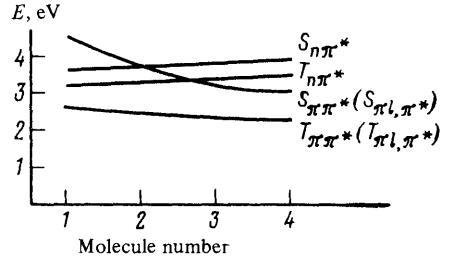


Figure 5. Electronic states of the following molecules: 1) nitrobenzene, 2) *p*-nitroaniline, 3) *m*-nitroaniline, 4) *o*-nitroaniline.

Another factor which influences the relative position of the $n\pi^*$ and $\pi\pi^*$ states is the hydrogen bond, or the formation of complexes with protonic solvents (in the limit, the protonation of the molecule). Hydrogen bond formation (or protonation) leads to bonding of the n-electrons, increases I_n in Eqn.(15), and hence causes a sharp increase in the energy of the $n\pi^*$ states, which can invert the relative position of the levels corresponding to $\pi\pi^*$ and $n\pi^*$ states[57,58].

In conclusion we shall summarise the properties of $n\pi^*$ and $\pi\pi^*$ states which can be used to distinguish these states experimentally. The energy of the $\pi\pi^*$ states decreases steeply as the length of the conjugation chain increases. At the same time the energy of the $n\pi^*$ states can decrease (though less markedly), it can remain unchanged, or it can even increase. The $S-T$ splitting of the $\pi\pi^*$ states is $\geq$1 eV, and substantially greater than the $S-T$ splitting of the $n\pi^*$ states (~0.2–0.5 eV). The $S-T$ splitting of the $\pi l, \pi^*$ (or $\pi\nu, \pi^*$) states lies between these two extremes. The introduction of l-electrons into the molecule produces a large increase in the energy of the $n\pi^*$ states and a decrease

in the energy of the $\pi\pi^*$ states (accompanied by their transformation into $\pi l, \pi^*$ states). Hydrogen bond formation (or protonation) produces a large increase in the energy of the $n\pi^*$ states and can lead to inversion of the levels. The most fundamental of these results is the conclusion that five types of relative position of the S, T, $n\pi^*$, and $\pi\pi^*$ states are possible. The factors listed above determine which of these five types is realised in practice.

V. SPIN–ORBIT INTERACTION IN ELECTRONIC STATES OF MOLECULES

The spin–orbit interaction (spin–orbit bond) of electronic states is characterised by the matrix element $\langle i|H_{so}|f\rangle$, where $|i\rangle$ and $|f\rangle$ are electronic wave functions of states of different multiplicity. The spin–orbit interaction operator is written[59]

$$H_{so}=\frac{1}{2c^2}\sum_q\sum_i\frac{Z_q}{r_{qi}^3}(\hat{l}_{iq}\cdot\hat{S}_i), \tag{21}$$

where c is the velocity of light, Z_q is the effective charge of the nucleus q, r_q is the distance between this nucleus and the electron i, and $\hat{l}_{iq}$ and $\hat{S}_i$ are the operators of the orbital and spin moment of the electrons. The brackets in Eqn.(21) contain the scalar product of the vector operators $\hat{l}_{iq}$ and $\hat{S}_i$. According to this approximation (whose justification is discussed in Ref.60) the H_{so} operator is a one-electron operator. Hence the matrix elements of the configurations included in $|i\rangle$ and $|f\rangle$, which differ only by one spin orbital, are non-zero[61]. This is one of the selection rules which the matrix elements of the H_{so} operator must satisfy: it implies, for example, that the $\pi\pi^*$ states are not bound to $\sigma\sigma^*$ states by spin–orbit interaction, though $\pi\pi^*$ states may be bound to $n\pi^*$ states.

Allowing for the effect of the spin moment projection operators on the spin functions[62] and considering the interaction of a singlet S_{ik} excited configuration (transition of an electron from the i-th orbital of the ground state configuration to the k-th vacant orbital) and of the three triplet configurations $T_{ik'}^0$, $T_{ik'}^{+1}$, and $T_{ik'}^{-1}$ (with projections of the spin moment on the z axis of 0 and ±1 respectively) we can write, after integration of the spin variables[63,64],

$$\begin{aligned}
\langle S_{ik}|H_{so}|T_{ik'}^0\rangle &= -\langle k|H_{so}^z|k'\rangle,\\
\langle S_{ik}|H_{so}|T_{ik'}^{+1}\rangle &= \frac{1}{\sqrt{2}}\langle k|H_{so}^x|k'\rangle+\frac{i}{\sqrt{2}}\langle k|H_{so}^y|k'\rangle,\\
\langle S_{ik}|H_{so}|T_{ik'}^{-1}\rangle &= -\frac{1}{\sqrt{2}}\langle k|H_{so}^x|k'\rangle+\frac{i}{\sqrt{2}}\langle k|H_{so}^y|k'\rangle,
\end{aligned} \tag{22}$$

where, for example,

$$H_{so}^z=\frac{1}{4c^2}\sum_q\frac{Z_q}{r_{iq}^3}\hat{l}_{iqz},$$

and $\hat{l}_{iqz}$ is the operator of the projection of the orbital moment on the z axis. Integration of Eqn.(22) is carried out with respect to the coordinates of one electron.

Similar formulae can be written for the matrix elements in the case of the integration of S_{ik} configurations with T_{jk} configurations, or of the interaction of ground state configurations with triplet configurations. If the multi-configuration approximation is used for the wave functions the expression for $\langle i|H_{so}|f\rangle$ contains a sum of matrix elements in the form of (22) with coefficients which define the contribution of each configuration to $|i\rangle$ and $|f\rangle$.

If the $|k\rangle$ and $|k'\rangle$ molecular orbitals are in LCAO form the matrix elements of (22) are evaluated by finding the effect of the $\hat{l}_x$, $\hat{l}_y$, and $\hat{l}_z$ operators on the atomic orbitals and calculating the one-, two-, and three-centre integrals for electron–nucleus interaction. We note that the one-centre integrals (when not identically equal to zero) are usually greater in absolute value than the two-centre integrals, and the latter are usually greater than the three-centre integrals.

In many important cases the coordinate system can be defined so that one of the matrix elements in (22) is non-zero: for example, the matrix element of the H_{so}^z operator. The effect of the $\hat{l}_x$, $\hat{l}_y$, and $\hat{l}_z$ operators on the p-functions is easily found from the explicit form of these operators[13] and of the atomic orbitals (Eqn.(13)):

$$\hat{l}_z p_z=0,\ \hat{l}_z p_x=ip_y,\ \hat{l}_z p_y=-ip_x. \tag{23}$$

In these expressions the $\hat{l}_z$ operator and the p-functions are given for the same centre. The action of the $\hat{l}_x$, $\hat{l}_y$, and $\hat{l}_z$ operators on the s-functions is to make these functions vanish, since they are eigenfunctions of the $\hat{l}_x$, $\hat{l}_y$, $\hat{l}_z$ operators with eigenvalues of zero. If the operators and the functions are given for different centres appropriate formulae can be obtained[64].

We shall now turn to specific cases. For the interaction of the $S_{\pi\pi^*}$ and $T_{\pi\pi^*}$ states of planar molecules the $\langle\pi_k^*|H_{so}^z|\pi_k^*\rangle$ matrix element (the only non-zero one if the z axis is perpendicular to the plane of the molecule) is expressed in terms of one-, two-, and three-centre integrals containing only p_z atomic functions (or $2p_z$ in the case of aromatic hydrocarbons). One-centre integrals are identically equal to zero as a consequence of the first of formulae (23). The two-centre integrals are also zero[59,64]. In this case only the three-centre integrals are finite[59], and even these are small in absolute value because the overlap of the $2p_z$-functions of the different atoms is not very marked and the interaction energy falls off very rapidly ($\propto r^{-3}$) with increasing interatomic distance. Calculations allowing for the terms of the spin–orbit interaction operator not included in (21) give ~0.3 cm^{-1} for the spin–orbit bond energy of the $\pi\pi^*$ states[65]. The matrix elements of the spin–orbit interaction of the $n\pi^*$ states also have approximately this value, since π^* orbitals appear as the k and k' orbitals in this case. A spin–orbit interaction of ~0.3 cm^{-1} should be interpreted as small.

However even this level of spin–orbit interaction is not always realised in the $\pi\pi^*$ states. The matrix elements of the H_{so} operator for molecules possessing symmetry elements must obey the selection rules (which are fully discussed in Ref.41). For the present discussion it is important to note that as a consequence of the symmetry properties the lower triplet state of many aromatic hydrocarbons is not connected by spin–orbit interaction to the electronic ground state[41]. This conclusion is highly relevant to the mechanism of $T-S$ conversion in aromatic hydrocarbons.

In the case of $n\pi^*$ and $\pi\pi^*$ states of different multiplicity the $\langle k|H_{so}^z|k'\rangle$ matrix element will include (for $|k\rangle$) the wave function of the n-electron orbital, and for $|k'\rangle$ the wave function of the π-electron orbital. We choose a coordinate system such that the x axis is perpendicular to the plane of the molecule and the axis of symmetry of the wave function of the n-orbital (in the one-centre approximation) coincides with the y axis. From the second formula (23) we can easily obtain

$$\langle S_{n\pi^*}|\hat{H}_{so}|T_{\pi\pi^*}\rangle\cong -ic_{k'n}b\,\frac{1}{4c^2}\left[np_y np_y\left|\frac{Z_n}{r^3}\right|\right], \tag{24}$$

where $c_{k'n}$ is the expansion coefficient of the k' π-orbital for an atom containing n-electrons. The one-centre integral $\left[np_y np_y\left|\frac{Z}{r^3}\right|\right]$ describes the interaction of the electron density $|np_y(r)|^2$ with the nucleus of the atom containing n-electrons, which has an effective charge Z. The other integrals in (24) are ignored (see below). An identical expression (but with

the opposite sign) can be obtained for the $\langle S_{\pi\pi^*}|H_{SO}|T_{n\pi^*}\rangle$ matrix element.

The integral in formula (24) can be evaluated analytically: the result is $1/3Z^4n^{-3}$, where n is the principal quantum number of the p-orbital. Equating Z to the Slater charges on the nuclei, and taking the $c_{k'n}$ values obtained in any of the π-MO approximations, we can find the value of (24). Calculations of this type[24,60,63,66-70] show that the spin–orbit interaction energy of the $n\pi^*$ and $\pi\pi^*$ states of different multiplicity is greater than ~10 cm^{-1} in the case of molecules containing N, O, and S atoms, and greater than ~100 cm^{-1} in molecules with heavy atoms (Br, I).

The one-centre integral $\left[np_y np_y \left|\frac{Z}{r^3}\right.\right]$ is used in the theory of atomic spectra to express the multiplet splitting constant ζ (given[71] as $1/6c^{-2}Z^4n^{-3}$). Hence the matrix element (24) can be written

$$\langle S_{n\pi^*}|H_{so}|T_{\pi\pi^*}\rangle = -ic_{k'n}b\frac{\xi}{2}. \qquad (25)$$

Calculations by formula (25) with experimental values of ζ give values of the spin–orbit bond of $n\pi^*$ and $\pi\pi^*$ states in good agreement with those given by formula (24). Allowance for the delocalisation of n-electrons and for the two-centre integrals in the expression for the matrix elements, and the use of multi-configuration wave functions[24], have very little effect on the result of the calculation.

The order of magnitude of the matrix element in formula (24) can be determined (with low precision, and with some *ad-hoc* assumptions) from data on the life time of the $T_{n\pi^*}$ states[72]. These "experimental" values of the spin–orbit coupling of $T_{n\pi^*}$ and $S_{\pi\pi^*}$ states are consistent with calculated values[73].

Formula (24) was obtained by assuming that the molecule contains only one pair of n-electrons. In more complicated cases the expression for the $\langle S_{n\pi^*}|H_{SO}|T_{\pi\pi^*}\rangle$ matrix element contains a summation over the different (equivalent) atoms with n-electrons. In these circumstances the one-centre integrals could mutually cancel out, making the matrix element small. In practice this does not happen. Because of the small splitting of the $n\pi^*$ states (in this case, $S_{n\pi^*}$) the vibronic interaction with non-fully-symmetrical vibrations leads to almost complete mixing[33]. The order of magnitude of the matrix element is found to be independent of the symmetry of the wave functions of the n-electrons.

These considerations lead to the very important conclusion that the spin–orbit interaction of states of different orbital type ($n\pi^*$ and $\pi\pi^*$) exceeds more than 30-fold the spin–orbit interaction of states of the same orbital type. The ratio of the square of their moduli, which appears in all calculations, is 10^3–10^4 for molecules containing N, O, and S atoms and over 10^4 for molecules containing halogen and other heavy atoms. This conclusion was reached[72] for molecules of aromatic azines from measurements of the life-time of $T_{n\pi^*}$ and $T_{\pi\pi^*}$ states, and from a theoretical study[63] of azines and of the carbonyl derivatives of thiocarbonyl compounds and nitro compounds. This large difference between the spin–orbit coupling between the different states is not surprising, since in the case of $n\pi^*$ and $\pi\pi^*$ interactions the matrix element contains one-centre integrals, whereas in the interaction of states of the same orbital type the matrix element contains only three-centre integrals.

The following general statement appears to be valid: if the $|k\rangle$ and $|k'\rangle$ orbitals (or one of them) contain different p-functions in their expansion with respect to atomic orbitals we can expect to find non-zero one-centre integrals in the expression (22) for one of the matrix elements. In general this matrix element is quite large, and increases rapidly with the charge on the nucleus of the atoms present in the molecule.

Other electronic states may be mentioned briefly. The matrix elements of the spin–orbit interaction operator for $\pi\pi^*$ and $\sigma\pi^*$ (or $\pi\sigma^*$) states of aromatic molecules contain non-zero one-centre integrals, leading to large interaction energies. The spin–orbit interaction amounts to 2–5 cm^{-1} for molecules of aromatic hydrocarbons[64,65,74], and exceeds 10 cm^{-1} for their derivatives containing atoms with a nuclear charge greater than that of carbon atoms. The spin–orbit interaction of $\sigma\sigma^*$ states is also large, which explains the low quantum yield of fluorescence in aliphatic molecules[64].

Non-planar molecules containing π-electrons are especially interesting. Typical of these are many aromatic and unsaturated amines in which the nitrogen atom is in an sp^3 hybrid state. As was pointed out in Section III, in these molecules the orbitals corresponding to the π-orbitals of the planar configuration include a small contribution from σ-orbitals, and their expansion in general contains not only p_z functions but also other p-functions (with a small statistical weight). Accordingly, the matrix elements of the spin–orbit interaction operator for the S_0, $S_{\pi l,\pi^*}$, and $T_{\pi l,\pi^*}$ states contain one-centre integrals, and their value is estimated[36] to be of the order of 1 cm^{-1}, i.e. intermediate between the corresponding quantities for the $\pi\pi^*$ states and the $n\pi^*$ and $\pi\pi^*$ states. When the amines form complexes with electron-acceptor systems (protons) the contribution of $l\pi^*$ configurations to the excited states decreases, and the spin–orbit interaction decreases at the same time[75]. These effects are manifest in the luminescent properties of the amines[76].

All the above statements apply equally to non-planar molecules with ν-orbitals, but so far no calculations of spin–orbit interactions have been reported for these molecules.

The spin–orbit interaction of $\pi l,\pi^*$ and $n\pi^*$ states is slightly smaller than that of $\pi\pi^*$ and $n\pi^*$ states in molecules which do not contain l-electrons. This is due to the spatial separation of the n- and l-orbitals[24].

The fundamental conclusion from this discussion is the statement[63,72] that the spin–orbit interaction of S and T states of different orbital type in planar molecules is over 30 times greater than the spin–orbit interaction of states of the same orbital type. This conclusion is crucially important to an understanding of the luminescence-spectral properties of molecules.

VI. RADIATIVE TRANSITIONS IN AROMATIC MOLECULES

The term radiative transition denotes transitions between vibronic states of molecules accompanied by the absorption or emission of photons. The photon emission process (luminescence) may or may not involve a change in the multiplicity of the states. In the latter case it is termed fluorescence, in the former case phosphorescence.

The probability of a transition from the state $|i\{n\}\rangle$ to the state $|f\{n'\}\rangle$ is proportional to the square of the matrix element $\langle i\{n\}|\mathbf{r}|f\{n'\}\rangle$, where integration is carried out over the variables r and R, and $\mathbf{r} = \sum_i \mathbf{r}_i$ is the sum of the radius vectors which define the position of the electrons in the molecule[13].

The probability of transitions which are allowed by symmetry and multiplicity can usually be calculated quite satisfactorily by the Condon approximation

$$\langle i\{n\}|\mathbf{r}|f\{n'\}\rangle = d_{if}\langle\{n\}|\{n'\}\rangle, \qquad (26)$$

where $\mathbf{d}_{if} = \langle i|\mathbf{r}|f\rangle$. The second multiplier in Eqn.(26) is the Franck–Condon factor, which defines the intensity of the individual spectral lines of the vibronic band. In the case of transitions allowed by multiplicity but forbidden by

symmetry the Condon approximation becomes invalid because the quantity d_{if} vanishes. If the transition is from the ground state to an electronically excited state we only need to allow for the dependence on R of the electronic wave function of the excited state. If the Herzberg–Teller expansion (9) is applicable we can write the following expression for the matrix element (26):

$$\langle i\{n\}|\mathbf{r}|f\{n'\}\rangle = \sum_{f'\neq f,q} \mathbf{d}_{if'} a^q_{f'f} \langle\{n\}|\delta R_q|\{n'\}\rangle = \\ = \sum_q \mathbf{d}^q_{if} \langle\{n\}|\delta R_q|\{n'\}\rangle, \quad (27)$$

where the subscript f' denotes the number of the electronically excited state, $a^q_{f'f}$ is defined by Eqn.(10), and δR_q is the deviation of the coordinate of the oscillator (q) from the equilibrium position. The matrix elements $\langle i\{n\}|\mathbf{r}|f\{n'\}\rangle$ for pure spin functions of different multiplicity are zero because of the orthogonality of the spin functions. The probability of transitions between states of different multiplicity can be made finite only by allowing for spin–orbit interaction. In this case, by analogy with (27) we obtain

$$\langle i\{n\}|\mathbf{r}|f\{n'\}\rangle = \sum_{f'\neq f} \mathbf{d}_{if'} b_{f'f} \langle\{n\}|\{n'\}\rangle = \tilde{\mathbf{d}}_{if}\langle\{n\}|\{n'\}\rangle, \quad (28)$$

where $b_{f'f} = \langle f'|H_{SO}|f\rangle (E_f - E_{f'})^{-1}$ and the multiplicity of the state $|f'\rangle$ is different from that of the state $|f\rangle$ but equal to that of the state $|i\rangle$. If necessary we can allow for the mixing of the wave function of the ground state $|i\rangle$ with the wave functions of the excited states in the derivation of formulae (27) and (28). By comparing the expressions (26), (27), and (28) we can understand the origin of the matrix element of a transition forbidden by multiplicity and symmetry[77] but which is allowed in the second-order perturbation theory for the vibronic interaction operators (10) and H_{SO}.

Transitions involving the absorption of a photon are usually characterised by their oscillator strength f, and the reverse transitions with emission of a photon by the rate constant for the radiative dissociation of the state (k_r) or by the radiative life time $\tau = 1/k_r$. In most cases the quantities f and k_r denote summations over all values of $\{n'\}$ in the last term with averaging (using the Boltzmann factor) over the vibrational states of the first term. Allowing for normalisation and for the full set of vibrational wave functions in the Condon approximation we have[13]

$$f = \frac{2\omega}{3}|\mathbf{d}_{if}|^2 = \frac{2\omega}{3}(x^2_{if} + y^2_{if} + z^2_{if}), \quad (29)$$

$$k_r = \frac{4\omega^3}{3c^3}|\mathbf{d}_{if}|^2 = \frac{4\omega^3}{3c^3}(x^2_{if} + y^2_{if} + z^2_{if}), \quad (30)$$

where ω is the frequency corresponding to the maximum of the vibronic band, c is the velocity of light, $x_{if} = \langle i|x|f\rangle$, etc. Eqns.(29) and (30) apply to non-degenerate states. In the case of a multiplicity-forbidden transition the value of $\mathbf{d}_{if}$ given by formula (28) must be used in formulae (29) and (30). From (29) and (30) we obtain the useful relationship $k_r = (\omega^2/1.5)f$ s^{-1} (if ω is expressed in cm^{-1}). In the case of symmetry-forbidden transitions, and assuming that the equilibrium position of the oscillators (q) involved in the transition is the same in states $|i\rangle$ and $|f\rangle$, we obtain (for low temperatures)

$$f = \frac{2\omega}{3}\sum_q |\mathbf{d}^q_{if}|^2 (2\mu_q\omega_q)^{-1}, \quad (31)$$

$$k_r = \frac{4\omega^3}{3c^3}\sum_q |\mathbf{d}^q_{if}|^2 (2\mu_q\omega_q)^{-1}, \quad (32)$$

where μ_q and ω_q are the reduced mass and frequency of the oscillator q. We note that the f and k_r values for symmetry-forbidden transitions are a function of temperature.

Let us examine the characteristic quantities f and k_r. We shall begin with the symmetry-allowed singlet–singlet transitions. In the case of $\pi \to \pi^*$ transitions the matrix element $\mathbf{d}_{ij}$ equals $\sqrt{2}\langle\pi_i|\mathbf{r}|\pi^*_f\rangle$, where π_i and π^*_f are the molecular orbitals between which the electronic transition takes place. From symmetry considerations the matrix components of the vector $\mathbf{r}$ lying in the plane of the molecule are non-zero. It follows that the $\pi \to \pi^*$ transitions are polarised in the plane of the molecule. The matrix elements $|\langle\pi_i|\mathbf{r}|\pi^*_f\rangle|$ are relatively large (~2 a.u.). According to formula (29) the value of f is approximately 0.1.[37–39,78–80]. For large conjugated molecules (e.g. dyes) f could approach or even exceed unity. From formula (30) we find that k_r for $S_{\pi\pi^*}$ states is ~10^8–10^7 s^{-1}, and the radiative life time is ~10^{-8}–10^{-7} s. In dye molecules the k_r value can be as high as 10^9 s^{-1}.[41] Singlet–singlet $n \to \pi^*$ transitions are allowed in many aza-aromatic molecules, in which the n-orbital includes a contribution from the 2s atomic function. The matrix element of the transition contains the non-zero one-centre integrals $[2s2p_z|z]$, which can be evaluated[9] and found to be ~1 a.u. Calculations of f in azines[80–82] give ~5×10^{-3}–10^{-2}, and ~10^6 s^{-1} for k_r in $S_{n\pi^*}$ states. These values agree with experiment[41]. The allowed $n \to \pi^*$ transitions are polarised perpendicular to the plane of the molecule. The mechanism of $\sigma \to \pi^*$ and $\pi \to \sigma^*$ transitions in aromatic hydrocarbons is entirely analogous: these transitions have f values of the same order and they are polarised perpendicular to the plane of the molecule[78].

In the molecules of carbonyl, thiocarbonyl, and nitro compounds, in which the n-orbitals have some p-character, and also in some azines, singlet–singlet $n \to \pi^*$ transitions are symmetry-forbidden in the Condon approximation. In order to calculate their probability we must allow for the vibronic interaction. Since we can put $(2\mu_q\omega_q)^{-1} \cong 10^{-1}$ in Eqn.(28), and $a_{f'f}$ has a similar value[70], we obtain ~5×10^{-4} and ~10^5 s^{-1} for f and k_r respectively in the case of symmetry-forbidden $n \to \pi^*$ transitions[81,83,84]. The polarisation of these transitions is determined by the polarisation of the transitions which limit the intensity, and it can therefore vary[83,85]. The probability of the symmetry-forbidden $\pi \to \pi^*$ transitions is similar to that of allowed $n \to \pi^*$ transitions in azines[41,86,87].

Singlet–triplet $\pi \to \pi^*$ transitions are allowed because of the spin–orbit interaction of the $T_{\pi\pi^*}$ states with $S_{\pi\pi^*}$, $S_{\sigma\pi^*}$, $S_{\pi\sigma^*}$, and $S_{n\pi^*}$ states (if n-electrons are present in the molecule), and of the interaction of the S_0 state with the $T_{\pi\pi^*}$, $T_{\sigma\pi^*}$, $T_{\pi\sigma^*}$, and $T_{n\pi^*}$ states. The spin–orbit coupling between the $T_{\pi\pi^*}$ state and the $S_{\sigma\pi^*}$, $S_{\pi\sigma^*}$, and $S_{n\pi^*}$ states is fairly strong (see Section V), but the oscillator strengths of the $S_0 \to S_{\sigma\pi^*}$, $S_0 \to S_{\pi\sigma^*}$, and $S_0 \to S_{n\pi^*}$ transitions are small. The oscillator strengths of the $S_0 \to S_{\pi\pi^*}$ transitions are large, but the spin–orbit coupling between $T_{\pi\pi^*}$ and $S_{\pi\pi^*}$ states is weak. It follows that the terms of the summation in Eqn.(28) contain a small multiplier for these transitions, and $\tilde{\mathbf{d}}_{if}$ is small. The situation is unchanged if allowance is made for the interaction of the S_0 state with the T states. The values of f and k_r for S–T transitions are calculated[88,89] to be ~10^{-7}–10^{-8} and ~10–1 s^{-1} respectively. Hence the radiative life time of the $T_{\pi\pi^*}$ states is ~0.1–1 s, i.e. these states are relatively long-lived (see below). In the case of symmetry-forbidden S–T transitions the life time of the $T_{\pi\pi^*}$ states is an order of magnitude greater[41,77]. It was shown experimentally[90,91,96] that $T_{\pi\pi^*} \to S_0$ transitions in aromatic hydrocarbons are polarised almost perpendicular to the plane of the molecule, and therefore k_r is determined by the spin–orbit interaction of $\pi\pi^*$ states with $\sigma\pi^*$ and $\pi\sigma^*$ states.

Singlet–triplet $n \to \pi^*$ transitions are allowed because of the spin–orbit interaction of the $T_{n\pi^*}$ states with the $S_{\pi\pi^*}$ and S_0 states: their energy is greater than ~10 cm^{-1}. Since the

f value for $\pi \rightarrow \pi^*$ singlet–singlet transitions is also large, the life time of the $T_{n\pi^*}$ states should be small. Calculation[66-68,89] gives $f \cong 10^{-5}$ for the $S_0 \rightarrow T_{n\pi^*}$ transitions, and $k_r \cong 10^3-10^2$ s^{-1} for the $T_{n\pi^*}$ states. Thus the $T_{n\pi^*}$ states are relatively short-lived. Since the $S_0 \rightarrow T_{n\pi^*}$ transitions determine the intensity of the $S_0 \rightarrow S_{\pi\pi^*}$ transitions they are polarised in the plane of the molecule. These results are consistent with experiment[41,72].

The probability of $S_0 \rightarrow S_{\pi l, \pi^*}$ and $S_0 \rightarrow T_{\pi l, \pi^*}$ transitions in substituted hydrocarbons is usually greater than the probability of long-wave $\pi \rightarrow \pi^*$ transitions in unsubstituted aromatic hydrocarbons. In the case of $S_0 \rightarrow S$ transitions this is because the presence of the substituent often leads to removal of the symmetry prohibition[29]. In the case of $S-T$ transitions the increase in probability arises from the decrease in the energy of the $\sigma\pi^*$ and $\pi\sigma^*$ states (decrease in the quantity $E_j - E_{j'}$ in Eqn.(28)), from the increase in the energy of the spin–orbit bond between the states (since the charge of the nuclei in the substituent is greater than the charge of the carbon nucleus, see Section V), and also from the non-planar structure of the molecule (for example, in the case of many amine molecules)[36]. The increase in probability is specially marked in the case of $S-T$ transitions in halogen-substituted molecules, for which the k_r value of the $T_{\pi l, \pi^*}$ states is ~$10-10^2$ s^{-1}. All these statements apply also to molecules with ν-orbitals, but this case has not been discussed theoretically (with one exception[30]), though it has been studied experimentally[92].

Let us examine briefly the problem of the vibrational structure of the absorption and luminescence bands, which has attracted much experimental[93-105] and theoretical[106-108] work. In the harmonic and in the Condon approximation the probability of a transition from the zero vibrational state $|0\rangle$ with excitation of the n-vibrational state of a normal oscillator in the molecule is proportional to the square of the Franck–Condon factor

$$|\langle 0|n\rangle|^2 = e^{-\gamma}\gamma^n (n!)^{-1}, \qquad (33)$$

where $\gamma = 0.5\Delta^2\mu\omega$, Δ is the change in the equilibrium position of the normal coordinate of this oscillator, and ω and μ are the frequency and mass of the oscillator. Formula (33) often describes the distribution of line intensities in vibrational progressions quite satisfactorily[98,106,108]. However in many cases we must go beyond the Condon approximation[99,100].

The following two observations are specially relevant to this discussion. Firstly, the vibrational structures of fluorescence and phosphorescence bands due to transitions of the same orbital type are approximately the same[41,95,106]. This means that the geometric characteristics of a molecule in the $S_{\pi\pi^*}$ and $T_{\pi\pi^*}$ (or $S_{n\pi^*}$ and $T_{n\pi^*}$) states are not very different. The γ parameter has been shown[95] to differ by less than 30% between the fluorescence and the phosphorescence spectra of aromatic molecules. Secondly, the vibrational structure of bands arising from $\pi \rightarrow \pi^*$ transitions is very different from that of bands arising from $n \rightarrow \pi^*$ transitions. This means that molecules in the $\pi\pi^*$ and $n\pi^*$ states have very different geometrical structures. Thus the most active vibrations (with $\gamma \cong 1$) in the bands of $\pi \rightarrow \pi^*$ transitions in carbonyl compounds are those of the aromatic rings, whereas in the bands of $n \rightarrow \pi^*$ transitions the stretching vibrations of the C=O group are the most active, with $\gamma \geq 1$.[93,94,99-101]. In thiocarbonyl compounds the vibrations of the C=O group are replaced by those of the C=S group[102], and in nitro compounds by the symmetrical stretching vibrations of the NO_2 group[105]. In aza-aromatic compounds the vibrations of the aromatic ring are active in the $\pi \rightarrow \pi^*$ bands, and those of the  corner are active in the $n \rightarrow \pi^*$ bands[96,97,103,104]. This difference in the vibrational structure of the bands is due to the nature of the transitions and is consistent, in particular, with localisation of the $n \rightarrow \pi^*$ transitions.

The vibrational structure of the absorption and luminescence bands associated with $\pi l, \pi^*$ and $\pi, \nu\pi^*$ states is usually much more diffuse than the vibrational structure of $\pi \rightarrow \pi^*$ bands[26,27]. This is due to the contribution of the $l\pi^*$ (or $\pi\nu$) configurations to the wave functions of the excited states, and to the consequent change in bond length and in bond angle in the group with l- or ν-orbitals[29,30]. The contribution from these configurations decreases as the length of the chain of conjugated bonds increases, and also on going from singlet to triplet states. Therefore the vibrational structure is less diffuse in the phosphorescence spectra, and in molecules with a large number of π-electrons[26].

We note that even in very complex molecules the parameter γ is significantly different from zero for a small number (1–3) of oscillators[93-108]. In most aromatic molecules the highest-frequency vibrations of the C–H bonds are inactive, and therefore the γ value for these vibrations is close to zero. All these results are highly relevant to the mechanism of non-radiative conversion processes (see Section VII).

Thus the radiative life time of $S_{\pi\pi^*}$ states is typically ~$10^{-7}-10^{-8}$ s, i.e. one or two orders of magnitude smaller than the radiative life time of $S_{n\pi^*}$ states. The radiative life times of triplet states show the opposite relationship: the life time of $T_{n\pi^*}$ states is ~$10^{-2}-10^{-3}$ s, and is two or three orders of magnitude shorter than the life time of $T_{\pi\pi^*}$ states. The radiative life time of the $T_{\pi l, \pi^*}$ states is intermediate between the life time of the $T_{\pi\pi^*}$ states in aromatic hydrocarbons and that of the $T_{n\pi^*}$ states. The vibrational structures of the bands due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions differ very substantially as a result of the difference in geometric structure of the molecule in the $\pi\pi^*$ and $n\pi^*$ states, and of the localised nature of the $n \rightarrow \pi^*$ transitions. The bands associated with transitions into (or from) the $\pi l, \pi^*$ (or $\pi, \nu\pi^*$) states are usually more diffuse than bands due to $\pi \rightarrow \pi^*$ transitions.

Early measurements of luminescence quantum yields have shown[109] that the yield is almost invariably less than unity, even in the absence of photochemical reactions. This effect is due to the non-radiative conversion processes discussed in the next Section.

VII. NON-RADIATIVE CONVERSION PROCESSES

The term non-radiative conversion denotes transitions between electronic states in molecules for which the electronic excitation energy is fully or partly converted into vibrational energy of the system as a whole. Conversion processes are a special case of intramolecular non-radiative transitions, which include various photochemical molecular transformation or pre-ionisation processes. Non-radiative transitions have been discussed in detail[110-114]: for our present purpose we only need to consider the dependence of the rate constant of the conversion upon the type of transition, the energy spectrum of the molecule, and the structure of the molecule.

One of the basic problems in the theory of non-radiative transitions concerns the nature of the interaction giving rise to the transition. This problem is directly associated with the problem of defining the state into which a molecule is converted upon electronic excitation. The problem was solved relatively recently[115-117] when it was shown that excitation by a broad-band source of light brings the molecule to a state whose wave function is not an eigenfunction of the full Hamiltonian of the system. (The case of monochromatic or quasi-monochromatic excitation is discussed in Refs.118 and

119.) This result, assumed without proof¶ until recently[115-117], is valid provided that (as is usually the case) the excitation region includes one pure spin adiabatic state into which an optical transition from the ground state is allowed. The pure spin adiabatic state is not a stationary state because its wave function is not an eigenfunction of the full Hamiltonian of the system, and such a state can dissociate non-radiatively under the influence of the operators V and H_{SO}. The dissociation is irreversible only if the system in its final state has a continuous (or quasi-continuous) spectrum of energy levels[13,115-117]. In the case of molecules in a condensed phase this condition is invariably satisfied.

Since only some of the intramolecular oscillators undergo a marked change in equilibrium position (and in frequency) during electronic transitions in substituted hydrocarbon molecules (see Section VI), sometimes accompanied by similar changes in some of the local vibrations of the solvent, the matrix elements of the non-adiabaticity and of the spin–orbit interaction operators will differ from zero, with a small number of oscillators excited in the final electronic state (see Section II). These oscillators (active in non-radiative conversion) are directly involved in the conversion process, accepting electronic energy and subsequently transferring it to other (inactive) vibrational modes of the molecule and of the solvent. In addition to the oscillators whose characteristics are different in the combined electronic states, the most anharmonic (and high-frequency) oscillators in the immediate vicinity of the part of the molecule where the electronic transition is localised are also active. All these conditions limit the number of modes which can be active in non-radiative transitions, and make it possible to calculate the rate constants of the conversion processes even in complex molecules.

At low temperatures ($kT < \omega$, where ω is the frequency of the active oscillators, $\omega \geq 500$ cm^{-1}), and if the vibrational relaxation rate constant (Γ) is greater than the conversion rate constant, we can write the following expression for the rate constant of the conversion between the levels i and f:[121,122]

$$k_{nr} = \sum_{\{n\}} \Gamma \left| \langle i\{0\}| \hat{R} | f\{n\} \right\rangle|^2 \cdot \left(\Delta^2_{\{n\}} + \frac{\Gamma^2}{4}\right)^{-1}, \qquad (34)$$

where the summation is taken over the vibrational states of the level f, for which $\Delta_{\{n\}} = E_{i(0)} - E_{f\{n\}} \leq 100$ cm^{-1}, and $\hat{R}$ is the level shift operator, defined by the expression

$$\hat{R} = V + H_{so} + (V + H_{so}) g_1 \hat{R} + V + H_{so} + (V + H_{so}) g_1 (V + H_{so}) + \ldots, \qquad (35)$$

and g_1 is given by

$$g_1 = \sum_{f'\{n'\}} \frac{|f'\{n'\}\rangle \langle f'\{n'\}|}{E_i - E_{f'\{n'\}}}.$$

The summation in this expression is taken over the states not included in Eqn.(34). If the value of k_{nr} given by (34) is greater than Γ the conversion rate constant is $\Gamma/2$.[118]

We can define different types of non-radiative conversion. If the multiplicity of the state is unaffected by the transition the process is termed internal conversion. If there is a change in the multiplicity of the state the process is called intercombinations ($S-T$ or $T-S$) conversion. For a transition of the system to the ground state the term "conversion" is sometimes replaced by "degradation" (internal, $S_1 \rightsquigarrow S_0$, or intercombinational, $T \rightsquigarrow S_0$).

Two rules on the rate of internal conversion processes have been formulated empirically: Kasha's rule[25] and Ermolaev and Sveshnikova's rule[123-125]. The first states that in most molecules internal conversion processes between electronically excited states (of the same resultant spin) take place in times shorter than ~10^{-11} s, and a significant quantum yield ($\geq 10^{-3}$) can be expected only for transitions from the lower excited state of the given multiplicity. The Ermolaev–Sveshnikova rule states that in many light-stable molecules in a condensed phase the conversion between S_1 and S_0 states can be ignored in comparison to fluorescence processes.

The theory of internal conversion processes in aromatic molecules containing additives has been developed in the writer's laboratory[126]. The expression for the internal conversion rate constant is

$$k_{IC} = \sum_{\{n\}} |V^{if}_{\{n\}}|^2 \Gamma (\Delta^2_{\{n\}} + \Gamma^2/4)^{-1}, \qquad (36)$$

where $V^{if}_{\{n\}}$ is a matrix element of the non-adiabaticity operator, calculated from the vibronic functions $|i\{0\}\rangle$ and $|f\{n\}\rangle$.

The main contribution to k_{IC} in the case of transitions between $\pi\pi^*$ (or $\sigma\sigma^*$) states, or between an $S_{\pi\pi^*}$ state and the ground state, comes from the matrix elements containing differentials with respect to the coordinates of the stretching vibrations of the C–H bonds (promoting modes[113]). This is because these vibrations have the greatest anharmonicity and the highest frequency of all the vibrations in the molecule. Ignoring the dispersion of the C–H stretching vibration frequencies, which is small even for small n [11] and decreases rapidly as n increases[127], we can re-write the expression for k_{IC} as[126]

$$k_{IC} \cong 10^{15} E^2_{if} \sum_{\nu,\{n\}} |c_{\nu i} c_{\nu f}|^2 \left| \left\langle 0 \left| \frac{\partial}{\partial x_\nu} \right| n \right\rangle \right|^2 \prod_{\nu' \neq \nu} |\langle 0 | n_{\nu'} \rangle|^2 \ (s^{-1}), \qquad (37)$$

where E_{if} is the difference in electronic energy of the i and f levels (in eV), the summation over ν includes all the C–H bonds in the molecule, $c_{\nu i}$ and $c_{\nu f}$ are the coefficients of the expansion of the π-orbitals, whose population is different in the $|i\rangle$ and $|f\rangle$ states, and x_ν is the coordinate of the C–H stretching vibrations. The ν' product in Eqn.(37) is taken for all the vibrations of the molecule whose characteristics are different in the $|i\rangle$ and $|f\rangle$ states (acceptor modes).

Using the Morse potential to describe the vibrations of the C–H bonds we can convert the formula for $|\langle 0|\frac{\partial}{\partial x}|\rangle|^2$ into

$$\left| \left\langle 0 \left| \frac{\partial}{\partial x} \right| n \right\rangle \right|^2 = \frac{\alpha^2 \Gamma^2 (2s - n + 1)}{n! \, \Gamma(2s - 2n) \, \Gamma(2s - 2n + 1) \, \Gamma(2s)} \cdot \eta^{2s} \rho^{-4s+2n} \times$$
$$\times \left[\frac{\eta}{2\rho} F\left(-n, 2s - n + 1; 2s - 2n + 1; \frac{1}{\rho}\right) - \right. \qquad (38)$$
$$\left. - \frac{s}{2s - n} F\left(-n, 2s - n; 2s - 2n + 1; \frac{1}{\rho}\right) \right]^2,$$

where α is the parameter of the Morse potential (~1 a.u.), $\eta = e^{\alpha\Delta}$, $\rho = \frac{1}{2} + \eta/2$, $\Gamma(x)$ is the gamma-function, $F(\alpha, \beta; \gamma; x)$ is a hypergeometric function, $s = 2D/\omega - \frac{1}{2}$, D is the dissociation energy of the C–H bond, ω is its vibration frequency, and Δ is the difference in length of the C–H bond between states $|i\rangle$ and $|f\rangle$. The Franck–Condon factors $\langle 0|n_{\nu'}\rangle$ are easily calculated because the $n_{\nu'}$ values are small and we can use the harmonic approximation in which $|\langle 0|n_{\nu'}\rangle|^2$ is given by Eqn.(33).

As was pointed out in Section VI electronic transitions in polyatomic molecules do not give rise to significant changes in the length of the C–H bonds. The γ parameter (formula (33)) for the stretching vibrations of the C–H bonds of the benzene molecule is ~10^{-2} ($\Delta = -0.014$ Å [128]). As the number of aromatic rings in the molecule increases the value of γ falls off rapidly to ~10^{-3} or less for a molecule containing two or more rings[99]. It follows that the most characteristic case is when $\Delta = 0$.

¶ The need for a proof was first stated in Ref. 120.

In Fig.6 the logarithm of the function $\theta = k_{IC} E_{if}^2 [\Sigma_\nu |c_{\nu i} c_{\nu f}|^2]^{-1}$ is plotted against the energy of the electronic transition for different values of Δ for C–H bonds, assuming typical values of $\gamma = 1$ for stretching vibrations of the aromatic nuclei at a frequency of ~1400 cm^{-1} and $\gamma = 0.5$ for bending vibrations at a frequency of ~400 cm^{-1}. The summation with respect to ν is easily evaluated because the $c_{\nu i}$ and $c_{\nu f}$ values are known for many molecules[37-40]. It is of the same order of magnitude as N_{C-H}/N^2, where N_{C-H} is the number of C–H bonds and N is the number of π-electrons in the molecule.

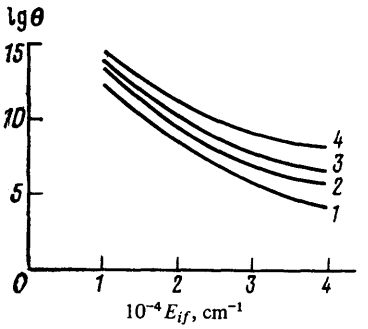


Figure 6. Variation of the factor θ with the energy of the transition: *1*) $\Delta = 0$, *2*) $\Delta = -0.01$ a.u., *3*) $\Delta = -0.02$ a.u., *4*) $\Delta = -0.03$ a.u.

These calculations lead to a number of conclusions. The internal conversion rate constant for $E_{if} \lesssim 10^4$ cm^{-1} is $\gtrsim 10^{11}$ s^{-1}, irrespectively of the value of Δ, and this is the main dissociation process available to the state $|i\rangle$. A similar (or smaller) value of E_{if} is characteristic of transitions between electronically excited states, and this calculation of k_{IC} is a theoretical justification of Kasha's rule. For E_{if} values lying between 10^4 and 2×10^4 cm^{-1} the internal conversion rate constant is of the same order as the rate constants for allowed radiative transitions. This is observed, for example, for the $S_2 \rightsquigarrow S_1$ transition in the azulene molecule, with an E_{if} value of 1.4×10^4 cm^{-1}. Formula (37) gives $\leq 10^9$ s^{-1} for the k_{IC} value of this transition, confirming that the luminescence properties of this molecule infringe Kasha's rule[129].

For $E_{if} \geq 2 \times 10^4$ cm^{-1} (as found in the transitions between S_1 and S_0 states in many aromatic molecules) the parameter k_{IC} depends not only on E_{if} but also on the Δ value of the C–H bonds. For many molecules we can write $\Delta = 0$: in this case (see Fig.6) k_{IC} is smaller than the radiative dissociation constant (k_r) of the S_1 states. It is also smaller than the rate constants for the $S-T$ conversion (see below). This result is a theoretical verification of the Ermolaev–Sveshnikova rule. It can also apply, with acceptable precision, for slightly smaller values of E_{if} if one of the following conditions obtains: 1) fast (~10^{-11} s) $S-T$ conversion processes between $n\pi^*$ and $\pi\pi^*$ states are possible; 2) the molecules have narrow luminescence bands and the γ parameter for their skeletal vibrations is $\gamma \leq 0.5$; 3) the radiative life time of the S_1 states is small (~10^{-9} s). The last two conditions are obeyed by many dye molecules, which can show strong fluorescence corresponding to transitions between S_1 and S_0 states even for $E_{if} < 2 \times 10^4$ cm^{-1} (but nevertheless $E_{if} > 10^4$ cm^{-1}).

In small aromatic molecules the Δ value of the C–H bonds can be relatively large in absolute value, so that $\pi \rightarrow \pi^*$ excitation may produce a decrease in length of the C–H bonds: for example, in benzene[128] and phenol[130] $\Delta \cong -0.03$ a.u. As a result the k_{IC} values can be close to the k_r values for the S_1 states even for $E_{if} \cong 4 \times 10^4$ cm^{-1}. This is an example of deviation from the Ermolaev–Sveshnikova rule. A similar behaviour may be discovered in other small molecules (for example, azabenzene), for which we can expect $|\Delta| \cong 0.03$ a.u. However in most aromatic molecules $|\Delta| < 10^{-2}$ a.u.[99], and the Ermolaev–Sveshnikova rule is accurately obeyed.

Internal conversion processes between $n\pi^*$ and $\pi\pi^*$ states have also been studied[126], as well as conversion between $S_{n\pi^*}$ and S_0 states. For $E_{if} > 5000$ cm^{-1} these processes are found to be slower than the conversion between $\pi\pi^*$ states, because the stretching vibrations of the C–H bonds in planar molecules do not act as promoting vibrations in this case. This result has been confirmed experimentally for the thioxanthone and thioxanthione molecules[102].

The probability of singlet–triplet conversion is very sensitive to the spin–orbit interaction of the states involved in the conversion. Using the calculations of spin–orbit interaction given in Section V we obtain the following expression[89,131] for the rate constant of the $S-T$ conversion between $\pi\pi^*$ (or $n\pi^*$) states in planar molecules in the Condon approximation and in first-order perturbation theory for the H_{SO} operator:

$$k_{ST} \cong 10^9 \sum_{\{n\}} \prod_q |\langle 0 | n_q \rangle|^2 \ (s^{-1}), \qquad (39)$$

and the following expression for the rate constant of the $S-T$ conversion between $S_{n\pi^*}$ and $T_{n\pi^*}$ (or between $S_{\pi\pi^*}$ and $T_{\pi\pi^*}$) states:

$$k_{ST} \cong 10^{12} \sum_{\{n\}} \prod_q |\langle 0 | n_q \rangle|^2 \ (s^{-1}). \qquad (40)$$

In Eqns.(39) and (40) the summation extends over the vibrational quantum numbers of the high-frequency ($\omega > 500$ cm^{-1}) oscillators whose characteristics differ in the S and T states and for which the squares of the Franck–Condon factor are a maximum. The n_q values must satisfy the condition of minimum $|E_{if} - \sum_q n_q \omega_q|$. Thus the calculation of k_{ST} reduces to a calculation of the Franck–Condon factors.

An estimate of $|\langle 0|n_q\rangle|^2$ can easily be obtained by using the Robinson–Frosch semi-empirical formula[132]. This approach gave the following results[89]. The rate constants for the $S-T$ conversion between states of the same orbital type lie between 10^6 and 10^8 s^{-1}, which is of the same order as the rate constants for the radiative dissociation of singlet states. The characteristic rate constants for $S-T$ conversion between states of different orbital type are ~10^{10}–10^{11} s^{-1}, i.e. more than two or three orders of magnitude greater than the rate constants for the radiative dissociation of singlet states. These calculations have led to the classification of molecules into five types according to their luminescence spectra[53,89].

In recent years a great deal of experimental information has been obtained on the spatial structure of aromatic molecules in different electronic states (see Section VI). Therefore we can now evaluate k_{ST} more reliably by using expressions of the type of (33). This was done in Ref.131 for molecules of carbonyl, thiocarbonyl, aza-heterocyclic, and nitro compounds, and the results were consistent with the estimates of k_{ST} given in Ref.89. It was shown that the spin–orbit coupling of combining states is not the only reason for the large difference (three orders of magnitude) between the k_{ST} values for transitions between states of different orbital type and states of the same orbital type, or the k_r values for singlet states. As pointed out in Section VI, the spatial structure of the molecules is different in the $n\pi^*$ and $\pi\pi^*$ states. As a result, the Franck–Condon factor for the

$S \rightsquigarrow T$ transition between $n\pi^*$ and $\pi\pi^*$ states is significantly higher than the factor for transitions between states of the same orbital nature.

These considerations lead to the important conclusion that if $S-T$ conversion can occur between states of different orbital nature it has a rate constant of $10^{10}-10^{11}$ s^{-1}, and it gives rise to fluorescence quenching. Recent experimental measurements[133-135] on transitions between $n\pi^*$ and $\pi\pi^*$ states have given $k_{ST} \cong 10^{11}$ s^{-1}.

By using data on the spatial structure of molecules in electronically excited states and on the structure of their energy spectrum we can calculate not only the most probable range of k_{ST} values but also the dependence of k_{ST} on the structure of the molecule. Thus it has been shown[131,136] that the probability of $S-T$ conversion between $\pi\pi^*$ states increases sharply in the presence of a $T_{\pi\pi^*}$ state. But even in this case the k_{ST} value does not exceed ~10^9 s^{-1}. Other conditions being equal the k_{ST} value for a transition between $\pi\pi^*$ states is lower, the lower the value of γ in formula (33). However γ decreases as the length of the chain of conjugated bonds increases[98], and this is why many dye molecules have a high fluorescence quantum yield.

The effect of highly excited $n\pi^*$ states on the probability of $S-T$ conversion between $\pi\pi^*$ states has been studied[70]. In molecules containing N, O, and S atoms and having spin–orbit coupling between $n\pi^*$ and $\pi\pi^*$ states of intermediate magnitude the vibronic mixing effects do not substantially increase k_{ST} for transitions between $\pi\pi^*$ states. As before, k_{ST} is of the same order of magnitude as k_r for $S_{\pi\pi^*}$ states. However this parameter decreases quite markedly as the energy difference between the $\pi\pi^*$ and $n\pi^*$ states increases (for example, as the length of the conjugation chain increases, in the presence of electron-donor substituents, or when proton-donor substituents are used, see Section IV). All these factors tend to increase the fluorescence yield of the molecules in which the lower S and T states are of the $\pi\pi^*$ type ($\pi l, \pi^*$ and $\pi, \nu\pi^*$).

In molecules containing atoms with a large nuclear charge (Br, I, Cl) the vibronic mixing effects affecting $n\pi^*$ and $\pi\pi^*$ states can make k_{ST} take a value of ~10^{10} s^{-1} for conversion between $\pi\pi^*$ states in molecules with a small ($\leq$10) number of electrons; as the number of electrons increases this value rapidly decreases[70]. Thus in molecules containing heavy atoms fluorescence is possible if the number of π-electrons is large. Deviations of k_{ST} from the usual behaviour can occur in small molecules, and are related to the weakening of the LS coupling in heavy atoms.

In molecules with $S_{\pi\pi^*}$ and $T_{\pi\pi^*}$ states lying above the lower $S_{n\pi^*}$ state (see Figs.3 and 4) the vibronic interaction effects can cause quenching of the fluorescence from $S_{n\pi^*}$ states. This is due to the smallness of k_r for $S_{n\pi^*}$ states and also to the fact that the difference in energy between $T_{n\pi^*}$ and $T_{\pi\pi^*}$ states can be small (2000–3000 cm^{-1}). This explains the absence of fluorescence in many aromatic carbonyl compounds such as benzophenone and anthrone[137]. However the situation is made more complicated by the lack of planarity of these molecules.

Deviation from planarity in molecules leads to mixing of the π and σ orbitals, to an increase in the spin–orbit interaction of states of the same orbital type (Section V), and to an increase in k_{ST}. The $\pi l, \pi^*$ states of non-planar aromatic molecules can be taken as an example[96]. Another example is provided by aliphatic hydrocarbon molecules[64], and by the non-planar aromatic carbonyl molecules mentioned above.

We can now turn to a discussion of the role of internal conversion processes in the dissociation of excited states. The variation of the internal conversion constant k_{IC} with E_{if} is shown diagrammatically in Fig.7 for $\Delta_{C-H} = 0$. The cross-hatched region shows the most characteristic values of the rate constant for the dissociation of an S state by the radiative mechanism and by the $S-T$ conversion mechanism (k) on the assumption that $\pi\pi^*-n\pi^*$ conversion is not involved. Three energy regions can be defined: the Kasha region, in which $k_{IC} > k$, an intermediate region ($k_{IC} \cong k$), and the Ermolaev–Sveshnikova region ($k_{IC} < k$). When $S-T$ conversion processes between $\pi\pi^*$ and $n\pi^*$ states are possible the k value increases sharply and the Ermolaev–Sveshnikova region expands. We shall examine the case of molecules which obey the Ermolaev–Sveshnikova rule, even if only approximately, i.e. molecules in which the first singlet excited state has an energy in excess of ~1.5 eV.

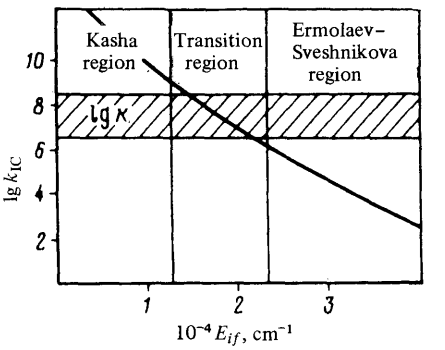


Figure 7. Relative values of k_{IC} and k as a function of the energy of the transition.

We have to consider processes of intercombination conversion from the lower triplet state to the ground state, which compete with the phosphorescence process. These processes have been studied in depth, both experimentally and theoretically, and they are discussed in the monograph literature[8,41] and in reviews[111,112]. In spite of their different approaches, all the theoretical studies conclude that the rate constant for conversion between S_0 states (k_{TS}) increases rapidly as the difference in energy between the states decreases[132,138,139]. This result, which follows directly from the simple formula (33) for the Franck–Condon factor, is consistent with experiment. However order-of-magnitude quantitative agreement between experimental and theoretical values of the constant has not yet been obtained, or has been obtained by postulating unrealistic potential energy surfaces for the molecules in excited states[111].

The difficulty of calculating the constant k_{TS} arises from the fact that, since E_{if} is large ($\geq$1 eV), the Franck–Condon factors for the $T \rightsquigarrow S_0$ transitions are small, and therefore the second- and higher-order terms in formula (35) cannot be ignored. (This is the difference between $T-S_0$ conversion and $S-T$ conversion.) The situation is made even more complex by the fact that in many aromatic molecules the matrix element of the operators of the spin–orbit interaction between the lower T state and the S_0 state is identically equal to zero in the Condon approximation (see Section V). In this case the transition is forbidden in the first-order (and in the Condon approximation) for the operator H_{SO}, and agreement between calculated values of k_{TS} and experiment cannot be obtained simply by improving the precision of the calculated Franck–Condon factor.

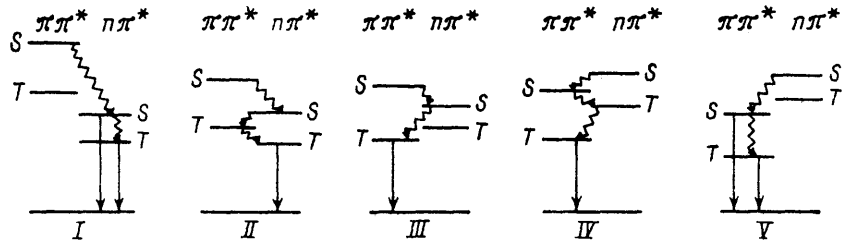


Figure 8. Most probable conversion processes between excited states, and radiative processes, involving molecules of the five luminescence-spectral types.

An important contribution[140] to our understanding of the mechanism of $T-S$ conversion in aromatic molecules points out that the constant k_{TS} is proportional to the constant k_r of the triplet state and to the overlap integral of the phosphorescence spectrum and of the infrared absorption spectrum of the molecule corresponding to the upper vibrational states of the C–H bonds, into which transitions are allowed as a result of the anharmonicity of the vibrations. This means[141,142] that k_{TS} is determined by a non-adiabatic interaction, and it should be calculated with allowance for second- and higher-order terms in the operators V and H_{SO}. It follows that k_{TS} should be proportional to the spin–orbit coupling of the T states with the S states, and to the constant k_{IC} for the conversion between these S states and the S_0 state (calculated for an E_{if} value equal to the energy of the T state[136]). Since the vibrational factor in the calculation of k_{IC} contains differentials with respect to the coordinates of the C–H bonds, and allowance for the anharmonicity of the vibrations is essential, the vibrational factor cannot be reduced to a Franck–Condon factor. In particular, the quantity $\langle 0|n\rangle$ for $n \neq 0$ and $\Delta = 0$ vanishes, and the quantity $\langle 0|\frac{\partial}{\partial x}|n\rangle$ for the anharmonic oscillator under these conditions cannot vanish for any value of n.

Conversion between $T_{\pi\pi^*}$ and the S_0 state can be achieved by mixing $S_{\pi\pi^*}$, $S_{n\pi^*}$, $S_{\sigma\pi^*}$, and $S_{\pi\sigma^*}$ states with the $T_{\pi\pi^*}$ state, and by mixing the appropriate triplet states with the S_0 state. In this case both the spin–orbit interaction and k_{IC} are small, since internal conversion between an $n\pi^*$ (or $\sigma\pi^*$, or $\pi\sigma^*$) state and the S_0 state cannot be promoted by stretching vibrations of the C–H bonds (see above, and Ref. 126). Therefore the conversion rate constants (k_{TS}) in the solid phase and at low temperatures are relatively small: in most molecules these constants differ by less than an order of magnitude from the k_r value for the $T_{\pi\pi^*}$ states[41,143]†. Under these conditions the dependence of the rate constant for the $T-S$ conversion on E_{if} is determined by the dependence of the matrix elements of (38) upon n, and is not very different from the dependence of k_{IC} on E_{if}. Theoretical calculations of k_{TS} as a function of E_{if} agree satisfactorily with experiment[140,136]. For $E_{if} \lesssim 1.5$ eV the constant k_{TS} becomes greater than k_r: in these molecules phosphorescence is impossible. At these energies the predominant contribution to k_{TS} can be obtained by the first-order perturbation theory if $\langle T_S|H_{SO}|S_0\rangle \neq 0$.[136]

The $T_{n\pi^*} \rightsquigarrow S_0$ intercombination conversion is much faster than conversion from a $T_{\pi\pi^*}$ state. This is because the spin–orbit interaction of $T_{n\pi^*}$ states with both S_0 and $S_{\pi\pi^*}$ states is large. In the condensed phase at low temperatures the constant k_{TS} for conversion from $T_{n\pi^*}$ states is similar in value to k_r for $T_{n\pi^*}$ states in many molecules[41,143]. The theory of $T-S_0$ conversion processes is still far from being fully developed.

To conclude this Section we shall list the main features of the conversion processes. Internal conversion between electronically excited states occur in ~10^{-11} s. In photochemically-stable molecules in a condensed phase we can usually ignore the $S_1 \rightsquigarrow S_0$ internal conversion (degradation) process. The rate constant for $S-T$ conversion between $n\pi^*$ and $\pi\pi^*$ states is ~10^{10}–10^{11} s^{-1}. The rate constant for $S-T$ conversion between states of the same orbital type in planar molecules is ~10^6–10^8 s^{-1}. The only exception are molecules containing heavy atoms (e.g. halogen) and having a small number ($\lesssim 10$) of π-electrons, for which the constant k_{ST} can be as high as 10^{10} s^{-1}. In the case of transitions between $\pi\pi^*$ states k_{ST} decreases as the energy difference between the $\pi\pi^*$ and $n\pi^*$ states increases and as the length of the conjugated bond chain increases. In non-planar molecules k_{ST} is higher than in planar molecules. The rate constants for $T \rightsquigarrow S_0$ conversion in the solid phase are similar in magnitude to the k_r values for triplet states. As the energy of the T state decreases the constant k_{TS} increases, lowering the phosphorescence yield.

VIII. CLASSIFICATION OF MOLECULES BY LUMINESCENCE SPECTRA

Let us now consider the luminescence-spectral properties of molecules in relation to the relative position of their electronically excited states#. We shall show that each of the five types of relative position of the $\pi\pi^*$ and $n\pi^*$ states (see Section IV) has its own set of luminescence-spectral characteristics, i.e. it corresponds to a type of molecule[53,89]. We shall assume that the molecules obey the Kasha and the Ermolaev–Sveshnikova rules, that they do not contain heavy atoms, and that their structure is planar.

Type I. The sequence of states is: S_0, $T_{n\pi^*}$, $S_{n\pi^*}$, $T_{\pi\pi^*}$, $S_{\pi\pi^*}$. Since the rate constants k_r (for $S_{n\pi^*}$ states) and k_{ST} (for the $S_{n\pi^*} \rightsquigarrow T_{n\pi^*}$ conversion) are similar in value (see Sections VI and VII), both fluorescence and (in the solid

†With rare exceptions, phosphorescence is not observed in the liquid phase because of the possibility of quenching of the T states by bimolecular processes.

#In this discussion the electronically excited states are arranged in order of increasing energy.

phase) phosphorescence are possible in these molecules. The fluorescence yield cannot be large because the constant k_r is relatively small. These molecules have a long-lived fluorescence and a short-lived phosphorescence. In the absorption spectra of molecules of the first luminescence-spectral type the bands corresponding to $n \to \pi^*$ and $\pi \to \pi^*$ transitions are separated by a relatively large ($\geq$1 eV) energy difference. Examples of this type of molecule are acetone, diacetyl, thiobenzophenone, and other molecules[4,53].

Type II. The sequence of states is: S_0, $T_{n\pi^*}$, $T_{\pi\pi^*}$, $S_{n\pi^*}$, $S_{\pi\pi^*}$. Because of the possibility of fast (~10^{-11} s) $S_{n\pi^*} \rightsquigarrow T_{\pi\pi^*}$ interconversion this type of molecule has a short-lived phosphorescence from the $T_{n\pi^*}$ state, and the fluorescence yield cannot exceed 10^{-3}. The $n \to \pi^*$ and $\pi \to \pi^*$ absorption bands are also well resolved in molecules of type II. Typical type II molecules are acetophenone, naphthoquinone, anthraquinone, and others[2-4].

Type III. The sequence of states is: S_0, $T_{\pi\pi^*}$, $T_{n\pi^*}$, $S_{n\pi^*}$, $S_{\pi\pi^*}$, Fast $S_{n\pi\pi^*} \rightsquigarrow T_{\pi\pi^*}$ interconversion is possible also in molecules of this type. Therefore these molecules can have only long-lived phosphorescence from the $T_{n\pi^*}$ states; the fluorescence yield cannot be greater than 10^{-3}. In the absorption spectra the $n \to \pi^*$ band is close to the $\pi \to \pi^*$ band, with the possibility of partial overlap. Examples of this type of molecule are benzoic acid, phthalic anhydride, etc.[4].

Type IV. The sequence of states is: S_0, $T_{\pi\pi^*}$, $T_{n\pi^*}$, $S_{\pi\pi^*}$, $S_{n\pi^*}$. Because of the possibility of $S_{\pi\pi^*} \rightsquigarrow T_{\pi\pi^*}$ interconversion processes in times of the order of 10^{-11} s the long-lived phosphorescence from $T_{\pi\pi^*}$ states is predominant in the radiation from these molecules. The fluorescence yield is small, but it can exceed the fluorescence yield of type-III molecules because the k_r values for $S_{\pi\pi^*}$ states are substantially higher than those for $S_{n\pi^*}$ states. An important difference between the luminescence properties of type IV and type III molecules is the ability of the former to be converted into type-V molecules (see below) under the influence of solvents giving rise to hydrogen bonds, since the energy difference between the $S_{\pi\pi^*}$ and $T_{n\pi^*}$ states is ~1000 cm^{-1}. Activation of the fluorescence of type II and type III molecules requires a much greater increase in the energy of the $n\pi^*$ states, which can be realised by dissolving the molecules in acids[144]. The bands corresponding to $n \to \pi^*$ transitions in the absorption spectra of type-IV molecules show complete overlap with the much stronger $\pi \to \pi^*$ bands, and they are not observed in poorly resolved spectra. Typical molecules of this type are acridine and quinoline in non-polar solvents.

Type V. The sequence of states is: S_0, $T_{\pi\pi^*}$, $S_{\pi\pi^*}$, $T_{n\pi^*}$, $S_{n\pi^*}$. Since the relatively slow ($\geq 10^{-9}$ s) $S_{\pi\pi^*} \rightsquigarrow T_{\pi\pi^*}$ processes are the only interconversion processes possible in this type of molecule we can expect both fluorescence and phosphorescence, with comparable yields. The ratio of the yields is determined by the relative values of k_r for the $S_{\pi\pi^*}$ states and k_{TS} for the $S_{\pi\pi^*} \to T_{\pi\pi^*}$ conversion, and of k_r for the $T_{\pi\pi^*}$ states and k_{TS} for the $T_{\pi\pi^*} \rightsquigarrow S_0$ conversion, which were discussed in the last two Sections. The $n \to \pi^*$ bands in the absorption spectra of type-V molecules are usually overlapped by the stronger bands due to $\pi \to \pi^*$ transitions, and they can be observed only when they lie between two of these bands. Dye molecules are typical of the luminescence-spectral type V.

The most probable conversion processes between electronically excited states and radiation processes involving molecules of the five luminescence-spectral types are illustrated in Fig.8. The diagram corresponds to k_{ST} values obtained in the Condon approximation. By going beyond this approximation[70] we can, on the one hand, describe differences between molecules in the same spectral type, and on the other hand we can demonstrate the absence of sharp boundaries between the five spectral types. We shall justify the latter statement by considering the transition from type I to type II. As the $T_{\pi\pi^*}$ state approaches the $T_{n\pi^*}$ state the extent of mixing of these states due to vibronic interaction increases, and the constant k_{ST} for the $S_{n\pi^*} \rightsquigarrow T_{n\pi^*}$ transition also increases very markedly. The energy of the $T_{\pi\pi^*}$ state can be higher than that of the $S_{n\pi^*}$ state, but since the $S-T$ splitting of the $n\pi^*$ states and the constant k_r for the $S_{n\pi^*}$ state are both small the fluorescence may be suppressed. Similar arguments can be applied in the other cases.

In other words, great care is needed to describe the luminescence-spectral properties of molecules whose electronic states lie in the transition region between two of the types defined above. This conclusion is entirely consistent with the well known increase in complexity of the spectral properties of systems with degenerate or quasi-degenerate states (the Jahn–Teller effect or pseudo-effect)[145]. The criterion for the validity of the scheme shown in Fig.8 is that the vibronic interaction of $n\pi^*$ and $\pi\pi^*$ states must be small compared with the energy difference between these states. In most cases this criterion is obeyed and the scheme of Fig.8 is applicable[79].

In the light of these considerations, the differences in properties between $\pi\pi^*$ (or $n\pi^*$) states arising from differences in orbital nature, from the presence or absence of quasi-degeneracy of the lower $S_{\pi\pi^*}$ state with the upper $T_{\pi\pi^*}$ state, from the differences in the vibronic bond with the upper states, etc. are only second-order differences and can be allowed for in the scheme proposed here. This is because none of the rate constants for $S-T$ conversion suffers a catastrophic change (by several orders of magnitude) as a result of these effects. The scheme outlined in Fig.8 remains valid, though there may be a change in the designation of the states and (or) a limited change in the rate constants for the dissociation of the states leading to luminescence.

Possible luminescence-spectral types of molecules of different orbital classes*.

Class	Type					Class	Type				
	I	II	III	IV	V		I	II	III	IV	V
(σn)	–	–	–	–	+	($\sigma\pi n$)	+	+	+	+	+
($\sigma\pi l$)	–	–	–	–	+	($\sigma\pi ln$)	+	+	+	+	+
($\sigma n v$)	–	–	–	–	+	($\sigma n v n$)	+	+	+	+	+
($\sigma n l v$)	–	–	–	–	+	($\sigma n l v n$)	+	+	+	+	+

*The plus sign denotes that this type of molecule can exist, the minus sign that it cannot.

The luminescence-spectral type to be expected in molecules of various types can therefore be stated without difficulty. Aromatic (unsaturated) molecules can be divided into the following classes[146], depending on the set of orbitals which characterise their electronic structure: ($\sigma\pi$), ($\sigma\pi l$), ($\sigma\pi v$), ($\sigma\pi lv$), ($\sigma\pi n$), ($\sigma\pi ln$), ($\sigma\pi vn$), and ($\sigma\pi lvn$). These designations hardly need to be explained: for example, the ($\sigma\pi$) class includes the aromatic hydrocarbon molecules, the ($\sigma\pi l$) class the aromatic hydrocarbon molecules with donor substituents, etc. The possibilities of observing the various luminescence-spectral types are summarised in the Table[146].

A set of molecules of different classes but of the same luminescence-spectral type is termed a luminescence-spectral series. Molecules of one series have similar (but numerically different) properties owing to the differences in orbital nature of their states and to the other factors discussed above. Transitions between molecules of different types or classes can be brought about by changes in chemical structure and by external factors (see Section IV).

All the above statements apply to molecules which do not contain heavy atoms, i.e. atoms with a multiplet splitting constant ξ greater than ~500 cm^{-1}.[70] Infringement of this condition causes k_{ST} for transitions between $\pi\pi^*$ states in molecules formally classified as type V to reach values of the order of 10^{11} s^{-1}: these molecules will have a low ($\leqslant 10^{-3}$) fluorescence quantum yield. The effect is clearly shown by molecules with a small ($\leqslant 10$) number of π-electrons.

The agreement between the luminescence-spectral classification of molecules and experimental data has been demonstrated by many workers[2-4,53,58,92,99,100,147-150].

This method of classification offers a unified description of the properties of a large number of molecular systems. It has been applied in the chemistry of phosphors and scintillators[147], in biophysics[148], and in photochemistry[114], and it has helped in the selection of materials with good light-emitting properties (for the active regions of lasers operating in the visible and the u.v. region)[144,149,150]. It has also been valuable in molecular spectroscopy[4].

The validity of our classification is limited by the possibility of photochemical processes. The problem is by no means trivial, because conversion processes can be initiated by photochemical processes whose yield is immeasurably low. A special case is met in systems with two or more minima in the potential surface of one electronic state[151].

Since this paper was submitted for publication the following relevant papers have appeared: a discussion[152] of the general problems in systematising the luminescence-spectral properties of molecules, a study[153] of the initiation mechanisms of conversion by photochemical reactions, and an analysis[154] of the mechanism of triplet–singlet conversion processes.

REFERENCES

1. B.I.Stepanov and A.N.Rubinov, Uspekhi Fiz.Nauk, **95**, 45 (1968).
2. R.N.Nurmukhametov, Uspekhi Khim., **34**. 1629 (1967) [Russ.Chem.Rev., No.9 (1967)].
3. D.N.Shigorin, Zhur.Vses.Khim.Obshch.imeni Mendeleeva, **20**, 32 (1975).
4. R.N.Nurmukhametov, "Pogloshchenie i Lyuminestsentsiya Aromaticheskikh Soedinenii" (Absorption and Luminescence in Aromatic Compounds), Izd.Khimiya, Moscow, 1971.
5. K.G.Spears and S.A.Rice, J.Chem.Phys., **55**, 5561 (1971).
6. U.Boesl, H.J.Neusser, and E.W.Schlag, Chem.Phys. Letters, **31**, 17 (1975).
7. N.A.Borisevich, "Vozbuzhdennye Sostoyaniya Slozhnykh Molekul v Gazovoi Faze" (Excited States of Complex Molecules in the Gas Phase), Izd.Nauka i Tekhnika, Minsk, 1967.
8. J.G.Calvert and J.N.Pitts, "Photochemistry" (Translated into Russian), Izd.Mir, Moscow, 1968.
9. G.G.Gelman, "Quantum Chemistry" (Translated into Russian), Izd.ONTI, Moscow, 1937.
10. M.Born and J.R.Oppenheimer, Ann.Physik, **84**, 457 (1927).
11. M.V.Vol'kenshtein, L.A.Gribov, M.A.El'yashevich, and B.I.Stepanov, "Kolebaniya Molekul" (Molecular Vibrations), Izd.Nauka, Moscow, 1972.
12. P.M.Morse, Phys.Rev., **34**, 57 (1929).
13. A.S.Davydov, "Kvantovaya Mekhanika" (Quantum Mechanics), Fizmatgiz, Moscow, 1963.
14. A.Nitzan and J.Jortner, Chem.Phys.Letters, **11**, 458 (1971).
15. G.Herzberg and E.Teller, Z.phys.Chem., **B21**, 410 (1933).
16. C.C.J.Roothaan, Rev.Mod.Phys., **23**, 69 (1951).
17. R.Parr, "Quantum Theory of Molecular Electronic Structure", Benjamin Press, New York, 1963.
18. T.E.Peacock, "Electronic Properties of Aromatic and Heterocyclic Molecules" (Translated into Russian), Izd.Mir, Moscow, 1969.
19. V.A.Gubanov, V.P.Zhukov, and A.O.Litinskii, "Poluempiricheskie Metody Molekulyarnykh Orbitalei v Kvantovoi Khimii" (Semi-empirical Molecular Orbital Methods in Quantum Chemistry), Izd.Nauka, Moscow, 1976.
20. I.A.Misurkin and A.A.Ovchinnikov, Uspekhi Khim., **43**, 2195 (1974); **44**, 393 (1975) [Russ.Chem.Rev., No.12 (1974); No.3 (1975)].
21. V.G.Plotnikov, Optika i Spektrosk., **20**, 394 (1966).
22. T.R.Grinter and T.Edvards, Mol.Phys., **15**, 357 (1968).
23. V.M.Komarov and V.G.Plotnikov, Spectr.Letters, **8**, 363 (1975).
24. V.G.Plotnikov and V.M.Komarov, Spectr.Letters, **9**, 265 (1976).
25. M.Kasha, Discuss.Faraday Soc., **9**, 14 (1950).
26. V.L.Ermolaev, Optika i Spektrosk., **11**, 492 (1961).
27. R.N.Nurmukhametov and G.V.Gobov, Optika i Spektrosk., **18**, 227 (1965).
28. J.N.Murrel, "The Theory of the Electronic Spectra of Organic Molecules", Wiley, New York, 1963.
29. V.M.Komarov and V.G.Plotnikov, Teor.i Eksper. Khim., **10**, 62 (1974).
30. V.M.Komarov, K.L.Rogozhin, A.N.Rodionov, V.G.Plotnikov, and D.N.Shigorin, Zhur.Prikl. Spektrosk., **23**, 348 (1976).
31. J.M.Foster and S.F.Boys, Rev.Mod.Phys., **32**, 303 (1960).
32. J.M.Hollas, E.Gregorek, and L.Goodman, J.Chem. Phys., **49**, 1745 (1968).
33. M.F.Merienne-Lafore and H.P.Trommsdorf, J.Chem. Phys., **64**, 3790 (1976).
34. L.V.Orlovskaya and A.F.Terpugova, Izv.Vys.Ucheb. Zaved., Fizika, 134 (1974).
35. J.H.Lichtenbelt et al., J.Chem.Phys., **22**, 297 (1977).
36. V.M.Komarov, V.G.Plotnikov, and L.G.Belousova, Optika i Spektrosk., **29**, 1006 (1970).
37. R.Pariser, J.Chem.Phys., **24**, 250 (1956).
38. G.Favini, J.Vandoni, and N.Simoneta, Theor.Chim. Acta, **3**, 45 (1965).
39. M.M.Mestechkin, L.S.Gutyrya, and V.N.Poltavets, Optika i Spektrosk., **27**, 454 (1970); **30**, 1022 (1971).
40. Yu.B.Malykhanov, Optika i Spektrosk., **43**, 431 (1977).
41. S.P.McGlynn, T.Azumi, and M.Kinosita, "Molecular Spectroscopy of the Triplet State" (Translated into Russian), Izd.Mir, Moscow, 1972.
42. I.A.Misurkin and A.A.Ovchinnikov, Teor.i Eksper. Khim., **3**, 431 (1967).

43. V.N.Kondrat'ev (Editor), "Energii Razryva Khimicheskikh Svyazei. Potentsialy Ionizatsii i Srodstva k Elektronu" (Dissociation Energies of Chemical Bonds. Ionisation Potentials and Electron Affinities), Izd.Nauka, Moscow, 1974.
44. V.G.Plotnikov, Optika i Spektrosk., **20**, 589 (1966).
45. T.Anno and A.Sado, J.Chem.Phys., **26**, 1759 (1957).
46. L.Goodman and R.W.Harrel, J.Chem.Phys., **30**, 1131 (1959).
47. D.R.Kearns and M.A.El-Bayoumi, J.Chem.Phys., **38**, 1508 (1963).
48. L.V.Orlovskaya, I.V.Sokolova, and A.F.Terpugova, Optika i Spektrosk., **36**, 1508 (1963).
49. J.L.Whitten and M.Hackmeyer, J.Chem.Phys., **51**, 5584 (1969).
50. K.Yamaguchi and T.Fueno, Bull.Chem.Soc.Japan, **44**, 43 (1971).
51. K.Inuzuka and R.S.Becker, Bull.Chem.Soc.Japan, **45**, 1557 (1972).
52. V.M.Komarov, Thesis, Moscow, 1978.
53. R.N.Nurmukhametov, V.G.Plotnikov, and D.N.Shigorin, Zhur.Fiz.Khim., **40**, 1154 (1966)[Russ. J.Phys.Chem., No.7 (1966)].
54. M.Kasha and M.R.Rawls, Photochem.Photobiol., **7**, 561 (1968).
55. R.N.Nurmukhametov and I.A.Misurkin, Zhur.Fiz. Khim., **42**, 217 (1968).
56. S.F.Mason, J.Chem.Soc., 494 (1960).
57. R.N.Nurmukhametov et al., Optika i Spektrosk., 22, 740 (1967).
58. D.N.Shigorin, N.A.Sheglova, and Yu.I.Kozlov, "Proceedings of the International Conference on Luminescence", Budapest, 1966, p.528.
59. D.S.McClure, J.Chem.Phys., **20**, 682 (1952).
60. J.L.Ginsburg and L.Goodman, Molec.Phys., **15**, 441 (1968).
61. I.G.Kaplan, "Simmetriya Mnogoelektronnykh Sistem" (Symmetry of Many-electron Systems), Izd.Nauka, Moscow, 1969.
62. N.F.Mott and I.Sneddon, "Wave Mechanics and Its Applications" (Translated into Russian), Izd.Nauka, Moscow, 1966, p.119.
63. V.G.Plotnikov, Optika i Spektrosk., **22**, 735 (1967).
64. V.G.Plotnikov, Optika i Spektrosk., **27**, 928 (1969).
65. E.Clement, J.Mol.Spectroscopy, **6**, 497 (1961).
66. J.W.Sidman, J.Chem.Phys., **29**, 644 (1958).
67. E.Clement and M.Kasha, J.Mol.Spectroscopy, **2**, 297 (1958).
68. L.Goodman and V.G.Krishan, Rev.Mod.Phys., **35**, 541 (1963).
69. Pill-Soon Song and W.H.Gardon III, J.Phys.Chem., **74**, 4234 (1970).
70. V.G.Plotnikov and B.A.Dolgikh, Optika i Spektrosk., **44**, 450 (1978).
71. I.I.Sobel'man, "Vvedenie v Teoriya Atomnykh Spektrov" (Introduction to the Theory of Atomic Spectra), Fizmatgiz, Moscow, 1963.
72. M.A.El-Sayed, J.Chem.Phys., **38**, 2834 (1963).
73. D.N.Shigorin and N.A.Shcheglova, Optika i Spektrosk., **36**, 740 (1974).
74. B.R.Henry and W.Siebrand, J.Chem.Phys., **54**, 1072 (1971).
75. V.M.Komarov and V.G.Plotnikov, Zhur.Prikl. Spektrosk., **20**, 256 (1974).
76. V.A.Smirnov, V.A.Sapozhnikov, O.M.Andreev, and M.V.Alfimov, Khimiya Vys.Energii, **5**, 121 (1971).
77. A.C.Albrecht, J.Chem.Phys., **38**, 354 (1963).
78. L.Burnelle and M.Kranepool, J.Mol.Spectroscopy, **37**, 383 (1971).
79. C.P.Yue and D.P.Chong, Mol.Phys., **14**, 487 (1968).
80. A.Kaito, M.Hatano, and A.Tajiri, J.Amer.Chem.Soc., **99**, 5241 (1977).
81. J.W.Sidman, Chem.Rev., **58**, 689 (1958).
82. L.Goodman, J.Mol.Spectroscopy, 6, 109 (1961).
83. J.A.Pople and J.W.Sidman, J.Chem.Phys., **27**, 1270 (1957).
84. V.A.Kilin, A.F.Terpugova, and E.I.Cheglokov, Optika i Spektrosk., **41**, 770 (1976).
85. R.Shimada and L.Goodman, J.Chem.Phys., **43**, 2027 (1965).
86. J.N.Murrel and J.A.Pople, Proc.Phys.Soc.(London), **A69**, 245 (1956).
87. M.J.Robey et al., Chem.Phys., **23**, 207 (1977).
88. B.R.Henry and W.Siebrand, J.Chem.Phys., 51, 2396 (1969).
89. V.G.Plotnikov, Optika i Spektrosk., **23**, 39 (1967).
90. T.Azumi and S.P.McGlynn, J.Chem.Phys., **37**, 2413 (1962).
91. M.A.El-Sayed, Nature, **197**, 481 (1963).
92. A.N.Rodionov, Thesis, Moscow, 1976.
93. R.N.Nurmukhametov and D.N.Shigorin, Zhur.Fiz. Khim., **35**, 72 (1961)[Russ.J.Phys.Chem., No.1 (1961)].
94. V.L.Ermolaev and A.N.Terenin, Uspekhi Fiz.Nauk, 71, 137 (1960).
95. V.L.Ermolaev, Optika i Spektrosk., **16**, 704 (1964).
96. F.Dörr and H.Gropper, Z.Elektrochem., **67**, 193 (1967).
97. K.K.Innes, J.P.Byrne, and I.G.Ross, J.Mol. Spectroscopy, **22**, 125 (1967).
98. V.P.Kochkov and V.L.Bogdanov, Optika i Spektrosk., **34**, 70 (1973).
99. N.S.Strokach, E.A.Gastilovich, and D.N.Shigorin, Optika i Spektrosk., **35**, 239 (1973).
100. E.A.Gastilovich, G.T.Kryuchkova, et al., **39**, 235 (1975).
101. M.A.Souto and C.T.Lin, Chem.Phys., **17**, 129 (1976).
102. M.Mahaney and J.R.Huber, Chem.Phys., **9**, 371 (1975).
103. N.Kanamuru and E.C.Lim, J.Chem.Phys., **61**, 1582 (1974).
104. A.E.W.Knight, G.M.Lamburgh, and C.S.Parmenter, J.Chem.Phys., **63**, 4336 (1975).
105. O.S.Khalil and S.P.McGlynn, J.Luminescence, 11, 185 (1975).
106. E.F.McCoy and I.G.Ross, Austral.J.Chem., 15, 573 (1962).
107. K.K.Rebane, "Elementarnaya Teoriya Kolebatel'noi Struktury Spektrov Primesnykh Tsentrov Kristallov" (Elementary Theory of the Vibrational Structure of the Spectra of Impurity Centres in Crystals), Izd. Nauka, Moscow, 1968.
108. M.D.Frank-Kamenetskii and A.V.Lukashin, Uspekhi Fiz.Nauk, 116, 193 (1975).
109. S.I.Vavilov, Z.Physik, **42**, 311 (1927).
110. S.Lower and M.A.El-Sayed, Uspekhi Fiz.Nauk, 94, 289 (1968).
111. B.R.Henry and M.Kasha, Uspekhi Fiz.Nauk, **108**, 113 (1972).
112. J.Jortner, S.A.Rise, and R.M.Hochstrasser, Adv. Photochem., 7, 149 (1969).
113. K.F.Freed, Fortschr.Chem.Forsch., **31**, 105 (1972).
114. V.G.Plotnikov and A.A.Ovchinnikov, Uspekhi Khim., **47**, 444 (1978)[Russ.Chem.Rev., No.3 (1978)].
115. M.Bixon and J.Jortner, J.Chem.Phys., **48**, 715 (1968).

116. W.Rhodes, B.R.Henry, and M.Kasha, Proc.Nat.Acad. Sci.USA, **63**, 31 (1969).
117. V.G.Plotnikov and G.G.Konoplev, Optika i Spektrosk., **34**, 1101 (1973).
118. E.D.Trifonov and V.L.Shekhtman, Fiz.Tverdogo Tela, 11, 2984 (1969).
119. V.G.Plotnikov and G.G.Konoplev, Zhur.Eksper.Teor. Fiz., **65**, 960 (1973).
120. K.K.Rebane, Trudy Inst.Fiz.Akad.Nauk EstSSR, No.7, 62 (1958).
121. V.G.Plotnikov and G.G.Konoplev, Fiz.Tverdogo Tela, **15**, 680 (1973).
122. V.G.Plotnikov and G.G.Konoplev, Pre-print of the Institute of Theoretical Physics of the UkrSSR Academy of Sciences ITF-74-55R, Kiev, 1974.
123. V.L.Ermolaev, Optika i Spektrosk., **13**, 90 (1962).
124. V.L.Ermolaev and E.B.Sveshnikova, Optika i Spektrosk., **16**, 587 (1964).
125. V.L.Ermolaev and E.B.Sveshnikova, Acta.Phys. Polon., **34**, 771 (1968).
126. V.G.Plotnikov and B.A.Dolgikh, Optika i Spektrosk., **43**, 882 (1977).
127. A.A.Ovchinnikov and N.S.Erikhman, Optika i Spektrosk., **34**, 690, 887 (1973).
128. G.Herzberg, "Electronic Spectra and Structure of Polyatomic Molecules" (Translated into Russian), Izd. Mir, Moscow, 1969.
129. H.C.Longuet-Higgins and M.Beer, J.Chem.Phys., **23**, 1390 (1955).
130. K.D.Bist and J.S.Brand, J.Mol.Spectroscopy, **24**, 413 (1967).
131. V.G.Plotnikov, B.A.Dolgikh, and V.M.Komarov, Optika i Spektrosk., **43**, 1072 (1977).
132. G.W.Robinson and R.P.Frosch, J.Chem.Phys., **37**, 1962 (1962); **38**, 1187 (1963).
133. R.M.Hochstrasser, H.Lutz, and G.W.Scott, Chem. Phys.Letters, **24**, 162 (1974).
134. R.W.Anderson, R.M.Hochstrasser, H.Lutz, and G.W.Scott, Chem.Phys.Letters, **28**, 153 (1974).
135. Y.Hirata and I.Tanaka, Chem.Phys.Letters, **41**, 336 (1971); **43**, 568 (1976).
136. R.N.Nurmukhametov and V.G.Plotnikov, Izv.Akad. Nauk SSSR, Ser.Fiz., **39**, 2259 (1975).
137. T.Kobayashi and S.Nagakura, Chem.Phys.Letters, **43**, 429 (1976).
138. W.Siebrand, J.Chem.Phys., **44**, 4055 (1966).
139. R.Engelman and J.Jortner, Mol.Phys., **18**, 145 (1970).
140. V.L.Ermolaev and E.B.Sveshnikova, Chem.Phys. Letters, **23**, 349 (1973).
141. E.N.Bodunov and E.B.Sveshnikova, Optika i Spektrosk., **36**, 340 (1974).
142. E.N.Bodunov, Optika i Spektrosk., **40**, 942 (1976).
143. V.L.Ermolaev, Uspekhi Fiz.Nauk, **80**, 3 (1963).
144. V.V.Gruzinskii, L.A.Barkova, and N.M.Poltarak, Zhur.Prikl.Spektrosk., 20, 619 (1974).
145. Yu.E.Perlin and B.S.Tsukerblat, "Effekty Elektronno-kolebatel'nogo Vzaimodeistviya v Optich-eskikh Spektrakh Primesnykh Paramagnitnykh Ionov" (Vibronic Interaction Effects in the Optical Spectra of Paramagnetic Impurity Ions), Izd. Shtiintsa, Kishinev, 1974.
146. D.N.Shigorin and V.G.Plotnikov, Dokl.Akad.Nauk SSSR, **234**, 121 (1977).
147. B.M.Krasovskii and B.M.Bolotin, "Organicheskie Lyuminofory" (Organic Phosphors), Izd.Khimiya, Leningrad, 1976.
148. V.M.Komarov and L.P.Kayshin, Stud.Biophys., **52**, 107 (1975).
149. N.A.Borisevich and V.V.Gruzinskii, Symposium "Kvantovaya Elektronika i Lazernaya Spektroskopiya" (Quantum Electronics and Laser Spectroscopy), Izd. Inst.Fiz.Akad.Nauk BelorussSSR, Minsk, 1971, p.81.
150. A.N.Simonov, Thesis, Moscow, 1975.
151. B.S.Neporent, Optika i Spektrosk., **32**, 38 (1972).
152. D.N.Shigorin, Zhur.Fiz.Khim., **51**, 1894 (1977)[Russ. J.Phys.Chem., No.8 (1977)].
153. V.G.Plotnikov and G.V.Maier, Optika i Spektrosk., **47**, 113 (1979).
154. B.A.Dolgikh and V.G.Plotnikov, Optika i Spektrosk., **47**, 231 (1979).

Obninsk Branch of the Karpov
Physicochemical Research Institute

Translated from *Uspekhi Khimii*, **49**, 362-383 (1980) U.D.C. 541.515

Chemical Chain Reactions in the Devitrification of the Matrix

I.M.Barkalov

The results of studies of the mechanisms of chain reactions occurring in the devitrification of vitreous matrices are surveyed and the characteristics of the kinetics and the mechanisms of the chain reactions accompanying the devitrification process are examined: chlorination of hydrocarbons, polymerisation, copolymerisation, and graft polymerisation. The possible applied aspects of chain reactions in the devitrification of the matrix are also considered.
The bibliography includes 64 references.

CONTENTS

I. Introduction 190
II. Destruction of radicals 191
III. Polymerisation 191
IV. Graft polymerisation 195
V. Copolymerisation 196
VI. Chlorination of hydrocarbons 198
VII. Applied aspects 200

I. INTRODUCTION

With decrease of temperature, the short-range order structure in a low-molecular-weight liquid or in a polymer varies continuously at a rate which depends on the relaxation time of the system. The rate of this rearrangement decreases as the temperature is reduced and at a certain temperature, called the glass point (T_g), the structure of the liquid or polymer is fixed and the substances passes to the vitreous state.

We may isolate two main factors which determine the probability of the conversion of a liquid into a glass rather than a crystal: a sufficiently high rate of cooling of the melt and a high viscosity in the range of crystallisation temperatures. A high viscosity of the melt retards the migration of the structural units and the relaxation time increases. Therefore at sufficiently high rates of cooling the equilibrium structure of the liquid corresponding to temperatures $T \geq T_g$ is "frozen". However, if the rate of cooling is reduced, the same liquid can be crystallised. On the other hand, typically crystallisable substances can be obtained, in principle, in a vitreous state at very high rates of cooling.

The ability of organic low- and high-molecular-weight compounds, to the reactions of which this review is devoted, to pass to the vitreous state is associated as a rule with a fairly intense intermolecular interaction in the liquid. The vitreous state is formed readily by alcohols (particularly dihydric and trihydric), amines, branched paraffins, and high-molecular-weight compounds.

The vitreous state is thermodynamically unstable but is in practice extremely stable owing to kinetic obstacles to the migration of structural units. When a vitreous substance is heated slowly in the devitrification region, there is a transition to a supercooled liquid thermodynamically unstable at the given temperature. This transition is accompanied by a fairly sharp increase in heat capacity. On the other hand, the viscosity of the system falls under these conditions. For a vitreous substance at $T \leq T_g$, the viscosity exceeds 10^{14} P, while transition to a supercooled liquid entails a fall of the viscosity to 10^7 P for silica and 10^2 P for alcohol. Naturally the sharp change in molecular mobility in the medium over a narrow temperature change should lead to extremely specific features of the mechanism of a chain reaction occurring under these conditions.

Among the chain reactions developing against the background of such a rearrangement of the matrix, polymerisation has aroused most interest among investigators. As early as 1962, it was shown[1] that vinyl acetate can be obtained in both vitreous and crystalline states. On the other hand, the rates of polymerisation under identical conditions proved to be higher by an order of magnitude for vitreous vinyl acetate than for the crystalline substance. High rates of polymerisation of vinyl monomers have been noted for the postradiation polymerisation in vitreous solutions in liquid paraffin and other solvents capable of forming a glass. The results of this series of investigations have been described in reviews[2,3]. Extremely high rates of polymerisation on devitrification of the matrix have been demonstrated for a large number of vitreous solutions of various vinyl monomers. Chapiro[2] suggested that such high rates of polymerisation at comparatively low temperatures ($T_g \cong -100°$ to -150 °C) are associated with the fact that in a vitreous matrix the monomer exists in the form of liquid microdrops incapable of forming crystals. Therefore, in spite of the very low temperatures, polymerisation takes place in a liquid monomer. However, if this hypothesis were valid, then the temperature dependence of the rate of polymerisation would undergo no sharp changes on passing through the matrix vitrification region. Nevertheless, it was shown in Chapiro's later study[3] that in all the instances investigated there is a sharp maximum in the rate in the region of the devitrification of the matrix.

In general a significant deficiency of all the early studies was the use of the traditional gravimetric method for the determination of the yield of the polymer and of the corresponding rate of polymerisation. As a result of the application of this method, the yield of the polymer, for example, at temperatures in the devitrification region, was inferred from measurements carried out at room temperature after the disintegration of the matrix. On the other hand, quantitative kinetic studies, necessary to understand the mechanisms of the chain reactions on devitrification, required primarily the development of methods whereby one could follow the process directly at the instant of its occurrence and not after its completion and disintegration of the surrounding matrix. In the first place, direct measurements of the rates of reaction, the rate constants for the elementary steps, and their temperature variations were necessary. Phase analysis of the two-component "monomer–vitrifying matrix" system, the

determination of the limits of miscibility at the glass temperatures of the system, and finally the determination of the vitrification region itself were needed in each specific instance.

Further advances in the study of the mechanisms of chain reactions on devitrification are associated mainly with the employment of the calorimetric technique in which the above methodological problems have been solved successfully. The application of the EPR method, which made it possible to follow the conversion of the active centres in radical processes directly at the instant of their occurrence, both qualitatively and quantitatively, also proved to be very fruitful. The latest advances in research into the characteristics of chain reactions on devitrification, associated mainly with the application of calorimetry and EPR, will be examined in this review.

II. DESTRUCTION OF RADICALS

Stabilised active centres accumulate in vitreous substances during their low-temperature radiolysis ($T < T_g$). Translational migrations (leading, for example, to the encounter and recombination of radicals) are greatly hindered in both crystalline and vitreous solids. This factor is in fact responsible for the comparatively high limiting concentrations of radicals which can be attained in the low-temperature radiolysis. On the other hand, the transition of the matrix to the liquid state on fusion of the crystals or to a supercooled liquid on devitrification leads to a sharp decrease of the viscosity of the system and an increase of the rate of translational movements and consequently of the rate of recombination of the radicals accumulated.

We shall consider this process in greater detail in relation to the destruction of stabilised radicals in radiolysed methanol[4]. On freezing, pure methanol crystallises and the vitreous state is not observed. However, the addition of small amounts of salts soluble in methanol such as $CoCl_2$, leads to the transition of these solutions to the vitreous state when the rate of cooling is sufficiently high. The use of differential scanning calorimetry[5] makes it possible to follow the phase transformations of the given system. When a solution of $CoCl_2$ in methanol is heated in the calorimeter in the region of the devitrification of the system (110–115 K), a sharp change in the heat capacity of the system is observed—there is a "step" (Fig.1, curve *a*). The solution then passes from the vitreous to the supercooled liquid state. On further increase of temperature, the thermodynamically unstable supercooled liquid crystallises. The crystallisation is accompanied by the evolution of heat (exothermic peak on curve *a* in Fig.1). Further heating leads to the fusion of methanol (endothermic peak). With increase of the $CoCl_2$ concentration in methanol, the viscosity of the solution apparently increases and the crystallisation of the supercooled liquid becomes increasingly more difficult. Thus, whereas approximately half of the methanol crystallises for a 2% concentration of $CoCl_2$, in 10% solution appreciable crystallisation and hence also fusion are no longer observed (Fig.1, curve *b*).

The radiolysis of such a vitreous $CoCl_2$ solution in methanol at 77 K leads to the accumulation of stabilised radicals. Measurement of the concentration of radicals by EPR shows that the stabilised radicals recombine effectively when the matrix passes from the vitreous to the liquid state. This recombination process can be followed also calorimetrically on the basis of the heat evolution accompanying it. Indeed heat evolution in irradiated specimens is observed precisely in the temperature range of the devitrification process (Fig.1, shaded exothermic peak) and the amount of evolved heat increases with increase of the dose until the attainment of a limiting concentration of radicals. The observed heat evolution is related precisely to the recombination of radicals. For a dose of approximately 100 Mrad, when the limiting concentration of radicals is attained, the contribution of charge recombination to the heat evolution can be neglected, because the concentration of charges is small compared with that of the radicals[6].

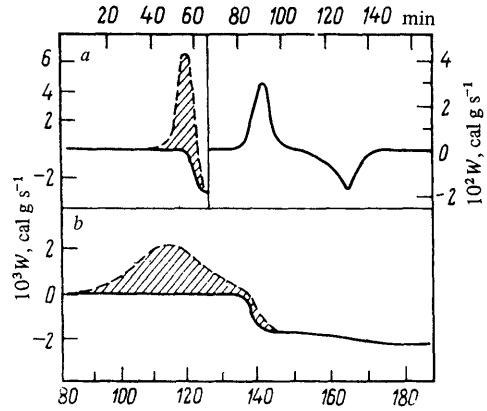


Figure 1. Calorimetric heating curves before (continuous lines) and after (dashed lines) irradiation of 2% (*a*) and 10% (*b*) solutions of $CoCl_2$ and CH_3OH with a dose of 100 Mrad at 77 K. Shaded regions—heat evolution associated with the recombination of radicals.

The radicals $^{\cdot}CH_2OH$, which are stabilised and accumulate in the low-temperature radiolysis, recombine with formation of ethylene glycol. On recombination, 70 ± 8 kcal mol^{-1} is evolved. The concentration of stabilised $^{\cdot}CH_2OH$ radicals can be calculated from the measured heat evolution. It was found that the EPR method and calorimetry yield virtually concordant results.

Thus, following the sharp change in the translational mobility of molecules, which occurs on transition from the vitreous to the supercooled liquid state, relatively small radicals recombine effectively. This takes place in systems where there exists virtually only one possible interaction channel—the recombination of radicals. In systems where the radicals liberated on devitrification are capable of initiating a chain reaction a different behaviour is observed, as will be shown below.

III. POLYMERISATION

As mentioned in the introduction, it has been shown in relation to a large number of examples that the polymerisation of vinyl monomers is sharply accelerated on devitrification of the matrix. The calorimetric method, which makes it possible to measure the rate of polymerisation directly at the instant of its occurrence, has been used successfully in an attempt to elucidate the causes of such acceleration of the polymerisation process. It has been shown by the calorimetric method[7] that the polymerisation of vitreous vinyl acetate and butylene dimethacrylate does not occur in the low-temperature radiolysis ($T < T_g$) and takes place only when the irradiated specimen

is heated in its devitrification region. It has also been established by the calorimetric technique[8] that the polymerisation of monomers in a vitrifying polymeric matrix proceeds vigorously immediately after the devitrification of the system.

Butyl methacrylate forms a complex with anhydrous zinc chloride, which passes to the vitreous state on freezing. The application of the calorimetric method in combination with EPR in the study of the postpolymerisation in the devitrification of this complex demonstrated the growth of radical chains after devitrification without termination[9]. The sharp inhibition of the termination of polymer chains in the supercooled liquid in the vicinity of the devitrification region itself provides a qualitative explanation of the high rates of polymerisation under these conditions. However, the problem of the rate of chain growth under such conditions remained open. In order to understand the mechanism of the polymerisation process on devitrification it was necessary to compare the propagation rate constants in the supercooled liquid, in the intrinsic crystal lattice of the monomer, and in the thermodynamically stable liquid.

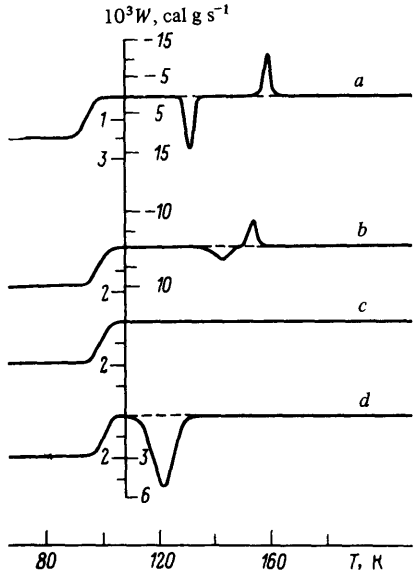


Figure 2. Calorimetric heating curves for pure ethanol (*a*), 10% (*b*) and 17% (*c*) acrylic acid solutions in ethanol, and a 17% acrylic acid solution in ethanol irradiated with ^{60}Co γ-rays for a dose of 2 Mrad at 77 K (*d*).

A system comprising a solution of acrylic acid in ethanol was studied[10] in order to solve these problems. Fig.2 shows that, when rapidly frozen (~100 K min^{-1}) solutions of acrylic acid in ethanol are warmed, the calorimeter reveals a characteristic change in heat capacity, a "step" associated with the transition of the system from the vitreous to the supercooled liquid state. On further increase of temperature in pure ethanol and dilute solutions (≤10 wt.%) of acrylic acid, the supercooled liquid crystallises and the calorimetric curve shows the corresponding heat evolution (Figs.2*a* and 2*b*). At higher temperatures the crystallised system melts (endothermic peak). With increase of acrylic acid concentration, the crystallisation of the supercooled solution after its devitrification becomes increasingly difficult and, in the presence of 17 wt.% of acrylic acid in alcohol, the solution does not crystallise at all (Fig.2*c*). All further studies were carried out[10] precisely for this simpler system—a non-crystallising 17% vitreous solution of acrylic acid in alcohol. Direct calorimetric measurements in the field of ^{60}Co γ-radiation showed that there is virtually no polymerisation in the vitreous solution of acrylic acid in alcohol at $T < T_g$. The calorimetric curve, obtained on heating the vitreous solution irradiated by ^{60}Co γ-rays at 77 K, shows an intense heat evolution, associated with polymerisation of acrylic acid, immediately after the devitrification step (i.e. after the transition to the supercooled liquid state) (Fig.2*d*). The overall yield of the polymer then reaches 80%.

At approximately 108 K the EPR spectra indicate the conversion of the monomeric radicals and the radicals of the alcohol matrix R_M, formed on radiolysis, into the radicals of the growing polymer chain R–C$_\beta$H$_2$–$^{\cdot}$C$_\alpha$H–COOH (R_p) (Fig.3).[10] In the supercooled liquid this radical assumes a non-equilibrium conformation with an angle $\phi \cong 75°$ between the axis of the unpaired electron orbital and the projection of the R–C$_\beta$ bond on to a plane perpendicular to the C$_\beta$–C$_\alpha$ bond; the EPR spectrum then consists of a doublet of triplets (Fig.3*b*). On raising the temperature to 120 K, the destruction of R_p begins, because the growing macroradicals now acquired sufficient translational mobility. Under these conditions they apparently "roll up", become surrounded by the polymer units, acquire a conformation normal for the polymer matrix with $\phi = 15°$, and give rise to a triplet EPR spectrum (Fig.3*c*).[11] The conformational transformations at the end of the growing radical in such systems has been examined in greater detail by Bol'shakov et al.[12]

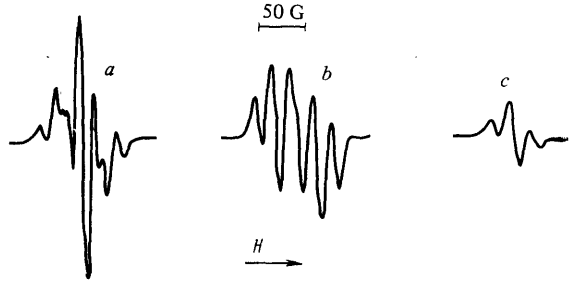


Figure 3. EPR spectra of a 17% acrylic acid solution in ethanol γ-irradiated with a dose of 2 Mrad at 77 K: *a*) at 77 K (R_M); *b*) specimen heated to 110 K (R_p); *c*) at 121 K.

Chain initiation is accompanied by the recombination of some of the monomeric radicals and only approximately half of them are converted into growing polymer radicals. On further increase of temperature, in the temperature range where acrylic acid is vigorously polymerised, the concentration of growing polymer radicals remains unchanged. Thus, over a comparatively narrow temperature range in the region of the devitrification of the matrix, the polymerisation process proceeds virtually without chain termination. This extremely important conclusion was convincingly confirmed experimentally for a whole series of systems[9,10,13,14].

Rates of polymerisation of the kind observed in a supercooled alcoholic solution of acrylic acid are reached in solid acrylic acid only at temperatures higher by 70–80 °C [15] and there is no termination of macroradicals in either case. This comparison clearly demonstrates the decisive role of the intermolecular interactions of the matrix. The translational mobility of the monomeric radicals, which is close to the mobility of the monomeric molecules, was estimated from the initial sections of the curves for the destruction of the radicals[15]. It proved to be $\nu_t \cong 2 \times 10^{-2}$ s^{-1}, while the frequency of the addition of monomeric molecules to the active centre is $\nu_p \cong 1.3 \times 10^{-3}$ s^{-1}. The frequencies of the reorientational mobility in this system are $\nu_r \cong 10^8$ s^{-1}. Thus $\nu_r \gg \nu_t > \nu_p$, i.e. the types of molecular mobility examined do not limit the polymer chain growth step.

However, the Arrhenius parameters of the propagation rate constant are very high[10]. The chain propagation rate constant in the temperature range 110–120 K has been estimated for the postpolymerisation of acrylic acid in the devitrification of the alcohol matrix[16]:

$$k_p \simeq 5 \cdot 10^{-3} \exp(-10700/RT), \text{ cm}^3 \text{ s}^{-1}.$$

The high Arrhenius parameters and their variation with increasing preliminary irradiation dose[10] indicate a cooperative nature of the process manifested by the compensation effect[17]. Consequently the monomer addition step continues to be limited by some third type of molecular movement.

After the mutual approach of the monomeric molecule and the active centre as a result of the translational and reorientational migrations, the rate-limiting stage is apparently the steric deformation of the molecules in the addition step[1c,12], for which mainly barriers to intermolecular interactions are overcome.

The monomeric radicals formed in the low-temperature radiolysis of glasses, should be destroyed when the matrix passes to the supercooled liquid state, unless they have attained during the growth process a critical length, which, when exceeded, precludes bimolecular recombination. Naturally, the rate of heating of the system by radiolysis will have a significant influence on the process mechanism: depending on the rate of heating, there either is or is not sufficient time for the monomeric radicals to be stabilised by conversion into growing polymer radicals[13]. Indeed constant heating of the system prevents the "setting" of the polymer chains and a fairly low rate of heating ensures the stabilisation of growing macroradicals[14].

On comparatively rapid (~2 K min^{-1}) heating of radiolysed vitreous butyl methacrylate, a polymer is hardly formed, while on slow heating (~0.05 K min^{-1}), virtually complete conversion is observed[13]. The postpolymerisation of pure butyl methacrylate during its devitrification is a radical process occurring in the absence of the destruction of radicals and chain transfer, i.e. proceeding via the mechanism of "living chains"[13].

A characteristic feature of the polymerisation of allylamine on devitrification of the matrix is the suppression of the "allylic termination" typical for the polymerisation of this monomer in the liquid state, this leads to the formation of a product with a very high molecular weight in such systems[18].

The nature of the chain process occurring on devitrification of the matrix depends significantly on the rigidity of the latter, the width of the devitrification temperature range, and the differences between the viscosities of the medium in the vitreous and supercooled liquid states. Thus it has been shown[19] that the radiation-induced polymerisation of vinyl chloride takes place solely in long-chain paraffin matrices, whereas in glasses consisting of low-molecular-weight paraffins a polymer is not formed. It has been suggested[20] that the supermolecular structure of the glass has a decisive influence on the development of polymerisation in the glass; in glasses comprising long-chain molecules the supermolecular formations consist of "packets" in which particularly favourable conditions may arise for the growth of polymer chains.

The polymerisation of vinyl chloride, vitrified in liquid paraffin, has been investigated on the basis of the changes in the energy losses by the ultrasonic emitter in the course of the radiolysis of the system at 77 K.[20] A change in the resistance to waves was observed in the course of the radiolysis, which the authors attributed to the formation of a polymer in the vitreous matrix at 77 K ($T_g \cong 183$ K for this system). Unfortunately the technique employed in the above study[20] did not permit the estimation of the amount of polymer formed at such low temperatures. Nevertheless, the

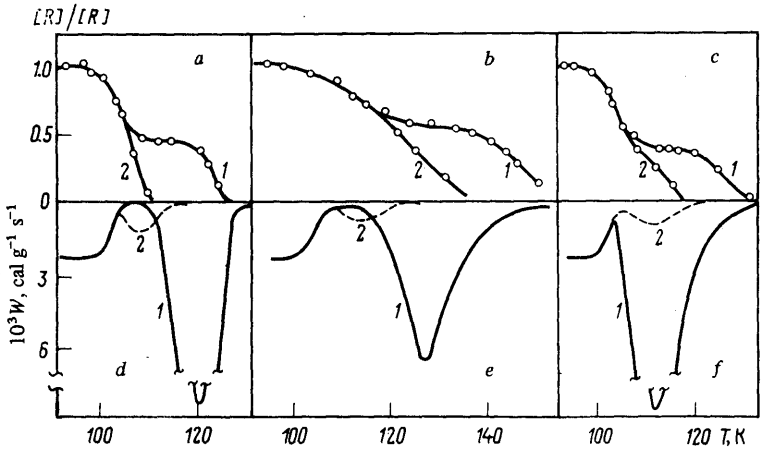


Figure 4. Temperature dependence of the stationary concentration of radicals [R_{st}] (*a*–*c*) and of the rate of polymerisation (*d*–*f*)(calorimetric heating curves) in γ-irradiated solutions (17 wt.%): *1a*) and *1d*) acrylic acid; *1b*) and *1e*) acrylamide; *1c*) and *1f*) methyl acrylate; *2a*) and *2d*) methacrylic acid; *2b*) and *2e*) methacrylamide; *2c*) and *2f*) methyl methacrylate.

main bulk of the polymer in these systems is formed on devitrification of the matrix[2]. The growth of polymer chains in the vitreous matrix at temperatures much smaller than T_g is believed[20] to take place in the region of extended defects in the glass, at the boundary between the ordered elements of the type of packets and the disordered medium.

Infrared spectroscopy has been used to investigate the characteristics of the chain propagation and termination reactions in the polymerisation of vinyl chloride vitrified in liquid paraffin[21]. It was established that, under isothermal conditions, the polymerisation is retarded in the system investigated, a further increase of temperature resulting in its acceleration. The phenomenon is extremely similar to the problem of the "setting" and "reviving" of polymer chains, first established[22] for solid-phase polymerisation.

It has been shown that, in postpolymerisation in supercooled alcoholic solutions, the reactivities of acrylic and methacrylic derivatives differ sharply[23]. Whereas on raising the temperature of vitrified alcoholic solutions of acrylic acid, acrylamide, and methyl acrylate, the yield of the polymer is 80%, the corresponding yield for their methacrylic analogues—methacrylic acid, methacrylamide, and methyl methacrylate—does not exceed 3–5% under identical conditions (Figs.4*d*–4*f*, cf. curves *1* and *2*).[23]

When solutions irradiated at 77 K are heated above T_g, the chain initiation and propagation are accompanied by the partial recombination of the radicals. The first monomer addition step, leading to the formation of an oligomeric radical, can be detected from the EPR spectra. For acrylic and methacrylic derivatives, the relative concentrations of the oligomeric radicals proved to be similar (Figs.4*a*–4*c*). Consequently the sharp difference between the rates of polymerisation of acrylic and methacrylic derivatives is not associated with the difference between the efficiencies of the initiation processes. With increase of the length of the growing polymer chain, its translational mobility falls and hence there is also a decrease of the probability of the destruction of the chain by recombination. For acrylic derivatives the concentration of the growing polymer radicals remains constant over a temperature range (Figs.4*a*–4*c*) and the polymer chain grows virtually without termination (Figs.4*d*–4*f*). On the other hand, a completely different picture is observed for methacrylic derivatives, The oligomeric radicals R_{ol} possess a fairly high translational mobility, are not stabilised, and recombine rapidly (Figs.4*a*–4*c*, curve *2*).

In order to elucidate the causes of such a sharp difference, the EPR spectra were analysed and the conformations of the terminal macroradicals in acrylic and methacrylic derivatives were determined from the hyperfine splitting by β-protons[23]. As a result of the interaction with the alcohol matrix, the terminal macroradicals of acrylic monomers exist in a specific conformation (Fig.5*a*, spectrum *2*), which differs from the conformation characteristic of the polymerisation of monomers in the crystalline state[10]. Methacrylic monomers do not give rise to a specific conformation and the terminal macroradicals have the same conformation as in their polymerisation in the crystal lattice of the monomer. The EPR spectra of the growing macroradicals are virtually identical in the polymerisation of methacrylic acid in a supercooled alcohol matrix (Fig.5*b*) and in its own crystal matrix (Fig.5*c*). Hence it follows that the presence of the CH_3 group near the reaction centre prevents the interaction of the growing macroradicals with the alcohol matrix, which leads to an increase of the probability of chain termination and to a decrease of the yield of the polymer. On the other hand, for acrylic monomers, the growing macroradical is associated with the alcohol molecules surrounding it, which leads to the formation of a specific conformation and the "coat" formed prevents its destruction. This is apparently the main cause of the sharp difference between the characteristics of the polymerisation of acrylic and methacrylic monomers[24]. On the other hand, the difference between the propagation rate constants is small and cannot account for the large difference in behaviour. Thus in a liquid medium $k_p = 1.45 \times 10^6 \exp(-4700/RT)$ for methyl acrylate and $k_p = 5.35 \times 10^5 \exp(-4700/RT)$ litre mol^{-1} s^{-1} for methyl methacrylate[25].

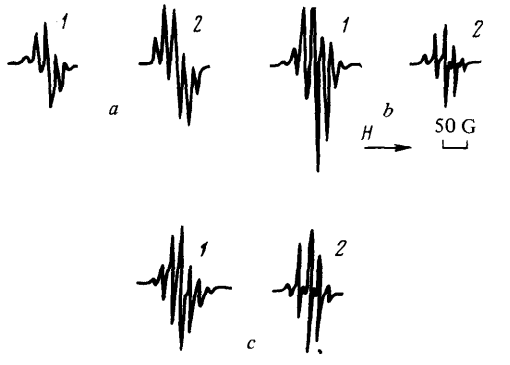


Figure 5. EPR spectra of 17% solutions γ-irradiated with a dose of 2 Mrad at 77 K: *a*) acrylic acid in ethanol at 77 K (curve *1*) and 120 K (curve *2*); *b*) methacrylic acid in ethanol at 77 K (curve *1*) and 112 K (curve *2*); *c*) spectrum of a polycrystalline methacrylic acid specimen at 77 K (curve *1*) and of the growing radical at 300 K (curve *2*).

Thus, in contrast to the usual liquid-phase polymerisation, a sharp difference is observed in the capacities of acrylic and methacrylic monomers for polymerisation on devitrification, which is associated with the more intense interaction with the growing acrylic macroradicals with the medium.

On heating irradiated vitreous monomers or their solutions, the following picture is thus observed: in the vicinity of the devitrification region the matrix is softened to such an extent that the conversion of monomeric radicals into the oligomeric radicals of the growing chain becomes possible. However, the characteristic times for the elementary chain propagation step are in this region extremely long and the chain growth is limited by the supply of the monomer to the growing active centre. With increase of temperature, the viscosity of the system is significantly reduced on passing to the supercooled liquid state, which facilitates the supply of the comparatively small monomer molecules to the growing polymer radical. At the same time, the viscosity of the supercooled liquid is still sufficiently high to prevent the bimolecular destruction of the macroradicals of the growing polymer chains. In this temperature range the polymerisation develops in accordance with the "living chain" mechanism. At high temperatures the matrix softens to such an extent that the bimolecular destruction of the growing macroradicals becomes possible and leads to the cessation of polymerisation. Such ideas concerning the mechanism of the polymerisation process on transition of radiolysed vitreous solutions of monomers to the supercooled liquid state proved to be applicable to a wide range of systems.

The polymerisation processes occurring on devitrification of the matrix by an ionic mechanism have also been investigated in fair detail. Not only radicals but also trapped electrons are known to be stabilised in glasses on low-temperature radiolysis. It has been found that there exist conditions under which ionic active centres stabilised in glasses can initiate ionic polymerisation. The anionic postpolymerisation of acrylonitrile has been observed on heating its vitrified solutions in methyltetrahydrofuran[26], dimethylformamide, and triethylamine[3] after the latter have been subjected to low-temperature radiolysis. The polymerisation process in these systems reached a maximum immediately after the transition of the system from the vitreous to the supercooled liquid state.

The polymerisation of the above systems at temperatures exceeding T_g was not observed, but it was possible to observe postpolymerisation via an ionic mechanism. It was found that the addition of acetone during the heating of vitreous acrylonitrile solutions fully suppresses its anionic polymerisation. It is noteworthy that, in a study of this system, the authors[26] noted for the first time the decisive role of the rate of heating of the radiolysed glass, showing that, when the system is heated slowly, a much greater amount of polymer is produced.

The anionic mechanism of postpolymerisation on devitrification has been demonstrated most clearly in the study of the polymerisation of nitroethylene vitrified in a methyltetrahydrofuran glass[27]. Electrons stabilised in the low-temperature radiolysis of glasses can be ejected from traps by visible and ultraviolet light, whereupon they recombine with holes. This optical "bleaching" method was first used to suppress ionic polymerisation[28] in order to demonstrate the ionic mechanism of the polymerisation of solid acrylonitrile. By subjecting nitroethylene glasses in methyltetrahydrofuran radiolysed at 77 K to optical bleaching before heating, the authors[27] showed that the postpolymerisation of this monomer is fully suppressed on devitrification of the matrix.

A cationic mechanism of the polymer chain propagation has been observed in the postpolymerisation of styrene vitrified in hexachlorobutadiene and methylene chloride[26]. Under comparable conditions, the amount of polymer formed in the above systems is smaller by an order of magnitude than in the anionic polymerisation of acrylonitrile on devitrification. However, here too a sharp maximum of the rate of polymerisation is observed in the region of the devitrification of the system. A qualitatively identical picture has been found for the polymerisation of a whole series of other systems on devitrification[29]. Cationic polymerisation on devitrification has also been observed for the postpolymerisation of isobutene vitrified in a poly(vinyl chloride) matrix[26].

Thus one must conclude that the characteristics of the polymerisation process on devitrification of the matrix, namely (1) the formation, before the transition of the system from the vitreous to the supercooled liquid state, of growing active centres sufficiently long to prevent their destruction and (2) the occurrence of the polymerisation reaction over a narrow temperature range above T_g without the termination of the growing active centres, are associated mainly with the specific physical nature of the rearrangement of the matrix on devitrification and are qualitatively the same for the radical and ionic mechanisms of chain propagation.

IV. GRAFT POLYMERISATION

Not only low-molecular-weight compounds but also polymers can be used as vitrifying matrices. As will be shown below, the same qualitative behaviour has been observed for vitreous solutions of a monomer in a polymer matrix as in the post-polymerisation of acrylic acid in an alcohol matrix. However, whereas the formation of macroradicals before the transition to the supercooled liquid state was necessary for polymerisation on devitrification of alcoholic solutions of the monomer in order to reduce the probability of the termination of the growing chains, when polymers are used as matrices, this condition is fulfilled automatically.

On cooling to 77 K, polyisobutylene passes to the vitreous state (Fig. 6*a*).[8] At low concentrations the monomers dissolved in it, for example acrylonitrile (the monomers were introduced into polyisobutylene by swelling it in the monomer vapour at room temperature), pass to the vitreous state without phase separation. The calorimetric heating curve for such solutions does not show peaks corresponding to the fusion of the individual monomers, although the sensitivity of the calorimeter was quite sufficient. Consequently, at these monomer concentrations the system consists of a solution over the entire temperature range. At higher temperatures part of the monomer becomes segregated as a separate phase on cooling and the calorimetric curve shows a monomer fusion peak (Fig. 6*b*). We may note that the calorimetric method is in this case convenient for the determination of the limiting solubility of the monomer in the polymer at the low temperatures employed.

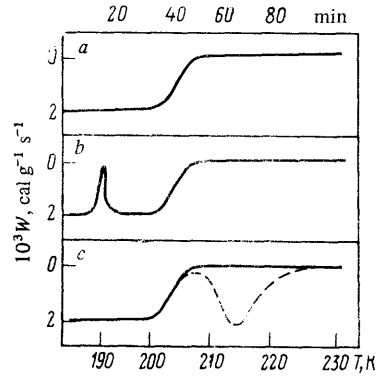


Figure 6. Calorimetric heating curves: *a*) polyisobutylene; *b*) 2% acrylonitrile solution in polyisobutylene; *c*) 1% acrylonitrile solution in polyisobutylene irradiated with 5 Mrad dose at 77 K.

As for monomers vitrified in an alcohol matrix, intense polymerisation is observed in radiolysed vitreous solutions of a monomer in a polymer on their devitrification (Fig. 6*c*). It can be easily shown that, in the low-temperature radiolysis of such vitreous solutions (monomer concentration 1–2%), mainly macroradicals of the polymer matrix are formed and stabilised. On devitrification, they acquire a sufficient mobility for the initiation of the polymerisation of the monomer introduced. Thus the polymerisation of the polymer matrix is initiated by macroradicals under the given conditions, i.e. graft polymerisation takes place. Since the monomer was first dissolved in the polymer matrix, polymers grafted in the bulk phase are formed.

In contrast to the usual methods of radiation-induced graft polymerisation—joint radiolysis of the polymer and the monomer (as a rule at temperatures higher than T_g for the polymer) and postpolymerisation of monomers on a radiolysed polymer matrix (*in vacuo* or in the presence of oxygen)[30,31]—graft polymerisation on devitrification makes it possible to employ most efficiently the macroradicals formed on radiolysis for the initiation of the grafted chains. The above factor is associated with the fact that, near T_g for the polymer matrix, conditions are created under which the destruction of the macroradicals formed is still difficult, while the supply of small monomer molecules to the growing active centres proceeds readily. This explains the high rates of graft copolymerisation observed under these conditions.

Intense graft polymerisation on devitrification of monomer solutions in polyisobutylene has been observed for a whole series of vinyl monomers: styrene, methyl acrylate, methyl methacrylate, etc.[8] Intense grafting of acrylonitrile, dissolved in poly(vinyl chloride), has been observed in the devitrification of the polymer matrix[32]. In the grafting of acrylonitrile, effective cross-linking of the macromolecules of the polymer matrix was also observed on devitrification of polyisobutylene as a result of the involvement of the C≡N group in the reaction[8]. Subsequently the grafting of acrylonitrile was used to cross-link polyethylene, and the cross-linking of macromolecules as a result of the dissociation of the C≡N groups of the grafted chains was demonstrated experimentally[33].

Radiation-induced graft polymerisation of readily polymerisable monomers such as tetrafluoroethylene by the method involving the joint irradiation of the monomer and polymer is extremely difficult. The point is that under these conditions the homopolymerisation of the monomer becomes the dominant process. Grafting on to polymers subjected to preliminary irradiation is also ineffective (for example, only 2–3% of tetrafluoroethylene can be grafted onto polyethylene[34]). The yield of the graft polymer can be increased only by employing polyethylene with an extremely high surface area and by carrying out the reaction at reduced temperatures[35]. However, under these conditions too the rate of reaction is low. The method of postradiation grafting on devitrification proved to be the most satisfactory in this instance[36].

To achieve partial dissolution of tetrafluoroethylene in powdered polyethylene (grain size 10–20 μm) and to fill the micropores in the polymer grains by the monomer, the polymer was first kept in liquid tetrafluoroethylene under a small pressure. The system was then cooled to 77 K and radiolysed. The calorimetric heating curve for this system (Fig.7) shows that the heat evolution associated with the graft polymerisation of tetrafluoroethylene is recorded starting from approximately 225 K. The grafting process takes place most effectively in the range 230–250 K, i.e. in the region of the devitrification of the amorphous portions of the polyethylene matrix. The yield of the graft polymer then reaches 200–300% (relative to the weight of the initial polyethylene). The graft polymer is soluble in boiling xylene and its infrared spectra clearly reveal absorption bands at 1160–1200 cm^{-1}, which are absent from the spectrum of polyethylene and are characteristic of polytetrafluoroethylene[36].

This method of grafting tetrafluoroethylene on devitrification of the matrix could be extended also to other polymeric supports. Treatment of polypropylene and ethylenepropylene rubber in liquid tetrafluoroethylene leads to the partial dissolution of the monomer in the polymer. When such a solution is cooled, it passes to the vitreous state without phase separation. When specimens of this kind, subjected to low-temperature radiolysis, are heated, vigorous polymerisation takes place on devitrification of the matrix[37].

Thus, when polymers are used as vitrifying matrices, the same qualitative picture is observed as for low-molecular-weight matrices with the sole difference that graft copolymers are formed. The advantages of the method of postradiation grafting on devitrification of the polymer matrix are as follows: (1) decrease of the irradiation dose required to obtain a specific yield of the graft polymer relative to the usual methods; (2) the formation of polymers grafted in the bulk phase—in the usual methods grafting takes place as a rule in the surface layer; (3) the possibility of grafting readily polymerisable monomers such as tetrafluoroethylene.

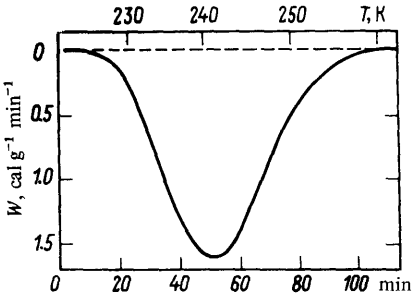


Figure 7. Postradiation grafting of tetrafluoroethylene in the devitrification of a polyethylene matrix. Irradiation dose 5 Mrad at 77 K.

V. COPOLYMERISATION

When the copolymerisation reaction is carried out in liquid and gas phases, the composition of the copolymer is determined by the relative reactivities of the comonomers and a homogeneous copolymer is obtained only in the initial stage of the copolymerisation. As one of the monomers is consumed, the resulting copolymer is as a rule enriched in the less reactive monomer and the polymer chains have an inhomogeneous composition.

As already mentioned above, a characteristic feature of the supercooled liquid state obtained on devitrification is a comparatively high viscosity. This feature must be manifested in some way in altering, compared with the usual liquids, the capacity of monomers for polymerisation. The preceding section presented examples of the sharp differences between the polymerisation capacities of acrylic and methacrylic derivatives on devitrification, while on polymerisation in the liquid state the propagation rate constants for these monomers were comparable as regards order of magnitude. Hence it was natural to expect that copolymerisation on devitrification can lead to a composition of the copolymer different than in the liquid phase copolymerisation.

The copolymerisation of methyl methacrylate with styrene on devitrification of an aniline matrix has been investigated[38]. A 30% solution of the monomer in aniline was devitrified at approximately 170 K. The copolymerisation was carried out by irradiating the system at 178 K, i.e. already in the supercooled liquid state. The authors claim that the composition

of the copolymer formed under these conditions is identical to that obtained on radical polymerisation, but they do not quote experimental data confirming this[38]. Subsequently these results were not confirmed either.

A series of studies on the mechanism of alternating copolymerisation in a vitreous system were carried out at Moscow State University[39-43]. Copolymerisation on devitrification in systems such as methyl methacrylate and methyl acrylate in the presence of $ZnCl_2$ and other complex-forming agents[39], butyl acrylate and 2,3-dimethylbutadiene, also in the presence of a complex forming agent[40], maleic anhydride and dimethylbutadiene[41], and sulphur dioxide together with a series of electron-donating monomers[43] takes place with formation of alternating copolymers. The introduction of a complex-forming agent into these systems entails a sharp increase of the cross chain propagation rate constant. Thus the copolymerisation proceeds via a mechanism involving the consecutive addition of monomers to the end of the growing chain. The cause of this mechanism is the possibility of donor–acceptor interactions between the chain growth radical and the monomer[41].

Another cause of the formation of an alternating copolymer is the formation of a charge-transfer complex between two monomeric species. Its reactivity is higher than that of each monomeric species and the alternation is thus explained by the homopolymerisation of this complex[43]. Sulphur dioxide probably forms a charge-transfer complex with dimethylbutadiene; on cooling, the system passes to the vitreous state. When a radiolysed glass of this kind is heated in the range $T_g \cong 113-133$ K, vigorous copolymerisation is observed. A 1:1 alternating copolymer is formed and its composition is almost independent of that of the initial mixture. The mechanism of the alternation consists in the addition of the complex formed by the monomers to the end of the growing chain[43].

The copolymerisation on devitrification of radiolysed alcoholic solutions of monomers in the absence of complex formation has been studied by Bol'shakov et al.[44] It was investigated for two pairs of comonomers: acrylic acid with acrylamide and acrylamide with methyl acrylate. For an overall concentration of comonomers in ethanol of 17 wt.%, the solution passes fully to the vitreous state on cooling. On subsequent heating, the solution devitrifies at $T_g \cong 102$ K and the supercooled liquid does not crystallise. When the monomer ratio is altered (but the overall concentration of the monomers in ethanol remains at 77 wt.%) over a wide range, the form of the calorimetric curve remains unaltered; consequently, over the entire temperature range from 77 to 300 K, when the monomer ratio is altered from 1:8 to 8:1, the monomers remain uniformly distributed throughout the bulk of the specimen, as in a liquid solution.

On devitrification of radiolysed solutions of this kind, vigorous heat evolution, associated with the copolymerisation, is observed. The yield of the copolymer increases monotonically with increasing preliminary irradiation dose and reaches approximately 95%. The copolymerisation could be interrupted, after the attainment of any required extent, by heating the specimen rapidly (at approximately 250 K min^{-1}) to room temperature. When the yield of the copolymer was altered from 1 to 90%, its composition hardly changed (Fig.8). Nevertheless, the composition of the copolymer in the systems investigated by Bol'shakov et al.[44] could be varied by altering the initial ratio of the monomers in solution. This means that the composition of the copolymer depends solely on that of the initial solution. For a solution of acrylic acid and acrylamide in ethanol, the composition of the resulting copolymer fully corresponds to that of the initial solution, while the composition of the copolymer obtained on radiation-induced copolymerisation of these monomers in the liquid phase at room temperature is determined by their relative reactivities, the copolymerisation constants being $r_1 = 0.25$ and $r_2 = 0.77$ respectively[45].

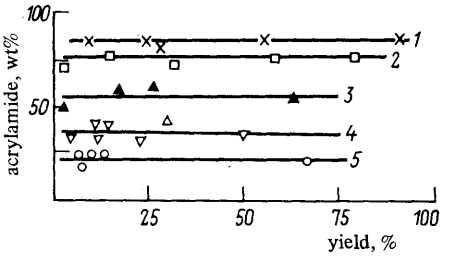


Figure 8. Dependence of the content of acrylamide in the copolymer on the degree of conversion for a 17% solution in ethanol; acrylamide : acrylic acid ratio (by weight): 1) 9:1; 2) 4:1; 3) 1:1; 4) 1:2; 5) 1:5.

The composition of the copolymer has also been found to be independent of the degree of conversion in the copolymerisation on devitrification of an alcoholic solution of acrylamide and methyl acrylate. However, up to an 80% content of acrylamide in the initial solution of this system, its content in the copolymer remains smaller throughout than in the initial mixture although it does continue to increase[44].

In the viscous supercooled liquid formed on devitrification of the solutions, the time of the mutual contact between the reacting species is much longer than in gas and liquid phases and the frequencies of the addition of the monomer to the active centre of the growing polymer chain are comparable in order of magnitude to the frequencies of the translational migrations of the monomers in the system[10]. Thus the increased viscosity of the supercooled liquid leads to a sharp increase of the time of mutual contact between the comonomers. On the other hand, the rate of growth of the polymer chain is not limited by diffusion under these conditions, because the frequency of the addition of the monomer to the growing macroradical is not limited by the rate of the translational migrations[10]. Presumably the increase of the time of mutual contact between the growing macroradical and the monomer in the systems indicated actually leads to the addition of the monomer in virtually every collision, in contrast to the behaviour observed in the usual liquids; this is in fact responsible for the identity of the compositions of the initial solution and the copolymer.

Such increase of the time of mutual contact between the reactants and the supercooled liquid gives rise to the hope that compounds which are not usually regarded as monomers can be involved in copolymerisation on devitrification. An interesting example of such copolymerisation and devitrification is provided by the acetone–acrylic acid system[46]. The polymerisation of acetone via the carbonyl group was first reported by Kargin et al.[47] Polyacetone was later obtained also by solid-phase radiation-induced polymerisation[48]. This polymer proved to be very unstable and decomposed rapidly to the monomer even at room temperature. Thermostable acetone–acrylic acid copolymers have been obtained by copolymerisation on devitrification[49]. When solutions of acrylic acid in acetone are cooled rapidly, partly or fully

vitreous specimens are formed. The amount of the vitreous phase then depends on the rate of cooling and on the concentration of the monomer in the solution. A fully vitrified specimen can be obtained by cooling a 10% solution of acrylic acid in acetone at a rate of 150 K min^{-1}. The calorimetric heating curve for such a specimen reveals devitrification at approximately 110 K; next, at approximately 133 K, a eutectic mixture crystallises from the supercooled liquid and then melts at 165 K.

When a vitreous solution of acrylic acid in acetone irradiated at 77 K is heated slowly in the calorimeter, heat evolution associated with polymerisation is observed immediately after the system passes to the supercooled liquid state. The conditions governing the formation of the polymer fully ruled out the possibility of the physical retention of acetone by the polymer matrix. The amount of unreacted acrylic acid was determined by titration and the yield of the polymer was calculated in relation to the amount of acrylic acid in the polymer. Fig. 9 illustrates the dependence of the yield of the polymer on the concentration of acrylic acid in the initial solution. In dilute solutions the yield of the polymer reaches 250%, which corresponds to the composition of the polymer: two acetone molecules per acrylic acid unit. With increase of the concentration of acrylic acid, the yield of the polymer falls rapidly to 130–140% and is then almost independent of the composition of the initial solution.

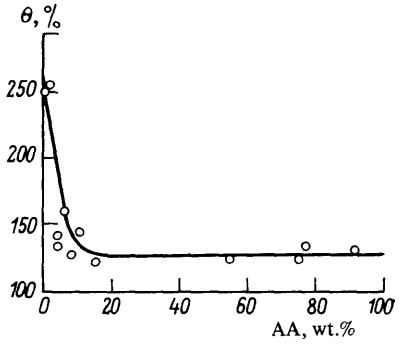
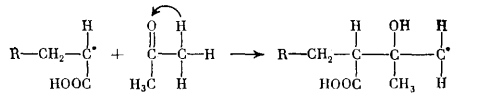
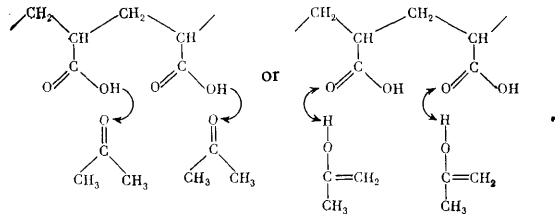


Figure 9. Dependence of the yield of the acrylic acid–acetone copolymer (θ) on the initial acrylic acid (AA) concentration in acetone. The yield of the polymer is referred to the acrylic acid which has reacted.

The incorporation of acetone into the composition of the polymer is observed also when the system is irradiated in the liquid state at 195 K.[50] 100% conversion is rapidly attained in the first stage of the polymerisation. This rapid stage is followed by a fairly slow stage, in which the conversion reaches 140–150% with respect to the acrylic acid which has reacted. It is extremely interesting that the incorporation of acetone into the copolymer is fully suppressed by traces of water. At the same time, traces of water do not have this kind of inhibiting influence on the homopolymerisation of acrylic acid. Two mechanisms, explaining the incorporation of acetone into the polymer formed have been proposed: (1) copolymerisation of acrylic acid and the enolic form of acetone:



[this mechanism is similar to that proposed previously for the polymerisation of acetaldehyde with formation of poly(vinyl alcohol)[51,52]]; (2) the formation of associated species comprising one or other tautomeric form of acetone and polyacrylic acid:



VI. CHLORINATION OF HYDROCARBONS

The chlorination of paraffinic hydrocarbons and their chloro-derivatives in the gas and liquid phases on radiation initiation and photoinitiation has been investigated in fair detail[53]. However, the characteristic features of the mechanism of these processes in solid and viscous media have been hardly studied. Investigations carried out recently have shown that the characteristics of the chain process occurring on devitrification of the matrix, demonstrated in relation to the polymerisation reaction, are maintained qualitatively also in reactions such as the chlorination of paraffins.

The characteristic features of low-temperature radiation-induced chlorination in vitrifying matrices have been studied for the butyl chloride–molecular chlorine system[54]. Solid chlorine undergoes no phase transformations and melts at 172 K (Fig. 10*a*). Butyl chloride passes to the vitreous state on fairly rapid cooling and, when such a specimen is heated, devitrification is observed at 96 K (Fig. 10*b*). On further increase of temperature, butyl chloride crystallises and then melts at a temperature as low as 150 K. A solution of chlorine in butyl chloride was prepared in the dark and no chemical reaction was observed. On cooling, this solution also passes to the vitreous state. The simplest phase transformations are observed on dissolution of one mole of Cl_2 in three moles of C_4H_5Cl—after devitrification the solution does not crystallise and does not melt (Fig. 10c). Consequently, for these proportions of the reactants, phase separation does not occur in the vitrifying solution. This finding is extremely important, because the interpretation of kinetic data for homogeneous one-component systems is significantly simplified.

The heat of the radiation-induced chlorination in the system investigated is 33 kcal per mole of chlorine. The relations presented in Fig. 11 shows that the radiation-induced chlorination takes place with acceleration at 114 K. The retardation of the process and the subsequent fall of the rate are associated with the consumption of the initial chlorine.

The radiation-induced chlorination of butyl chloride takes place in the solid phase, i.e. at temperatures below the devitrification region. When the system passes from the vitreous to the supercooled liquid state, the rate of reaction rises (Fig. 11). A characteristic feature of the process in this temperature range is a virtually linear increase of the rate of chlorination as a function of time. When the initiating γ-radiation is switched off, the rate of the process gradually falls. The characteristic time of the decrease of the rate of

chlorination after switching off γ-irradiation has been determined as $\tau_0 \cong 1500$ s. Such a slow decrease of the rate indicates a long lifetime of the active centres in the supercooled liquid at the temperatures indicated. This finding is in fact responsible for the non-stationary process kinetics—the accumulation of active centres in the course of the radiolysis entails an increase of the rate of the process with time in the initial stage.

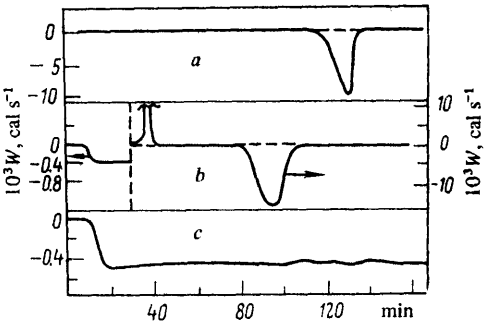


Figure 10. Calorimetric heating curves: *a*) chlorine (3.7×10^{-3} M); *b*) butyl chloride (5.26×10^{-3} M); *c*) chlorine solution (8.7×10^{-4} M) in butyl chloride (2.4×10^{-3} M).

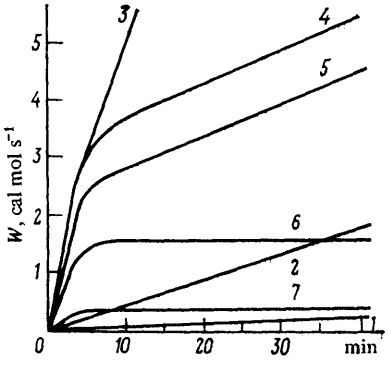


Figure 11. Time variation of the rate of radiation-induced chlorination of butyl chloride at different temperatures (K): 1) 98; 2) 107; 3) 113; 4) 118; 5) 122; 6) 127; 7) 150. Dose rate 30 rad s^{-1}.

The kinetics of the process change significantly with increase of temperature (Fig.11). The process takes place most vigorously at 114 K. On further increase of temperature, the matrix softens, which leads to a sharp decrease of the lifetime of the active centres. At 127 K a constant rate of the process is established immediately (more precisely after the characteristic time of the calorimetric apparatus has elapsed) when the ionising radiation is switched off. The increase probability of chain termination lowers the overall rate of the process over the increase of temperature.

The radiation-induced chlorination of butyl chloride on devitrification of the matrix can be described by the following simple scheme:

$$ClRH \overset{\gamma}{\rightsquigarrow} ClR^{\cdot} + H^{\cdot}, \quad (1)$$

$$ClR^{\cdot} + Cl_2 \rightarrow ClRCl + Cl^{\cdot}, \quad (2)$$

$$Cl^{\cdot} + ClRH \rightarrow ClR^{\cdot} + HCl, \quad (3)$$

$$\left.\begin{matrix} Cl^{\cdot} \\ ClR^{\cdot} \end{matrix}\right\} \rightarrow \text{termination}. \quad \begin{matrix} (4) \\ (5) \end{matrix}$$

In the temperature range 98–114 K the termination of the kinetic chains is extremely slow ($1/\tau_0 \cong 6.6 \times 10^{-4}$ s^{-1}). Judging from the data of Eckling and Goldfinger[55], the rate constant for reaction (2) in the photochemical chlorination of C_2H_5Cl in the temperature range in which we are interested can exceed by several orders of magnitude the rate constant for reaction (3). Consequently, reaction (3) will limit the rate of the given process. For the initial rate of the process (when chain termination can be neglected), we obtain the following expression[54]:

$$w_0 = -d[ClRH]/dt \simeq k_3 g I t [ClRH], \quad (6)$$

where g is the radiation yield of the centres initiating the chlorination and I the intensity of the γ-radiation.

Using this expression, the temperature variation of k_3 was determined from the initial sections of curves *1–3* in Fig.11. This relation is illustrated in Fig.12 (curve *1*). Assuming that $g \cong 1$ in Eqn.(6), we can estimate the constant k_3, which has the following value in the range 98–114 K:

$$k_3 \simeq 10^{11} \cdot \exp(-5600/RT) \text{ litre mol}^{-1} \text{ s}^{-1}. \quad (7)$$

As already mentioned, at higher temperatures the rate of termination increases sharply and a stationary rate of the chlorination process is established. Assuming that the kinetic chains are terminated mainly by reaction (5), the following expression is obtained for the stationary rate of chlorination:

$$w_{st} = -d[ClRH]/dt = k_3/k_4 g I [ClRH]. \quad (8)$$

An analogous expression for the stationary rate has been used[56] after the same assumptions to describe the radiation-induced liquid-phase chlorination of tetradecane. Indeed, in conformity with Eqn.(8), the rate in this temperature range rapidly attains a stationary value and ceases to depend on time (Fig.11, curves *6* and *7*). On substituting Eqn.(8) the values of k_3 calculated by Eqn.(7) and the value of w_{st} (Fig.11, curves *6* and *7*), we obtain $k_4 = 7$ s^{-1} (for 150 K) and $k_4 = 0.05$ s^{-1} (for 127 K). Taking into account the experimental value $k_0 = k_4 = 6.6 \times 10^{-4}$ s^{-1} for 107 K, we obtain the temperature variation of k_4 in the range 150–107 K (Fig.12, curve *2*) and the following expression for the termination rate constant:

$$k \simeq 10^{12} \cdot \exp(-7400/RT), \text{ s}^{-1}.$$

It follows from Eqn.(8) that the activation energy for the overall process $E_{OV} = E_3 - E_4 - 5.6 - 7.4 = -1.8$ kcal mol^{-1}. A similar activation energy in fact characterises the rate of the overall process in this temperature range (Fig.12, curve *3*).

Thus, as in polymerisation, the chain chlorination of chloroalkanes in the supercooled liquid state is characterised by a long lifetime of the active centres. With increase of temperature in the supercooled liquid, the rate of chain propagation reaches a maximum and, when the liquid passes to the thermodynamically stable state and the viscosity of the medium falls sharply, the probability of termination increases. Consequently the suppression of the chain termination process combined with the attainment of conditions ensuring

effective chain growth—conditions which are automatically obtained in the vicinity of the region of devitrification of the system—make it possible to increase significantly the overall rate of reaction.

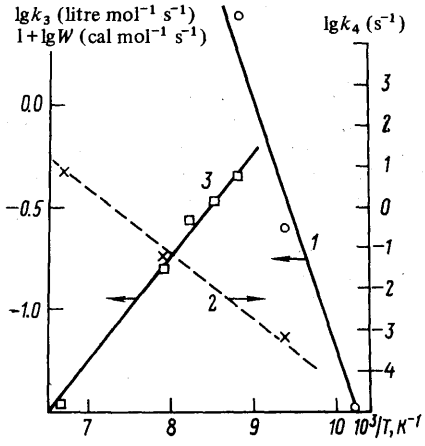


Figure 12. Temperature variation of the rate constants k_3 (line *1*) and k_4 (line *2*) and of the rate of radiation-induced chlorination of butyl chloride for a 4% degree of conversion of chlorine (curve *3*).

Possibly other low-temperature chain processes, such as, for example, hydrohalogenation and halogenation of olefins, the interaction of N_2O_4 with unsaturated compounds, etc.[57,58] under conditions corresponding to the devitrification of the matrix will be characterised by the suppression of chain termination with simultaneous attainment of conditions ensuring vigorous chain propagation.

VII. APPLIED ASPECTS

Graft polymerisation on devitrification of the matrix permits an effective use of the active centres and hence of the expensive ionising radiation energy which generates them. The employment of this process for the grafting of tetrafluoroethylene appears to be most promising. The prospect of the modification of polymeric materials and articles by grafting to impart to them properties close to the unique properties of polytetrafluoroethylene is extremely attractive. The grafted layer of polytetrafluoroethylene can significantly lower the coefficient of friction of the polymer surface and increase its thermal and chemical stabilities. The use of tetrafluoroethylene grafts in order to regenerate PTFE waste is also promising[59,60]. In all these processes the method of graft polymerisation on devitrification of matrices can be used successfully.

A new class of polymerisable oligomers—oligocarbonate-acrylates—is characterised by high rates of radiation-induced hardening[61,64]. All the oligocarbonate-acrylates investigated pass to the vitreous state on rapid cooling. When the oligomers irradiated in the vitreous state are heated, intense postpolymerisation is observed after the system passes to the supercooled liquid state (Fig. 13). The efficiency of the method is so high that a dose of only 100 krad is sufficient for the required degree of hardening[61,63].

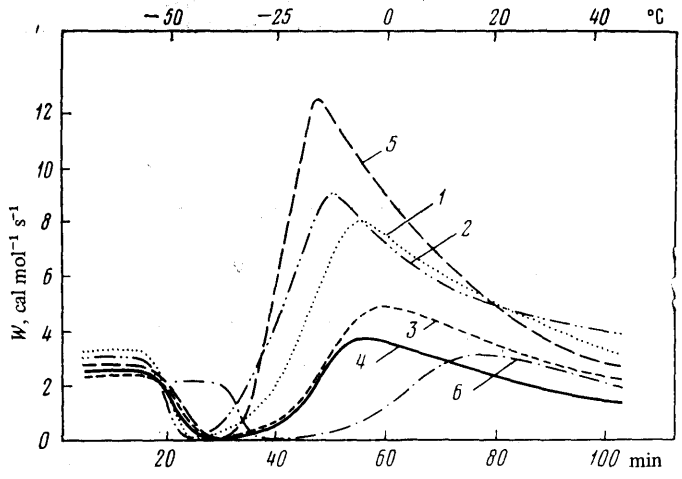


Figure 13. Calorimetric heating curves for oligocarbonate-acrylates irradiated with an 8 krad dose of ^{60}Co γ-rays at 77 K: 1) OKM-3; 2) OKM-4; 3) OKA-2; 4) OKM-1; 5) OKM-2; 6) OKM-7.

For low doses of the preliminary irradiation (1–5 krad), the presence of atmospheric oxygen dissolved in the oligomer causes sharp inhibition of the process and the appearance of an induction period. However, when the preliminary irradiation dose is increased to 50–100 krad, the inhibiting effect of oxygen ceases to influence the kinetics of the hardening process. This effect is probably associated with the increase of the rate of initiation of the process. The absence of an inhibiting influence of oxygen in a closed system even for a dose of 50–100 krad is of interest. Indeed, the elimination of the stickiness of the surface layers (insufficient hardening due to inhibition by oxygen) constitutes a serious problem in the radiation-induced hardening of coatings based on polymerisable oligomers.

The selection of the appropriate vitrifying matrix makes it possible to carry out the chain reaction at extremely low temperatures—as a rule significantly below the melting points of the reactants. On the other hand, the occurrence of a chain reaction in the crystal lattice is hindered by the low translational mobility of the reactants. Furthermore a chain reaction at the lowest possible temperature is of interest because a decrease of temperature entails a kind of selection of the possible reaction channels. Indeed, the channel with the lowest activation energy "survives" at low temperatures. Thus a decrease of the reaction temperature should lead to a high process selectivity. Furthermore, with decrease of temperature, the entropy factors, which are so important in the thermodynamics of chemical reactions, play a continuously decreasing role and the equilibrium in all the reactions is therefore displaced towards exothermic reactions, even those in which highly ordered systems are produced. On the other hand, the employment of vitrifying matrices permits chain reactions at temperatures close to 77–100 K.

REFERENCES

1. I.M.Barkalov, V.I.Gol'danskii, N.S.Enikolopyan, S.F.Terekhova, and G.M.Trofimova, Dokl.Akad.Nauk SSSR, **147**, 396 (1962).
2. A.Chapiro, Chimia (Switz.), **21**, 454 (1967).
3. A.Chapiro, A.M.Jendrychowska-Bonamour, and L.Perec, Amer.Chem.Soc., Advances in Chemistry Series, 1968, Vol.82, p.513.
4. E.F.Abdrashitov, D.P.Kiryukhin, L.A.Tikhomirov, and I.M.Barkalov, Khim.Vys.Energii, 7, 274 (1973).
5. A.M.Kaplan, D.P.Kiryukhin, I.M.Barkalov, and V.I.Gol'danskii, Khim.Vys.Energii, **3**, 460 (1969).
6. S.Fujii and J.E.Willard, J.Phys.Chem., **74**, 4313 (1970).
7. I.G.Gusakovskaya, V.G.Nikol'skii, and V.I.Gol'danskii, Khim.Vys.Energii, **4**, 434 (1970).
8. I.P.Kim, A.M.Kaplan, I.M.Barkalov, and V.I.Gol'danskii, Dokl.Akad.Nauk SSSR, **193**, 855 (1970).
9. G.S.Georgiev, A.M.Kaplan, V.P.Zubov, V.B.Golubev, I.M.Barkalov, V.I.Gol'danskii, and V.A.Kabanov, Vysokomol.Soed., **A14**, 177 (1972).
10. A.I.Bol'shakov, A.I.Mikhailov, I.M.Barkalov, and V.I.Gol'danskii, Dokl.Akad.Nauk SSSR, **205**, 379 (1972).
11. P.Yu.Butyagin, A.M.Dubinskaya, and V.A.Radtsig, Uspekhi Khim., **38**, 593 (1969)[Russ.Chem.Rev., No.4 (1969)].
12. A.I.Bol'shakov, A.I.Mikhailov, and I.M.Barkalov, Teor.Eksper.Khim., **9**, 831 (1973).
13. A.M.Kaplan, B.La.Serna, I.L.Stoyachenko, E.I.Shklyarova, V.B.Golubev, V.P.Zubov, V.A.Kabanov, and V.I.Gol'danskii, Dokl.Akad.Nauk SSSR, **224**, 829 (1975).
14. A.M.Kaplan, I.L.Stoyachenko, V.B.Golubev, and V.I.Gol'danskii, Vysokomol.Soed., **17B**, 259 (1975).
15. A.I.Bol'shakov, A.I.Mikhailov, I.M.Barkalov, and V.I.Gol'danskii, Vysokomol.Soed., **15A**, 470 (1973).
16. A.I.Bol'shakov, A.I.Mikhailov, and I.M.Barkalov, Vysokomol.Soed., **19B**, 906 (1976).
17. Ya.S.Lebedev, Yu.D.Tsvetkov, and V.V.Voevodskii, Kinetika i Kataliz, **1**, 496 (1960).
18. M.Ya.Kreindel', L.I.Andreeva, A.M.Kaplan, V.B.Golubev, M.N.Masterova, V.P.Zubov, L.S.Polak, and V.A.Kabanov, Vysokomol.Soed., **18A**, 2233 (1976).
19. G.N.Gerasimov, A.D.Smirnov, T.M.Sabirova, and A.D.Abkin, Vysokomol.Soed., **11B**, 636 (1969).
20. G.N.Gerasimov, A.D.Smirnov, T.M.Sabirova, and A.D.Abkin, Vysokomol.Soed., **16A**, 1530 (1974).
21. G.N.Gerasimov, T.A.Bespyatkina, T.M.Sabirova, and A.D.Abkin, Dokl.Akad.Nauk SSSR, **209**, 628 (1973).
22. A.M.Kaplan, D.P.Kiryukhin, I.M.Barkalov, and V.I.Gol'danskii, Vysokomol.Soed., **9B**, 639 (1969).
23. A.I.Bol'shakov, A.I.Mikhailov, and I.M.Barkalov, Vysokomol.Soed., **19B**, 781 (1976).
24. A.I.Bol'shakov, A.I.Mikhailov, and I.M.Barkalov, Vysokomol.Soed., **20A**, 1820 (1978).
25. Kh.S.Bagdasar'yan, "Teoriya Radikal'noi Polimerizatsii" (Theory of Radical Polymerisation), Izd. Nauka, Moscow, 1966.
26. M.Bodar, Thesis, University of Paris, 1967.
27. I.Katsu, K.Tsuji, K.Hayashi, and S.Okamura, J.Polymer Sci., **A-1**, 5, 1899 (1967).
28. I.M.Barkalov, "Kinetics and Mechanism of Polyreactions", IUPAC Symposium on Macromolecular Chem., Budapest, 1969, p.555.
29. H.Yamaoka, I.Ohama, K.Hayashi, and S.Okamura, J.Polymer Sci., **A-1**, **8**, 495 (1970).
30. B.L.Tsetlin, Doctoral Thesis, Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow, 1970.
31. A.Chapiro, "Radiation Chemistry of Polymeric Systems", Intersci.Publ., 1962.
32. A.Chapiro and A.M.Jendrychowska-Bonamour, French P.1479353 (1966).
33. M.S.Joshi, K.Singer, and J.Silverman, Radiat.Phys. Chem., 9, 475 (1977).
34. K.Jobst, "Kinetics and Mechanism of Polyreactions", Internat.Symp., Budapest, 1969, p.317.
35. Y.Tabata, J.Fujikawa, S.Shu, and K.Oshima, J.Macromolec.Sci.Chem., A5, 793 (1971).
36. T.I.Nevel'shaja, I.P.Kim, and I.M.Barkalov, J.Macromolec.Sci., A11, 91 (1977).
37. M.R.Muidinov, D.P.Kiryukhin, M.K.Asamov, and I.M.Barkalov, Vysokomol.Soed., **A20**, 360 (1978).
38. L.Azikonda and L.Perec-Jaulin, "IUPAC Symposium on Macromolecular Chemistry", Budapest, 1969, Vol.4, 8118, p.86.
39. V.P.Zubov and V.A.Kabanov, Vysokomol.Soed., **13A**, 1305 (1971).
40. G.S.Georgiev, N.P.Appolonova, V.B.Golubev, V.P.Zubov, and V.A.Kabanov, Vysokomol.Soed., **14A**, 643 (1972).
41. I.L.Stoyachenko, G.S.Georgiev, V.B.Golubev, V.P.Zubov, and V.A.Kabanov, Vysokomol.Soed., **15A**, 1899 (1973).
42. V.B.Golubev, V.P.Zubov, G.S.Georgiev, I.L.Stoyachenko, and V.A.Kabanov, J.Polymer Sci., **A-1**, **11**, 2463 (1973).
43. I.L.Stoyachenko, E.I.Shklyarova, A.M.Kaplan, V.B.Golubev, V.P.Zubov, and V.A.Kabanov, Vysokomol.Soed., 18A, 1420 (1976).
44. A.I.Bol'shakov, A.I.Mikhailov, and I.M.Barkalov, Dokl.Akad.Nauk SSSR, **241**, 1355 (1978).
45. G.Hardy and L.Nagy, "Internat.Symp.of Macromolec. Chem., Prague, 1965", p.319.
46. A.I.Bol'shakov, A.I.Mikhailov, I.M.Barkalov, and V.I.Gal'danskii, Dokl.Akad.Nauk SSSR, **222**, 633 (1975).
47. V.A.Kargin, V.A.Kabanov, V.P.Zubov, and I.M.Papisov, Dokl.Akad.Nauk SSSR, **134**, 1098 (1960).
48. S.Okamura and K.Hayashi, X Ann.Meeting of Soc. High Polymer, Japan, Tokyo, 1961.
49. A.I.Bolshakov, A.I.Mikhailov, I.M.Barkalov, and V.I.Goldanskii, US P.3896084 (1975).
50. I.M.Barkalov, A.Chapiro, and A.M.Jendrychowska-Bonamour, Applied Polymer Symp., **26**, 175 (1975).
51. T.Omoto and T.Matsubara, J.Polymer Sci., **56**, 669 (1962).
52. I.M.Papisov, T.A.Pisarenko, and V.A.Kabanov, Dokl.Akad.Nauk SSSR, **156**, 669 (1964).
53. R.V.Dzhagatspanyan and M.T.Filippov, "Radiatsionnaya Khimiya Galogensoderzhashchikh Organicheskikh Soedinenii" (Radiation Chemistry of Halogen-Containing Organic Compounds), Atomizdat, Moscow, 1973.
54. D.P.Kiryukhin, I.M.Barkalov, and V.I.Gol'danskii, Khim.Vys.Energii, 11, 438 (1977).
55. R.Eckling and P.Goldfinger, Chem.Ber., **93**, 3014 (1960).
56. R.V.Dzhagatspanyan and V.I.Kosorotov, Khim.Vys. Energii, **3**, 531 (1969).
57. G.B.Sergeev, Symposium, "Sovremennye Problemy Fizicheskoi Khimii" (Current Problems in Physical Chemistry), Izd.Moskov.Gos.Univ., 1970, Vol.**4**, p.**20**.

58. G.B.Sergeev and A.P.Shvedchikov, Zhur.Vses.Khim. Obshch.im.Mendeleeva, **18**, 52 (1973).
59. N.I.Kholodov, V.M.Kholodova, V.G.Chernakov, I.M.Barkalov, V.I.Gol'danskii, A.I.Mikhailov, A.N.Ponomarev, and V.S.Os'kin, USSR P.524813 (1976); Byul.Izobret., No.30, 66 (1976).
60. V.M.Kholodova, I.M.Barkalov, V.I.Gol'danskii, A.I.Mikhailov, and N.I.Kholodov, Vysokomol.Soed., **19A**, 1638 (1977).
61. I.M.Barkalov, A.A.Brikenshtein, V.I.Gol'danskii, D.P.Kiryukhin, V.M.Munikhes, and A.A.Radugina, Dokl.Akad.Nauk SSSR, **222**, 1357 (1975).
62. I.M.Barkalov, A.A.Brikenshtein, V.I.Gol'danskii, D.P.Kiryukhin, V.M.Munikhes, and A.A.Radugina, Dokl.Akad.Nauk SSSR, **231**, 641 (1976).
63. I.P.Kim, D.P.Kiryukhin, I.M.Barkalov, V.T.Shashkova, T.Ya.Kefeli, and A.A.Berdin, Vysokomol. Soed., **20A**, 23 (1978).
64. V.M.Munikhes, S.I.Kuzina, D.P.Kiryukhin, A.I.Mikhailov, and I.M.Barkalov, Vysokomol.Soed., **20A**, 810 (1978).

Division of the Institute of Chemical Physics of the USSR Academy of Sciences, Chernogolovka

RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

March 1980

Translated from *Uspekhi Khimii*, 49, 385-419 (1980)

U.D.C. 621.039 + 541.11

Thermodynamics of Isotope Exchange Reactions

N.M.Zhavoronkov, D.A.Knyazev, A.A.Ivlev, and G.D.Klinskii

The present state of the theory of the equilibrium chemical isotope effect is examined and the methods for the approximate and exact calculation of the partition functions of the isotopic forms of polyatomic molecules are analysed. Also analysed is the possibility of employing the chemical isotope effect for the interpretation of the force fields of molecules of transition complexes; relations between the isotope effects associated with the stepwise substitution of isotopes, coupled isotope effects, etc, are considered.
The relations between the isotope effects and the structural and general chemical phenomenological characteristics of compounds are discussed and a systematic treatment of chemical isotope effects together with the methods for the statistical prediction of the magnitude of these effects are considered.
The bibliography includes 117 references.

CONTENTS

I.	Introduction	203
II.	Thermodynamics of isotope exchange reactions	204
III.	Methods for the interpretation of chemical isotope effects	207
IV.	Characteristics of the variability of isotope effects	211
V.	Systematic treatment of chemical isotope effects and their prediction	216

I. INTRODUCTION

For a long time the interest in chemical isotope effects was concentrated on the possibility of using them for the separation of the isotopes of light elements. During the last 10–12 years, much more attention has been devoted to them but largely for other reasons. It was found that the measurement of isotope effects is useful for research in many fields of chemistry, biochemistry, and geochemistry. For example, the kinetic hydrogen and carbon isotope effects have been used successfully to study the mechanisms and activated complexes of organic reactions; the hydrogen, carbon, and sulphur effects have been employed to predict the presence of petroleum and natural gas in geometrical regions, the oxygen and hydrogen effects have been used in paleogeothermometry, and the effects of biogenic elements have found applications in the study of the mechanisms of cell metabolism.

The value of isotope effects as sources of information in research is due to one specific feature of their theory. Statistical thermodynamics reveals a relation, of rare simplicity, between the isotope effects and the characteristics of intramolecular force fields. This feature makes it possible to infer intramolecular characteristics directly from changes in macroscopic quantities—the isotope concentrations, but not conversely, which is in general characteristic of the applications of the molecular-statistical theory. Hence follows the possibility of securing information about the force fields not only of simple stable molecules, which can be studied by other

methods, but also of investigating short-lived compounds and fragments of large molecules, which play an important role in chemical, biochemical, and geochemical systems and mechanisms.

The general, extensive literature on chemical isotope effects has been reflected systematically in frequently published reviews, specialised compilations, and monographs. Being unable to analyse the state of the problem in fields adjoining chemistry, we shall indicate the reviews and monographs dealing with various aspects of the applications of isotope effects in biochemistry[1-5] and geochemistry[6-13]. Compilations and review articles have been devoted to chemical isotope exchange reactions used for the separation of stable isotopes of light, medium, and heavy elements (ranging from hydrogen to uranium inclusive)[14-20]. The results of the study of isotope effects[18-22] and their applications to the study of molecular structures[14-24], reaction kinetics and mechanisms[21,24-29], phase exchange[14,24,30], solutions, and the behaviour of solvents[14,24,30] are reflected in the reviews and monographs quoted above.

However despite their relatively large number, the aim of the review articles published in the last decade was to inform the reader about fairly narrow questions and they consisted too often of handbooks and bibliographic compilations. Owing to their specialist characteristics, both the reviews and monographs are concerned either only with the main features or only with special features of the general theory, so that a general picture of the scope of the theory is not built up.

Nevertheless, in many of the fields indicated, the interpretation of chemical isotope effects is invariably based on the thermodynamics of isotope exchange reactions. This is because the methods for the analysis of kinetic and equilibrium isotope effects are fundamentally the same and are based on the general theoretical apparatus of statistical thermodynamics and the theory of the vibrations of polyatomic molecules. Significant new theoretical results, which make it an effective weapon in the hands of research chemists, biochemists, and geochemists, have not as yet been described in one publication. Nor has any attempt been made to carry out a combined analysis of isotope effects which would reflect their relation to the chemical nature and specific features of the elements. The aim of the present review is to fill these gaps to some extent.

II. THERMODYNAMICS OF ISOTOPE EXCHANGE REACTIONS

1. General Theory

In the general case a chemical compound can contain an element undergoing isotope substitution in several different non-equivalent positions. Non-equivalent atoms are characterised by different equilibrium and kinetic isotope effects, while equivalent atoms have identical effects.

Following the procedure of Varshavskii and Vaisberg[31], we shall consider the equilibrium in the isotope exchange of an element X between two compounds AX_n and BX_m. The first contains n atoms X capable of isotope substitution in the given equivalent positions. The remainder of the molecule of A may contain exchangeable atoms of the element X, but in other equivalent positions, which are not taken into account in the present treatment. Similarly in the molecule BX_m account is taken only of the exchange of m equivalent atoms of the element X. If the numbers n and m are not unity, the exchange of isotopes X and X′ will proceed through a series of stages. Each stage can be formulated as:

$$AX_{n-i+1}X'_{i-1} + BX_{m-j}X'_j \rightleftarrows AX_{n-i} + X'_i + BX_{m-j+1}X'_{j-1}, \quad (1)$$

where $i = 1,2,\ldots,n$ and $j = 1,2,\ldots,m$.

The equilibrium constant K_{ij} for this stage can be expressed in terms of the concentrations of the isotopic forms:

$$K_{ij} = \frac{[AX_{n-i}X_i]\ [BX_{m-j+1}X'_{j-1}]}{[AX_{n-i+j}X'_{i-1}]\ [BX_{m-j}X_j]}. \quad (2)$$

In all there are nm independent stages in the reaction under consideration with equilibrium constants of the type defined by Eqn.(2). Their sequence, from the first to the last, corresponds to the overall exchange reaction between the fully substituted isotopic forms:

$$mAX_n + nBX_m' \rightleftarrows mAX'_n + nBX_m \quad (3)$$

whose equilibrium constant K_Σ is equal to the product of the constants K_{ij}:

$$K_\Sigma = \prod_{i=1}^{n}\prod_{j=1}^{m} K_{ij}. \quad (4)$$

The real equilibrium includes all nm stages and is characterised by the isotope separation factor α measured experimentally:

$$\alpha = \frac{[X'_{AX_n}]/[X_{AX_n}]}{[X'_{BX_m}]/[X_{BX_m}]}, \quad (5)$$

where [X] and [X′] are the overall mole fractions of the isotopes X and X′ in the compounds AX_n and BX_m.

The quantities K_{ij}, K_Σ, and α are related to one another and to the symmetry numbers of the isotopic forms of the molecules AX_n and BX_m by the following expressions:

$$K_{ij} = \alpha \frac{\sigma(AX_{n-i+1}X'_{i-1})\,\sigma(BX_{m-j}X'_j)}{\sigma(AX_{n-i}X'_i)\,\sigma(BX_{m-j+1}X'_{j-1})}, \quad (6)$$

$$K_\Sigma = \alpha^{nm}. \quad (7)$$

Statistical thermodynamics expresses the equilibrium constant K_{ij} in terms of the partition functions Q of the isotopic forms of the compounds AX_n and BX_m:

$$K_{ij} = \frac{Q'_{AX_n}/Q_{AX_n}}{Q'_{BX_m}/Q_{BX_m}}, \quad (8)$$

where the prime refers to forms AX_n and BX_m containing the larger number of atoms of the X′ isotope.

In the ideal gas approximation, usually employed for chemical equilibrium, one neglects the dependence of the partition functions on the phase state of the given substance, which makes it possible to calculate these quantities from molecular spectra and molecular constants without taking into account the interactions of the molecules. A further simplification is achieved by employing the Born–Oppenheimer approximation concerning the subdivision of the internal energy of molecules into the electronic, spin-nuclear, vibrational, rotational, and translational components[32]. For the majority of isotope equilibria, this approximation is also the only one possible, since more accurate calculations require much more detailed information about the molecular force field.

In the calculation of thermodynamic isotope effects there is no necessity to calculate the electronic and spin-nuclear components of the partition function. The electronic component does not differ from the statistical weight of the electronic ground state for the vast majority of molecules in the range 0–2000 K, since the excited electronic levels are usually much higher than the ground levels. For the rare molecules where there is a possibility of thermal excitation of even one electronic level, the total partition functions must be calculated for each level separately because excitation is accompanied by a sharp change in the vibrational characteristics and a very significant change in the rotational characteristics of the molecules[33,34]. An analogous situation obtains also for the spin-nuclear component, which plays a significant role only for molecular hydrogen, where it must be taken into account by

calculating separately the partition functions for the *ortho*- and *para*-forms[35].

The exclusion of the electronic and spin-nuclear components reduces the task of finding the thermodynamic isotope effects to the calculation of the vibrational, rotational, and translational partition functions or, in the refined version, to the calculation of the vibrational-rotational and translational partition functions.

In the most accurate studies the vibrational-rotational component is calculated taking into account the anharmonicity of the vibrations, the centrifugal stretching effect, and the effects associated with vibration-rotation interactions[36,37]. However, the information required for this purpose is available for very few molecules and in the calculation of the isotope effects of all elements except hydrogen one therefore employs simplified models of the vibrational and rotational motions, which are assumed to be independent. The simplest and most widely used harmonic oscillator–rigid rotator model neglects the three corrections enumerated above, and makes it possible to resolve completely the rotational and vibrational partition functions[38,39].

The calculation of the thermodynamic isotope effects does not require the separate determination of the partition functions for each isotopic form of the compound. It is more rational to calculate the ratio of the partition functions of the isotopic forms (RPFIF) of the given molecule.

In terms of the "rigid rotator–harmonic oscillator" approximation, the RPFIF, also denoted by f, can be formulated as follows[27,40]:

$$f = \frac{\sigma}{\sigma'}\left(\frac{M'}{M}\right)^{3/2}\left(\frac{I'_A I'_B I'_C}{I_A I_B I_C}\right)^{1/2}\exp\left[\frac{hc}{2kT}\left(\sum_i d_i\omega_i - \sum_i d'_i\omega'_i\right)\right]\frac{\prod_i [1-\exp(\omega_i hc/kT)]^{d_i}}{\prod_i [1-\exp(\omega'_i hc/kT)]^{d'_i}}, \quad (9)$$

where M is the molecular weight, $I_A I_B I_C$ the product of the moments of inertia of the molecule relative to the three (principal) Cartesian axes, ω_i the ith harmonic vibration frequency, and d_i the multiplicity of its degeneracy; the primes refer, as in Eqn.(8), to isotopic forms containing a greater number of atoms of the isotope X′. If the prime is attributed to isotopic forms of molecules containing a greater number of heavy isotope atoms involved in exchange while the symbols without prime are assigned to forms with a greater number of light isotope atoms, then Eqn.(9) leads to a convenient specific relation: $f\sigma'/\sigma \geq 1$.

Eqn.(9) can be significantly simplified by the application of the Teller–Redlich theorem[41,42], which relates the moments of inertia, the vibration frequencies, the molecular weights M and M', and the masses of the isotopes m and m' in the isotopic forms, which differ in the isotopes of a single element:

$$\frac{I'_A I'_B I'_C}{I_A I_B I_C}\left(\frac{M'}{M}\right)\left(\frac{m}{m'}\right)^{3n}\prod_i\left(\frac{\omega}{\omega'}\right)^2 = 1. \quad (10)$$

Substitution of Eqn.(10) in Eqn.(9) leads to the following relation:

$$f = \frac{\sigma}{\sigma'}\left(\frac{m'}{m}\right)^{3n/2}\frac{\prod_i \{\omega'_i \exp(-\omega'_i hc/2kT)[1-\exp(-\omega_i hc/2kT]^{-1}\}^{d'_i}}{\prod_i \{\omega_i \exp(-\omega_i hc/2kT)[1-\exp(-\omega_i hc/2kT]^{-1}\}^{d_i}}. \quad (11)$$

The multiplier $(m'/m)^{3n/2}$, determined by the masses of the pair of isotopes under consideration, enters into all the RPFIF referring to this pair of isotopes; in the calculation of isotope effects it always cancels out and is therefore omitted. In most studies the ratio σ/σ', which is equal to RPFIF when all isotope distributions are equally probable, is transferred to the left-hand side of Eqn.(11). The so-called reduced frequencies $\omega_i hc/kT$ are in general designated by u_i. When account is taken of these conventional procedures and notations, Eqn.(11) can be put in the form

$$\left(\frac{\sigma'}{\sigma}\right)f = \frac{\prod_i \{u'_i \exp(-u'_i/2)[1-\exp(-u'_i)]^{-1}\}^{d'_i}}{\prod_i \{u_i \exp(-u_i/2)[1-\exp(-u_i)]^{-1}\}^{d_i}} = \frac{\prod_i [\mathrm{sh}(u_i/2)/u_i]^{d_i}}{\prod_i [\mathrm{sh}(u'_i/2)/u'_i]^{d'_i}}. \quad (12)$$

The difficulty of the determination of the quantities $(\sigma'/\sigma)f$ by Eqn.(12) depends on the number of atoms in the molecule and on the symmetry of the isotopic forms under consideration. The symmetry numbers σ and the degree of degeneracy of the vibration classes d_i and d'_i depend on the latter. With decrease of the symmetry of the given form, the degrees of degeneracy diminish and the orders of the submatrices of the secular equations of vibrational motion increase. The latter implies an increase of the number of non-identical cofactors in the products in the numerator and denominator of Eqn.(12). In the limit one of the products can have $3N-6$ cofactors, but the main difficulties in the application of Eqn.(12) do not depend on the fact that the number of cofactors can be large. A large number of non-identical frequencies implies a sharp increase of the difficulty of their calculation, because the frequencies of isotopic forms are usually unknown and are found by solving the secular equations using particular models of the potential energy of the molecules.

Evidently the number of different isotopic forms $AX_{n-i}X'_i$ of the compound AX_n is $n+1$; in order to characterise fully the thermodynamic non-equivalence of these forms, it is necessary and sufficient to calculate n independent values of the RPFIF.

For equilibrium between the molecules of AX_n and BX_m, the calculation of the isotope effects requires the determination of $n+m$ values of the RPFIF, and, as just shown, each of these determinations can be very complicated. A successive radical simplification of the calculation of isotope effects is achieved by replacing the RPFIF for all possible pair combinations of the isotopic forms for any molecule by the simplest functions of a single RPFIF referring to the fully substituted forms AX_n and AX'_n. This replacement not only greatly reduces the number of RPFIF required for the consideration of the equilibrium (two instead of $n+m$), but also simplifies to the maximum extent the very calculation of these two necessary values of the RPFIF, since the high and identical symmetries of the fully substituted forms reduce to a minimum the number of different vibration frequencies.

The "rules of the sums of isotopic frequencies", first obtained by Sverdlov[45,46] and Decius and Wilson[47] and subsequently modified by Broderson[48], follow from the theory of the vibrations of polyatomic molecules[42–44]. These rules can be represented by the formula

$$\sum_i^{3N-6}\omega_i^{2p}(AX_{n-j}X'_j) - \sum_i^{3N-6}\omega_i^{2p}(AX_{j-k}X'_{n-(j+k)}) = \sum_i^{3N-6}\omega_i^{2p}(AX_{n-l}X'_l) - \sum_i^{3N-6}\omega_i^{2p}(AX_{n-(l+k)}X'_{l+k}), \quad (13)$$

where the symbols X and X′ refer to the light and heavy isotopes of the element X respectively and p is any integer.

Using Eqn.(13) with $p = 1,2$, Bigeleisen[17,49] showed that, for the values of $\ln(f\sigma'/\sigma)$ referring to different members of the isotope-homologous series $AX_{n-j}X_j$, the "geometrical mean rule", which assumes the general form

$$\frac{1}{j-k}\ln\left[\frac{\sigma'}{\sigma}f(AX_{n-j}X'_j/AX_{n-k}X'_k)\right] = \text{const}. \quad (14)$$

holds with an adequate degree of approximation. This rule, first discovered empirically in an early study by Urey[40], has been frequently subjected to numerical tests[15,17,49,50], which invariably confirmed its adequate accuracy [the deviation from the rule does not exceed 1.0% of $\ln(f\sigma'/\sigma)$].

When the isotopic equilibrium of a specific pair of isotopes is considered, the geometrical mean rule makes it possible to characterise the entire set of isotopic homologues by a single value of the RPFIF, which establishes an unambiguous (isomorphous) correspondence between the chemical compound (molecule, ion) and the characteristics of its possibilities as regards isotope separation. Varshavskii and Vaisberg[31] suggested that the concept of the β-factor, which is related to f, be used for this purpose. If the RPFIF refers to the fully substituted forms AX_n and AX'_n containing n equivalent atoms of X capable of isotope substitution, then, regardless of the complexity of the compounds and the value of n, the following very simple relation holds:

$$\ln\beta = \frac{1}{n}\ln f\,(AX_n/AX'_n). \tag{15}$$

The advantage of the concept of the β-factor over the RPFIF thus consists in the fact that it defines unambiguously the degree of thermodynamic non-equivalence of two isotopes in the given molecule, while the RPFIF includes in addition the equally probable distribution factor, which is equal to the ratio of the symmetry numbers. The expression for the β-factor can be written in the form

$$\ln\beta = \frac{1}{n}\sum_i d_i \ln\left\{\frac{u'_i \exp(-u'_i/2)\,[1-\exp(-u'_i/2)]^{-1}}{u_i \exp(-u_i/2)\,[1-\exp(-u_i/2)]^{-1}}\right\} \tag{16}$$

or

$$\ln\beta = \frac{1}{n}\sum d_i \ln\left[\frac{\mathrm{sh}\,(u_i/2)}{\mathrm{sh}\,(u'_i/2)}\Big/\frac{u_i}{u'_i}\right] \tag{17}$$

Eqn.(16) has become the main working relation in most studies devoted to the thermodynamics of isotope exchange and kinetic isotope effects, although the necessary stipulations concerning the conditions governing its application are not made in many investigations.

Brodskii[51] and Varshavskii and Vaisberg showed in the general case[31] that, when account is taken of the equal probabilities of the distributions of isotopes between all the isotopic forms of substances AX_n and BX_m, the isotope separation factor α, corresponding to the equilibrium in the entire set of type (2) reactions, is given by the very simple equation

$$\alpha = \beta_{AX_n}/\beta_{BX_m}. \tag{18}$$

The simplicity of Eqn.(18) constitutes yet another piece of evidence demonstrating the superiority of the concept of the β-factor compared with that of RPFIF.

In view of the difference in the significance of these concepts, we thought it essential to confine ourselves to only one of them in the present review, namely the β-factor. Nevertheless, in order to simplify and facilitate the exposition, both terms are used in the text below. Unless otherwise stated, here the significance of the term "RPFIF" is always identical to that of the term "β-factor".

2. Refined Quantum-Statistical Relations

The "harmonic oscillator–rigid rotator" approximation, to which Eqns.(12), (16), and (17) correspond, ensures an accuracy of the calculation of the RPFIF sufficient for the majority of practical problems in the thermodynamics of isotope exchange. Here we shall consider the refinements and corrections which follow from improved models and which are necessary in certain special situations. At the same time, such treatment should indicate the limits of the accuracy of Eqn.(12), (16), and (17).

Real molecules are anharmonic oscillators and non-rigid rotators. Different vibrations of polyatomic molecules are not independent. The same applies to the vibrational and rotational motions of the molecule as a whole. Furthermore, the energies of states with zero vibrational quantum numbers differ from the quantity $hc\omega_i/2$. Finally, account must be taken of the effects of the internal rotation of groups in the molecule and (at low temperatures) of the difference between the rotational partition functions and their classical values (quantisation effects). The influence of these factors on the RPFIF decreases approximately in the following sequence: (1) anharmonicity and interaction between the vibrations; (2) quantum effects of the rotation; (3) hindered internal rotation; (4) non-rigidity of the rotators (centrifugal stretching); (5) interaction between rotation and vibrations.

All these corrections are introduced in the form of the corresponding multipliers of the quantity β_{harm} found by Eqns.(12), (16), or (17) in terms of the "harmonic oscillator–rigid rotator" approximation:

$$\beta_{exact} = \beta_{harm}\, C_1 C_2 C_3 C_4 C_5. \tag{19}$$

The correction for anharmonicity C_1 includes simultaneously the effect of the deviation of the shape of the potential energy surfaces of the molecules from the parabolic form and the interaction of different normal vibrations[36,52,53]. The vibrational energy levels of polyatomic molecules are usually specified by the expression[39]

$$E_{vibr} = \sum_i hc\omega_i\left(v_i+\frac{1}{2}\right) + \sum_i hcx_{ii}\left(v_i+\frac{1}{2}\right)^2 + \sum_{i<j} hcx_{ij}\left(v_i+\frac{1}{2}\right)\left(v_j+\frac{1}{2}\right) + \ldots, \tag{20}$$

in which v_i and v_j are the vibrational quantum numbers of the vibrations i and j and x_{ii} and x_{ij} are anharmonicity constants. Since the forms of the potential energy surfaces have been little studied, we shall confine ourselves to the first terms of the expansion of E_{vibr} in Eqn.(20). In terms of this approximation, the correction for anharmonicity is[52,53]

$$C_1 = \exp\left[\frac{hc}{4kT}\sum (x'_{ij}-x_{ij})\,d_i d_j\right]\cdot\left\{1+\frac{hc}{kT}\sum d_i(d_i+1)\times\right. \tag{21}$$
$$\left.\times\left[\frac{x'_{ii}\cdot e^{u'_i}}{(e^{u'_i}-1)^2}-\frac{x_{ii}e^{u_i}}{(e^{u_i}-1)^2}\right]+\frac{hc}{kT}\sum d_i d_j\left[\frac{x'_{ij}(e^{u_i}+e^{u_j})}{(e^{u'_i}-1)(e^{u'_j}-1)}-\frac{x_{ij}(e^{u_i}+e^{u_j})}{(e^{u_i}-1)(e^{u_j}-1)}\right]\right\}$$

The first term in this expression, which reflects the influence of anharmonicity on the zero-point energy, makes the main contribution. The expression in braces corresponds to the thermal excitation of the vibrational levels and at the usual temperatures hardly differs from unity. Taking this factor into account, the correction for anharmonicity in relation to Eqns.(16) and (17) is expressed thus:

$$C_1 = \exp\left[\frac{hc}{4kT}\sum d_i d_j\,(x_{ij}-x_{ij})\right]. \tag{22}$$

According to the Darling–Dennison rule[54], we have for fully substituted isotopic forms

$$x_{ij}'/x_{ij} = \omega_i'\omega_j'/\omega_i\omega_j. \tag{23}$$

Eqn.(22) transforms into[53]

$$C_1 = \exp\left[\frac{hc}{4kT}\sum_{i<j} d_i d_j\left(\frac{\Delta\omega_i}{\omega_i}+\frac{\Delta\omega_j}{\omega_j}\right)\right];\quad \Delta\omega_i = \omega_i'-\omega_i. \tag{24}$$

Wolfsberg[24,55,56] showed that the correction to zero-point energy for anharmonicity, expressed by equations of type (20), suffers from a significant inaccuracy, because it does not take into account the component of the zero-point energy which is independent of the vibrational quantum numbers. A more accurate expression for the vibrational levels should include

the constant terms G_0, which converts Eqn.(22) into the following expression:

$$C_1 = \exp\frac{hc}{kT}\left[(G_0' - G_0) + \sum_{i<l}\frac{d_i d_l}{4}(x_{il}' - x_{il})\right]. \qquad (24')$$

Allowance for the constant terms G_0 introduces a contribution to the correction for anharmonicity which is comparable to the correction itself[56,57]. Using the Morse potential function, Ishida[58] expanded the analysis of the correction for anharmonicity and tabulated the increments in partition functions corresponding to it as functions of u and x.

The presence of a single hindered rotation in a molecule implies a decrease of the number of vibrational degrees of freedom by unity, a decrease of the number of cofactors in the expression for the partition function ratio, and hence an appreciable decrease of the ratio. The vanishing cofactor is replaced by the ratio of the internal rotation partition functions, which in the general case differs very little from unity[59]. This correction (C_2) amounts to several tenths per cent of $\ln\beta$ at the usual temperatures for the protium–deuterium substitution and falls to hundredths per cent for heavier elements.

The correction C_3 due to the quantisation of the rotational motion[36,37,60] is significant in the protium–deuterium substitution at low temperatures, while in other cases it is insignificant. The corrections for the centrifugal stretching of the bonds in the molecules[36,37,61] (C_4) and for the interaction of the vibrational and rotational motions[36,62,63] (C_5) are always negligible at temperatures above 100 K.

In a series of recent studies[64,65] the accuracy of the initial Born–Oppenheimer approximation itself was analysed in relation to diatomic molecules. A correction for its inaccuracy can be introduced into Eqn.(19) by means of a correction coefficient C_6. In the examples examined[65] the contribution of this correction to $\ln\beta$ does not exceed 0.1%.

3. Approximate Relations

The quite satisfactory accuracy of the "rigid rotator–harmonic oscillator" approximation, the low availability of more detailed information about the energy states of the molecules, and the applicability of the geometrical mean rule make Eqn.(16) the main mathematical relation of the thermodynamics of isotope effects. Despite its simplicity, its practical application is quite laborious. In order to develop computer programs for its calculation, a number of attempts have been made to reduce it to forms more suitable for calculations.

The method of Bigeleisen and Mayer[66] is widely used. They expressed RPFIF as the following function of reduced frequencies and their isotopic shifts:

$$\beta = 1 + \Sigma G(u_i)\Delta u_i; \quad \Delta u_i = u_i - u_i'; \qquad G(u_i) = 1/2 - 1/u_i + 1/(e^{u_i} - 1). \qquad (25)$$

Eqn.(25) significantly reduces the values of $\ln\beta$—the relative error of the calculation reaches 15–17%. Despite this, Eqn.(25) is frequently employed as a simple means of estimating the contributions of different vibrational frequencies to RPFIF and as a means of interpreting the different overall variations of RPFIF due to the absolute values of u_i and Δu_i.

Another expansion of β, in terms of functions of u_i and Δu_i, is sufficiently accurate for computational purposes[61]:

$$\ln\beta = \Sigma G(u_i)\left[1 + \frac{S(u_i)}{2G(u_i)}\cdot\left(\frac{\Delta u_i}{u_i}\right) + \frac{C(u_i) - 2S(u_i)}{6G(u_i)}\left(\frac{\Delta u_i}{u_i}\right)^2\right]\Delta u_i,$$
$$G(u_i) = 1/2 - 1/u_i + 1/(e^{u_i} - 1); \quad S(u_i) = 1/u_i - u_i e^{u_i}/(e^{u_i} - 1)^2; \quad C(u_i) = \qquad (26)$$
$$= 2u_i^2 e^{2u_i}/(e^{u_i} - 1)^3 - u_i(u_i + 2)e^{u_i}/(e^{u_i} - 1)^2.$$

The functions $G(u_i)$, $S(u_i)$, and $C(u_i)$ as well as their derivatives with respect to u have been tabulated using small steps in u[66,67].

III. METHODS FOR THE INTERPRETATION OF CHEMICAL ISOTOPE EFFECTS

As mentioned in the introduction, the theory of chemical isotope effects has two complementary aspects—the use of isotope effects as a research technique and the consequent problem of the analysis and interpretation of the measured effects, and the prediction of effects in order to select chemical systems for the separation of isotopes or in order to devise a research technique. Both problems involve the same mathematical procedures and differ solely in their formulation and the preference given to different methods of solution.

Depending on the means used for the analysis and prediction, it is possible to distinguish three levels in these problems: the level of the rigorous theory of the vibrations of polyatomic molecules; the level of semiempirical relations using the correlations between the isotope effects with separate exact or approximate characteristics of the molecular force field; the phenomenological level, operating with concepts such as the degree of oxidation of the element, the type of geometrical configuration of the compound or its fragment, and the type of donor atom or ligand attached to the element.

The first level is naturally of key importance, since a rigorous treatment of the values of α and β in terms of the theory of vibrations makes it possible to isolate the most important determining groups of molecular characteristics, which can then be expressed approximately in terms of the other two levels. Nevertheless the first level is used nowadays solely for the interpretation of isotope effects (in consequence of the complexity of the mathematical relations for this level and the existence of simpler but accurate procedures which make it possible to calculate the isotope effect directly); it is therefore the level of the rigorous interpretation of isotope effects.

1. Approximate Relations

The relative simplicity of the theoretical relations between chemical isotope effects and the intramolecular characteristics has already been mentioned. The simplest relation, whereby one can obtain a general estimate of the influence of various factors on $\ln\beta$, is the linear Bigeleisen–Mayer approximation, which is valid at high temperatures[66]:

$$\ln\beta = \frac{1}{24n}\sum_i [u_i^2 - (u_i')^2] = \frac{1}{24n}\left(\frac{h}{kT}\right)^2 \Delta\,\mathrm{Sp}\,(GF), \qquad (27)$$

where $\Delta\mathrm{Sp}(GF)$ is the isotopic increment in the trace of the product of the kinematic coefficients matrix G and the force constants matrix F.

Bearing in mind that the stretching vibration frequencies make the main contribution to $\ln\beta$, Bigeleisen proposed a modification of Eqn.(27) which is suitable in the region of all of the usual temperatures. This is achieved by introducing a correction coefficient $\gamma_S(u_S)$ determined by the reduced frequency u_S of the symmetrical stretching vibration[68,69]:

$$\ln\beta = \frac{\gamma_s}{24n}\left(\frac{h}{kT}\right)^2 \Delta\,\mathrm{Sp}\,(GF); \quad \gamma_s = 12G(u_s)/u_s. \qquad (28)$$

Subsequently he described[23] a method whereby one can fit to γ a finite Chebyshev polynomial as a function of u_{max}—the maximum stretching vibration frequency of the molecule. It has been shown[70] that, instead of u_S and u_{max}, it is more desirable to employ the weighted-mean frequency using the isotopic increments in the squares of the frequencies themselves as the weighting factors.

A simpler method has been proposed[71] for the determination of γ from the u_{as} (asymmetric stretching vibration frequencies) and $\Delta Sp(GF)$ whereby an expression can be fitted to $\ln\beta$ with a relative error of ±2% and the necessity to take into account the isotopic shifts of all the frequencies of the molecule is eliminated. The values of γ_{as} have been tabulated[71] as functions of u_{as} and the ratio of the isotope shift Δu to u.

The analytical value of Eqns.(27) and (28) consists in the fact that they reveal the principal intramolecular parameters which determine the values of $\ln\beta$. These are the force constants, geometrical characteristics, and atomic masses in the molecule. Analysis of $\Delta Sp(GF)$ makes it possible to estimate the relative role of each of the three groups of factors and the relative contributions of different components within these groups. In terms of their influence on $\ln\beta$, the above groups can be arranged in the following sequence. The influence of the masses of the atoms capable of undergoing isotope substitution is strongest, that of the force constants is weaker, and that of molecular geometry is weaker still. However, one should bear in mind that this subdivision of molecular parameters into groups is conventional, since the atomic weight of the element and the characteristics of the force fields of the molecules in which it is included depend on one another, and the force constants and molecular geometry are interrelated to an even greater extent.

Analysis of $\Delta Sp(GF)$ revealed a virtually rigorous proportionality of the quantity $\ln\beta$ and hence also $\ln\alpha$ to the square of μ, the reciprocal of the atomic weight of the element involved in isotope substitution, and explained the very rapid decrease of the chemical isotope effects with increasing atomic weight[66]:

$$\Delta Sp\,(GF) = \Delta\mu \sum_{ij} a_{ij} f_{ij} = \frac{\Delta m}{m\,(m+\Delta m)} \sum_{ij} a_{ij} f_{ij} \qquad (29)$$

where $\Delta m = m' - m$, m and m' are the atomic weights of the isotopes of the given element, μ and μ' are the reciprocals of the atomic weights of the isotopes, a_{ij} are coefficients in the elements g_{ij} of the matrix G which depend solely on the molecular geometry, and f_{ij} are the elements of the force constants matrix F.

Eqn.(29) permits a rough estimate of the degree of diminution of the chemical isotope effects on passing from the first element in the Periodic System (hydrogen) to the last—for example, uranium. The quantities $\ln\beta$ and $\ln\alpha$, recalculated in terms of a single increment in the mass difference Δm, should then diminish by a factor of $(2-3)\times 10^4$. Although in reality the scale of the decrease of the effects is somewhat smaller[72] owing to the influence of the second cofactor on the right-hand side of Eqn.(29), this equation imposes very stringent limitations on the overall scope of both chemical isotope separation methods and the applications of isotope effects as the basis of a research technique. The first factor on the right-hand side of Eqn.(29) is in fact the main factor, which determines the limits of the development of these fields at the present time and shows that they are applicable to the set of relatively light polyisotopic elements.

Another corollary of Eqn.(29) is the proportionality of the isotope effects to the difference between the isotopic masses Δm or, more precisely, the direct proportionality of $\ln\beta$ and $\ln\alpha$ to the increment in the reciprocal of the mass of the isotope Δu. This relation is responsible for the large magnitude of the isotope effects and the ease of their measurement and application in those cases where $\Delta m > 1$. At the same time it can be used to test the accuracy of the experimental determination of the effects, when the latter have been measured in relation to three or more isotopes of the given element.

The masses of other elements (incapable of isotopic substitution) do not enter into the expression for $\Delta Sp(GF)$, so that the values of RPFIF and $\ln\alpha$ depend only slightly on them[73]. The influences of the masses of other elements linked to those involved in isotope substitution are appreciable only in hydrides, where protium can be substituted by deuterium and tritium which are twice and three times as heavy.

Table 1. Algebraic expressions for $\Delta Sp(GF)/\Delta\mu$ for certain types of molecules XY_n and $X(YZ)_n$ with linear ligands (YZ) (r and R = XY and YZ distances; α = YXY angle; β = XYZ angle in the YXY plane; θ = XYZ angle in the plane orthogonal to the YXY plane; γ = angle defining the displacement of the XY bond from the plane; f_r = XY bond force constant; f_{rr} and f'_{rr} = force constants for the interaction of the adjacent and opposite XY bonds; f_α = YXY valence angle force constant; $f_{\alpha\alpha}$ and $f'_{\alpha\alpha}$ = force constants for the interaction of adjacent and opposite angles; f_β, $f_{\beta\beta}$, $f'_{\beta\beta}$, etc. are defined analogously).

Type of molecule and its symmetry	$\sum_{ij} a_{ij} f_{ij} = \Delta Sp\,(GF)/\Delta\mu$
$XY_2\,(D_{\infty h})$	$2\,(f_r - f_{rr}) + 8\,f_\alpha$
$X\,(YZ)\,(D_{\infty h})$	$2\,(f_r - f_{rr}) + 8\,f_\alpha - 16\sqrt{\frac{R}{r}}\,f_{\alpha\beta} + 4\left(\frac{R}{r}\right)(f_\beta + f_{\beta\beta})$
$XY_2\,(C_{2v})$	$2\,(f_r + \cos\alpha f_{rr}) - 4\sin\alpha f_{r\alpha} + 2\,(1-\cos\alpha)\,f_\alpha$
$X\,(YZ)_2\,(C_{2v})$	$2\,(f_r + \cos\alpha f_{rr}) - 4\sin\alpha f_{r\alpha} + 2\,(1-\cos\alpha)\,f_\alpha - 4\sqrt{\frac{R}{r}}\,(1+\cos\alpha)\times$ $\times f_{\alpha\beta} + 2\left(\frac{R}{r}\right)(f_\beta + f_\theta - \cos\alpha f_{\beta\beta} - f_{\theta\theta})$
$XY_3\,(D_{3h})$	$3\,(f_r - f_{rr}) - 6\sqrt{3}\,(f_{r\alpha} - f'_{r\alpha}) + 9\,(f_\alpha - f_{\alpha\alpha}) + 9\,f_\gamma$
$X\,(YZ)_3\,(D_{3h})$	$3\,(f_r - f_{rr}) - 6\sqrt{3}\,(f_{r\alpha} - f'_{r\alpha}) + 9\,(f_\alpha - f_{\alpha\alpha}) + 9\,f_\gamma - 6\sqrt{\frac{R}{r}}\times$ $\times f_{\alpha\beta} + \frac{27}{2}\sqrt{\frac{R}{r}}\,(f_{\gamma\theta} + f'_{\gamma\theta}) + 3\left(\frac{R}{r}\right)(f_\beta + f_\theta + f_{\beta\beta} - 2\,f_{\theta\theta})$
$XY_4\,(D_{4h})$	$4\,(f_r - f'_{rr}) - 16\,(f_{r\alpha} - f'_{r\alpha}) + 8\,(f_\alpha - f'_{\alpha\alpha}) + 8\,(f_\gamma - f_{\gamma\gamma})$
$X\,(YZ)_4\,(D_{4h})$	$4\,(f_r - f'_{rr}) - 16\,(f_{r\alpha} - f'_{r\alpha}) + 8\,(f_\alpha - f'_{\alpha\alpha}) + 8\,(f_\gamma - f_{\gamma\gamma}) -$ $- 16\sqrt{\frac{R}{r}}\,(f_{\alpha\beta} + f_{\alpha\theta}) + 4\left(\frac{R}{r}\right)(f_\beta + f_\theta - 2\,f_{\beta\theta} - f_{\theta\theta})$
$XY_4\,(T_d)$	$4\,(f_r - f_{rr}) - 16\sqrt{2}\,(f_{r\alpha} - f'_{r\alpha}) + 16\,(f_\alpha - f'_{\alpha\alpha})$
$X\,(YZ)_4\,(T_d)$	$4\,(f_r - f_{rr}) - 16\sqrt{2}\,(f_{r\alpha} - f'_{r\alpha}) + 16\,(f_\alpha - f'_{\alpha\alpha}) - 16\sqrt{\frac{R}{r}}\times$ $\times (f_{\alpha\beta} + f'_{\alpha\beta}) + 24\sqrt{\frac{R}{r}}\,(f''_{\alpha\beta} + f'''_{\alpha\beta}) + 8\left(\sqrt{\frac{R}{r}}\right)(f_\beta + f_{\beta\beta} -$ $- 3\,f'_{\beta\beta})$
$XY_6\,(O_h)$	$6\,(f_r - f'_{rr}) - 48\,f_{r\alpha} + 24\,(f_\alpha + 2\,f_{\alpha\alpha} - f'_{\alpha\alpha})$
$X\,(YZ)_6\,(O_h)$	$6\,(f_r - f'_{rr}) - 48\,f_{r\alpha} + 24\,(f_\alpha + 2\,f_{\alpha\alpha} - f'_{\alpha\alpha}) - 48\sqrt{\frac{R}{r}}\,(f_{\alpha\beta} + f'_{\alpha\beta} +$ $+ 2\,f''_{\alpha\beta}) + 12\left(\sqrt{\frac{R}{r}}\right)(f_\beta + f_{\beta\beta} - f'_{\beta\beta})$

In terms of the range of its accuracy, Eqn.(29) makes it possible to separate the influence of the isotopic masses from the influence of the force constants and molecular geometry within $\ln\beta$. The role of the last two factors can be seen from Table 1, which presents the algebraic expressions for the sums $\sum_{ij} a_{ij} f_{ij}$ for isotope substitutions of the central atoms X in compounds of the type XY_n and $X(YZ)_n$.[74] Both the force constants f_{ij} and the coefficients a_{ij}, which are determined by the molecular geometry, are derivatives of the

characteristics of the potential energy surface of the molecules and their effects can be separated only by convention. Nevertheless, inspection of the expressions in Table 1 shows that formally such subdivision can be readily achieved and this makes it possible to separate the influence of bond strength from the influence of molecular geometry. We shall take into account the fact that the force constants for the deformation of bonds f_r, the deformation of valence angles f_α, the interaction of bonds f_{rr}, the interaction of bonds and angles $f_{r\alpha}$, and the interaction of angles with one another $f_{\alpha\alpha}$ decrease in a specific sequence[75,76]:

$$f_r \gg f_\alpha \gg f_{rr} \geqslant f_{\alpha\alpha} \geqslant f_{r\alpha}. \qquad (30)$$

This means that the main contribution to $\Delta Sp(GF)$ comes invariably from $(f_r - f_{rr})$ combinations multiplied by the coefficients a_{ii}, equal to the number n of attached atoms Y or atomic groups YZ. Despite the much greater numerical values of the coefficients a_{ij} of other combinations of constants, the fraction of this contribution does not fall below 60% of $\Delta Sp(GF)$ and is in the range 80–90% for the vast majority of molecules. Thus the force constants f_r for the deformation of bonds and their number n make the main contribution to $\Delta Sp(GF)$.[66,76] If one is dealing with a molecule of the type $XY_1Y_2...Y_i...Y_n$ in which the atom X involved in isotope substitution is linked to different atoms or groups Y_i, then the dominant component of the sum $\sum_{ij} a_{ij} f_{ij}$ is $\sum_i f_{ri}$.

According to the concept of the transferability of force constants[75,76], the bond deformation force constants for series of related molecules have the same numerical value or change comparatively slightly. Together with the considerations described above, this justifies the treatment of the quantities $\ln\beta$ as sums of certain constant increments corresponding to each bond. It has been shown[74,77] that in isostructural series of the type CH_4, CH_3F, CH_2F_2, CHF_3, CF_4 or BF_3, BF_2Cl, $BFCl_2$, BCl_3 the additivity of the values of $\ln\beta$ for the central carbon and boron atoms holds with a high degree of accuracy. However, even for an approximate maintenance of the additivity of $\Delta Sp(GF)$, numerous conditions must hold, which are partly outside the scope of the concept of transferability of the force constants[78]. The next section of this review will show that the rigorous additivity of $\ln\beta$ is incompatible with the rigorous additivity of the higher terms of the expansion of $\ln\beta$ in series in terms of the quantities $\Delta Sp(GF)^j$ even for series of geometrically similar molecules. The assumption of the additivity of the thermodynamic isotope effects of carbon for arbitrary sets of organic compounds[7,79] is therefore erroneous.

2. Exact Relations

Eqns.(28)–(29) make it possible to interpret the values of $\ln\beta$ only to within a correction factor γ. Although in most cases the latter lies within a narrow range of values, the corrections which it introduces can reach 30% of the true value of $\ln\beta$. This is a result of the failure to take into account the non-linear terms of the expansion of $\ln\beta$ in terms of the characteristics of the force field.

An accurate expansion in a variable-sign power series with Bernoulli coefficients B_{2j-1} was obtained by Bigeleisen[68] for the range $u_{max} < 2\pi$:

$$\ln\beta = \sum_{j=1}^{\infty} \frac{(-1)^{j+1} B_{2j-1}}{2j\,(2j)!} \sum_{i=1}^{3N-6} \delta\,(u_i^{2j}) = \\ = \sum_{j=1}^{\infty} \frac{(-1)^{j+1} B_{2j-1}}{2j\,(2j)!} \left(\frac{hc}{kT}\right)^{2j} \Delta\,\mathrm{Sp}\,(GF)^j. \qquad (31)$$

The condition for the convergence of this series ($u_{max} < 2\pi$) holds only for molecules with comparatively weak bonds or at relatively high temperatures.

This limitation as well as the low rate of convergence of series (31) stimulated the derivation of approximate expressions for $\ln\beta$ over an arbitrary range of values of u. Considerable efforts were wasted in the search for ways of achieving a sufficiently accurate mathematical description of $\ln\beta$ with the aid of finite orthogonal Jacobi polynomials[14,23,80]. Analysis of different versions of this description by Bigeleison and Ishida[23] led to the conclusion that the following approximate expression, in which the terms of series (31) are modulated by finite first-order Chebyshev polynomials, is best:

$$\ln\beta = \sum_{j=1}^{n} T\,(n, j, u_{|max}) \frac{(-1)^{j+1} B_{2j-1}}{2j\,(2j)!} \left(\frac{hc}{kT}\right) \Delta\,\mathrm{Sp}\,(GF). \qquad (32)$$

The accuracy ensured by the Bigeleisen–Ishida expansion (32) is determined by the order n of the modulating Chebyshev function $T(n,j,u_{max})$ and the required range of values $u \in [0, u_{max}]$. The accuracy of Eqn.(32) is higher the higher the order n and the narrower the required range of values of u. The marked increase of the error of the approximate expression (32) with increase of u necessitates the application of a (third–fourth)-order function $T(n,j,u_{max})$ and the introduction into $T(n,j,u_{max})$ of exact values of u_{max} corresponding to the maximum frequency of the vibrations of the molecule in the "light isotope" form.

Nemeth et al.[81] used the minimax method in order to expand the components of $\ln\beta$ into a finite polynomial; the resulting approximate expression is

$$\ln\beta \simeq \sum_{j=1}^{n} a\,(n, j, u_{max}) \cdot \sum_{i}^{3N-6} \delta\,(u_i/u_{max})^{2j} = \\ = \sum_{j=1}^{n} a\,(n, j, u_{max}) \cdot \left(\frac{hc}{kT}\right)^{2j} \Delta\,\mathrm{Sp}\,(GF)^j \quad , \qquad (33)$$

where $a(n,j,u_{max})$ are modulating polynomials analogous to $T(n,j,u_{max})$, and their numerical values have been tabulated[81].

The difference between Eqn.(33) and (32) is that the $\ln\beta$ polynomials $a(n,j,u_{max})$ fit much better the components of $\ln\beta$ and over a wide range values of u. Although the accuracy of Eqn.(33) is ultimately comparable to that of Eqn.(32), the weak dependence of the error of the former equation on u makes it possible to employ the same numerical values with $a(n,j,u_{max})$ for large sets of molecules over a wide temperature range. This converts Eqn.(33) into an algebraically simple expression and greatly facilitates the mathematical analysis of the relations between the RPFIF and all its intramolecular characteristics.

Having used the perturbation technique, Singh and Wolfsberg[82] obtained a new relation expressing the RPFIF directly in terms of the force constants, masses, and geometrical parameters of the molecule. To a second approximation, this method ensures an error in the fitting of an expression to $\ln\beta$ at the level of several per cent. The resulting expression is not algebraically simple[83] and has not as yet been subjected to a general analysis from the standpoint of the possibility of using it for the investigation of the structural characteristics of the thermodynamics of isotope exchange.

Eqn.(32) has been used in a series of studies[50,83–88] in order to investigate in detail the relations between the RPFIF and the force constants. The following example provides an idea about the complexity of the resulting specific relations[85]: the overall form of the expression for $\Delta Sp(GF)^3$ for a non-linear triatomic molecule has 113 terms. If it is necessary to estimate the scale of the significance of various constants, this makes numerical analysis of specific molecules preferable and lowers the generality of the conclusions.

The estimation of the contributions of various force constants to $\ln\beta$ with the aid of equations of type (32) involves a significant difficulty: the replacement of the real (numerical) value of the force constant by zero has the physical

significance of either bond rupture (if one is dealing with the valence constant), or the complete elasticity of the valence angle (zero deformation constant for the angle), or the cessation of the interaction between unlike coordinates. Such substitution can influence the coefficients of the characteristic polynomial to such an extent that certain vibration frequencies of the molecule "modified" in this way can prove to be imaginary. A special method has therefore been proposed[87] for the extrapolation of $\ln\beta$, in terms of the force constants, from the region where all the frequencies of the "modified" molecule retains positive values to zero values of the force constant. This method must be used in estimating the contributions of the valence and deformation constants, which are largest. On the other hand, the constants for the interaction between unlike coordinates can be estimated directly with the aid of Eqn.(32).

This exact analysis confirmed the dominant role of the valence force constants f_r (which follows from the analysis of the approximate relations and empirical correlations), the secondary role of the deformation constants f_α, and the much smaller influence of constants of the type f_{rr}, $f_{\alpha\alpha}$, and $f_{r\alpha}$, which reflect the interaction of unlike internal coordinates of the molecule. It has been shown[87] that the contributions of the valence constants to $\ln\beta_H$, characterising polyatomic deuterium-substituted hydrides, are almost additive at normal temperatures (300 K) and are rigorously additive at higher temperatures. The isotope effects of oxygen and in general of any element whose atoms play the role of terminal atoms are similarly almost additive and cumulative with respect to the force constants[83,88]. On the other hand, additivity breaks down significantly for elements of the type of carbon, which form numerous bonds and play the role of central atoms[83].

Expansion (32) has been used[50] to test the accuracy of Eqn.(14), which postulates the thermodynamic equivalence of all the stages of the isotope substitution of equivalent atoms. In contrast to earlier studies, it was found that the corrections to the geometrical mean rule are appreciable and can amount to 0.1–1% of $\ln\beta$.

Table 2. The functions b_j in Eqn.(35) [$B_j = (3.55559\times 10^{-6}/T^2u_{max})^{2j}$, $a_ja_j = a(n,j,u_{max})$ according to Nemeth et al.[81] and n = degree of polynomial].

n	Function b_j
1	$b_1 = b_1$
2	$b_1 = B_1 + 2B_2\sigma_1$ $b_2 = -2B_2$
3	$b_1 = B_1 + 2B_2\sigma_1 + 3B_3\sigma_1^2 - 3B_3\sigma_2$ $b_2 = -2B_2 - 3B_3\sigma_1$ $b_3 = 3B_3$
4	$b_1 = B_1 + 2B_2\sigma_1 + 3B_3\sigma_1^2 - 3B_3\sigma_2 + 4B_4\sigma_1^3 - 8B_4\sigma_1\sigma_2 + 4B_4\sigma_3$ $b_2 = -2B_2 - 3B_3\sigma_1 - 4B_4\sigma_1^2 - 4B_4\sigma_2$ $b_3 = 3B_3 + 4B_4\sigma_1$ $b_4 = -4B_4$

A deficiency of Eqns.(32), (33), and other polynomial expansions of $\ln\beta$ in terms of the parameters $\Delta Sp(GF)^j$ is the algebraic complexity, already mentioned, of the increments in the traces of the degrees of the matrix (GF), which constitutes a significant obstacle in the mathematical analysis of the relations between the RPFIF and the characteristics of the molecules. A definite advance in this respect was made by the simplification achieved using Waring's formulae[89,90]. Their application replaces the parameters $\Delta Sp(GF)^j$ by $\Delta\sigma_j$ (isotopic increments in the coefficients σ_j of the characteristic polynomial for molecular vibrations):

$$\sigma_1 = 4\pi^2c^2\sum_i \omega_i^2,$$
$$\sigma_2 = (4\pi^2c^2)^2\sum_{i\neq k}\omega_i^2\omega_k^2, \qquad (34)$$
$$\sigma_3 = (4\pi^2c^2)^3\sum_{i\neq k\neq l}\omega_i^2\omega_k^2\omega_l^2.$$

This replacement of the parameters of the expansion reduces Eqns.(32) and (33) to the form

$$\ln\beta = \sum_j b_j\Delta\sigma_j + \sum_{j,k} b_{jk}\Delta\sigma_j\Delta\sigma_k + \sum_{j,k,l} b_{jkl}\Delta\sigma_j\Delta\sigma_k\Delta\sigma_l + \ldots, \qquad (35)$$

where b_j, $b_{j,k}$, and $b_{j,k,l}$ are functions of σ_j of different orders, which depend on the choice of modulating polynomials. If the functions b_j, $b_{j,k}$, ... are found by the method of Nemeth et al.[81] from the polynomials $a(n,j,u_{max})$, then their form is significantly simpler than in the case where $T(n,j,u_{max})$ is used for the same purpose (Table 2).

The advantages of Eqn.(35) compared with Eqns.(32) and (33) are as follows. Despite its apparent greater complexity, Eqn.(35) has a simpler structure and converges more rapidly, but Table 3 shows that the contribution of even the second sum on the right-hand side of Eqn.(35) is comparable to the error of the approximation and can therefore be neglected together with higher terms. The first sum $\sum_j b_j\Delta\sigma_j$ has a convenient structure. In contrast to the variable-sign sums on the right-hand sides of Eqns.(32) and (33), it includes only positive terms whose absolute magnitude decreases rapidly. Table 3 shows that the first term with $\Delta\sigma_1$ amounts to 70–90% of $\ln\beta$, the contribution of the second term with $\Delta\sigma_2$ is 10–30%, and that of the term with $\Delta\sigma_3$ is about 1% of $\ln\beta$, i.e. is comparable to the error of the approximation. This enables us to speak of the relative contribution of each term to $\ln\beta$, while a similar statement does not have such a clear-cut significance in relation to the terms of the variable-sign sums (32) and (33).

Table 3. The structure of the contributions of the terms of expansion (35) to $\ln\beta$ at 300 K (degree of polynomial fitted $n = 3$, n' = degree of secular equation).

Molecule	$\ln\beta_{harm}$ [Eqn.(16)]	n'	$\sum b_j\Delta\sigma_j$	$b_1\Delta\sigma_1$	$b_2\Delta\sigma_2$	$b_3\Delta\sigma_3$
NO_2	0.0976	2+1	0.0997	0.0737	0.0254	0.0006
NOF	0.0823	2+1	0.0838	0.0718	0.0119	0.0001
NOCl	0.0761	2+1	0.0775	0.0704	0.0070	0.0001
CO_2	0.1719	1+1+1+1	0.1678	0.1215	0.0450	0.0013
COF_2	0.1841	3+3	0.1840	0.1517	0.0317	0.0006
HCO^-	0.1773	3+3+3	0.1797	0.1290	0.0492	0.0015

Furthermore, the first sum $\sum_j b_j\Delta\sigma$ consists of simple functions. Table 2 shows that the values of b_j are power functions of the coefficients σ_j of the characteristic polynomial. These coefficients refer to an isotopically unperturbed molecule and can be readily expressed not only in terms of the frequencies [Eqn.(34)] but also in terms of the matrices G and F. The values of σ_j are equal to the sums of products of the principal minors of order j of the matrices G and F.[91] The isotopic increments $\Delta\sigma_j$ can be expressed quite similarly.

Overall, the properties of σ_j and $\Delta\sigma_j$ make it possible to separate relatively simply the influence on $\ln\beta$ of force characteristics, on the one hand, and of the geometry and mass of the molecules, on the other. This makes Eqn.(35) convenient for the interpretation of isotope effects and for the search for relations.

An example of useful applications of Eqn.(35) is the derivation of the quantitative coupling relations between the isotope effects of different elements and the frequency characteristics of the molecules[92]. For the reaction

$$HCO_3^- \rightleftarrows CO_2 + OH^- \qquad (36)$$

four isotope exchange processes are possible between all three substances and there can be four equilibrium isotope effects with respect to three elements:

$$\begin{aligned}
&H\overset{*}{C}O_3^- + CO_2 \rightleftarrows HCO_3^- + \overset{*}{C}O_2; \quad \alpha_C = \beta_{CO_2}/\beta_{HCO_3^-},\\
&\overset{*}{H}CO_3^- + OH^- \rightleftarrows HCO_3^- + \overset{*}{O}H^-; \quad \alpha_H = \beta_{OH^-}/\beta_{HCO_3^-},\\
&HCO\overset{*}{O}_2^- + CO_2 \rightleftarrows HCO_3^- + C\overset{*}{O}_2; \quad \alpha_O^{(1)} = \beta_{CO_2}/\beta_{HCO_3^-},\\
&HC\overset{*}{O}O_2^- + OH^- \rightleftarrows HCO_3^- + \overset{*}{O}H^-; \quad \alpha_O^{(2)} = \beta_{OH^-}/\beta_{HCO_3^-}.
\end{aligned} \qquad (37)$$

The coupling relation for Eqns.(37) or, what amounts to the same thing, for reaction (36), is as follows:

$$\begin{aligned}
&\frac{\mu_C}{\Delta\mu_C}\ln\alpha_C + \frac{\mu_H}{\Delta\mu_H}\ln\alpha_H + 2\frac{\mu_O}{\Delta\mu_O}(\ln\alpha_O^{(1)} + \ln\alpha_O^{(2)}) =\\
&= \sum_i jb_i(CO_2)\,\sigma_i(CO_2) + \sum_i jb_i(OH^-)\,\sigma_i(OH^-) - \sum_i jb_i(HCO_3^-)\,\sigma_i(HCO_3^-).
\end{aligned} \qquad (38)$$

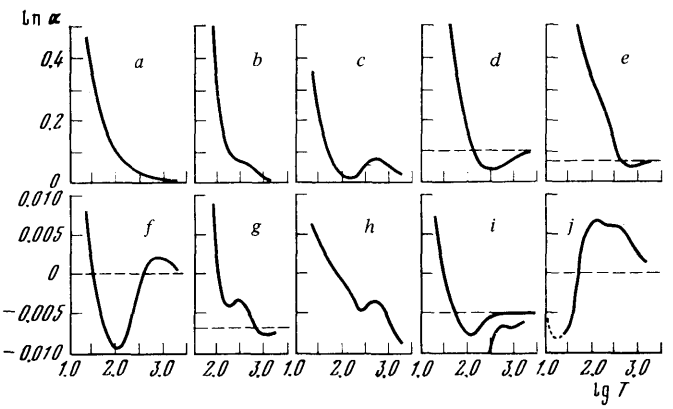


Figure 1. Types of temperature variations of theoretically calculated isotope separation factors for oxygen, carbon, and hydrogen in terms of the variables $\ln\alpha$ and $\lg T$ in the following systems: *a*) $^{18}OCS/CH_3CH^{18}O$; *b*) $Br_2C^{18}O/H^{18}OCO_2$; *c*) $CH_3{}^{13}CHO/H^{13}COO^-$; *d*) $CH_3CHDCH_3/DCOOH$; *e*) $CH^{18}OCH_3/Cl_2C^{18}O$; *f*) $CH_2{}^{13}CO/H^{13}COO^-$; *g*) $DONO_2$/*trans*-DONO; *h*) $^{13}CO_2/CH_3COCH_3$; *i*) $DONO_2/HCOOD$; *j*) $CH_2DCOCH_3/CH_2DCH_2CH_3$.

With the aid of coupling relations of type (38), it is possible to estimate isotope effects which have not been investigated experimentally, to test the reliability of the results, and to determine the characteristics of the transition complexes.

3. Temperature Variation of Isotope Effects

The most complete theoretical treatment of the nature of the temperature variation of $\ln\beta$ and $\ln\alpha$ has been achieved by Denisov et al.[71] and by Stern and coworkers[93,94]. The analysis was based on the study of the $\ln\beta_i$ components of the RPFIF corresponding to different vibration frequencies ω_i [see Eqn.(17)]. Each component $\ln\beta_i$ can be effectively fitted at low temperatures by a linear relation in terms of the reciprocal of the absolute temperature and at high temperatures by a quadratic relation. The transition from the first type of relation to the second occurs at higher temperatures for each frequency the higher the frequency. In the general case the resultant value of $\ln\beta$ in the region of moderate temperatures therefore depends on temperature in a complex way and, while obeying the linear and quadratic relations at low and high temperatures, always exhibits a monotonic decrease with increase of temperature. In contrast to $\ln\beta$, the values of $\ln\alpha$, which are equal to differences between the $\ln\beta$, can vary non-monotonically with increase of temperature. It has been shown[71,93,94] that there are several types of temperature variation of $\ln\alpha$, which include relations with inversion of the sign of $\ln\alpha$, with a maximum, with a minimum, and with points of inflection (Fig.1).

IV. CHARACTERISTICS OF THE VARIABILITY OF ISOTOPE EFFECTS

1. Semiempirical Structural Relations

The study of the correlations between the RPFIF and the exact or approximate characteristics of molecular force fields leads to the possibility of estimating the RPFIF with the aid of extremely limited spectroscopic or non-spectroscopic information. Conversely, measurement of isotope effects makes it possible to find the approximate values of the force constants, the stretching vibration frequencies, and other molecular parameters.

As shown above, the valence force constants f_r, corresponding to the longitudinal deformation of the valence bonds involving the atom undergoing isotope substitution, make the dominant contribution to the values of $\ln\beta$. In series of related compounds there are definite relations between the quantities f_r and other force constants of the molecules (f_α, f_{rr}, $f_{r\alpha}$, $f_{\alpha\alpha}$) or their simple combinations (elements of the *F*-matrix)[74,75,95,96], which permits a definite selection of the valence force constants f_r as the main argument in the study of RPFIF correlations. Since the valence force constants f_r are characteristics of the bond strength and there are many other bond properties correlated with them, the quantities $\ln\beta$ should exhibit fairly close correlations with many parameters of both the bonds themselves in the molecules and of the atoms involved in the bonds.

The density of such correlations and hence their reliability and usefulness are determined both by the selected method of expressing the bond strength and by the nature of the set of compounds for which such correlations are constructed For example, for simple sets such as those of diatomic molecules[97-99], the observed relations are so close and simple that the RPFIF can be expressed analytically as a function of the properties of the atoms forming the molecule. On the other hand, for the set of hydrides of different elements, it has been possible merely to conclude that the variation of the RPFIF is periodic[31]. In the general case of polyatomic molecules dense linear $\ln\beta - \Sigma f_r$ and $\ln\beta - \Sigma(f_r \pm f_{rr})$ correlations

are observed for sets formed by geometrically similar compounds. A variable phenomenological feature of the compounds in such sets is usually the nature of the donor atom attached to the atom undergoing isotope substitution. Examples of such correlations are presented in Figs. 2 and 3.[100-103] In series of the type XY_n and $XY_iY'_{n-i}$, where Y and Y' are different halogens, hydrogen, oxygen, and chalcogens, etc, these correlations are so close that methods of comparative calculation of the RPFIF become justified, for example, those based on the linear relations of the $\ln\beta_X - \ln\beta_{X'}$ type (Fig. 4).[103]

In compounds $XY_iY'_{n-i}$, where the geometry of the coordination sphere of the atom involved in isotope substitution is retained, $\ln\beta_X$ is nearly additive: the values of $\ln\beta_X$ can be obtained as the sums of certain increments for the X–Y and X–Y' bonds. As shown above, this is a consequence of the transferability of the force constants in such series of molecules.

The correlations between $\ln\beta$ and $\Sigma(f_r \pm f_{rr})$ for a set of compounds with different geometries have a much smaller density. For such sets (Fig. 5), the correlation coefficients are approximately 0.8. This is a natural consequence of the influence of the component of $\Delta Sp(GF)$, which is not proportional to Σf_r and reflects the differences associated with the geometrical variety of molecules.

Frequently only the stretching vibration (symmetric or anti-symmetric) frequencies are known for the compounds of interest. The knowledge of these frequencies is virtually equivalent to the knowledge of one of the combinations $(f_r \pm f_{rr})$ and the squares of the stretching vibration frequencies ν can therefore be used as bond characteristics for compounds where the central atom is linked to monatomic ligands. Such correlations are equally well applicable to sets containing the elements of a single Group or a single Period. It is also necessary to exclude the influence of masses by introducing the corresponding multiplier (Figs. 6 and 7).

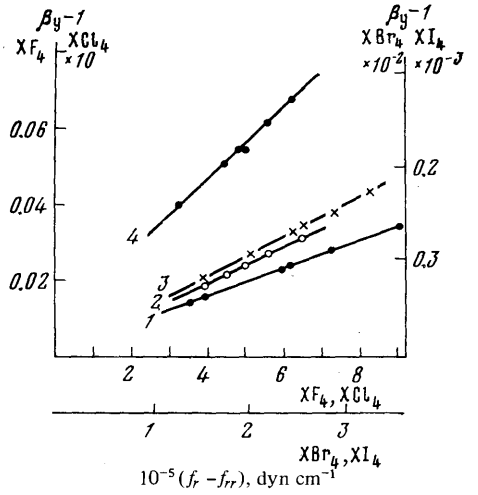


Figure 3. Dependence of $\beta_Y - 1$ for the terminal atoms Y in the tetrahalides XY_4 of the elements in the carbon subgroup on the combination of force constants $f_r + f_{rr}$ at 300 K; 1) XF_4; 2) XCl_4; 3) XBr_4; 4) XI_4.

The force constants are second derivatives of the bond energies E with respect to internuclear distances corresponding to equilibrium distances r_e. It is therefore natural to expect that relations of the type $\ln\beta - E$ or $\ln\beta - \sum_i E_i$ should be fairly simple. However, even for sets of related diatomic compounds such expectations are not borne out in practice[97-99]. For polyatomic molecules, the above relations are

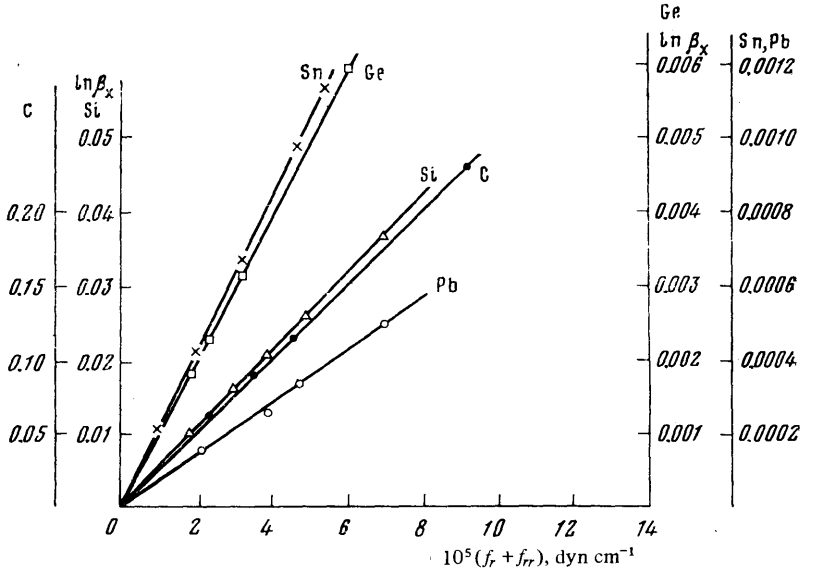


Figure 2. Dependence of $\ln\beta_X$ for the tetrahalides XY_4 of the elements in the carbon subgroup on the combination of constants $fr + f_{rr}$ at 300 K.

also not simple[103]. A much better correspondence is observed between $\ln\beta$ and the argument $\eta_0(y_X y_Y / y_X^0 y_Y^0)^{1/2} E/r_e$, where η_0 is a constant, y_X and y_Y are the first ionisation potentials of the atoms X and Y forming the molecule, and y_X^0 and y_Y^0 are the first ionisation potentials of the alkali metals belonging to the same Periods as X and Y. The use of this argument (Fig.7) is based on the familiar empirical relation $f_r = cE/r_e$, which Lippincott generalised[104]. The above relation has been confirmed for a fairly large set of compounds[105].

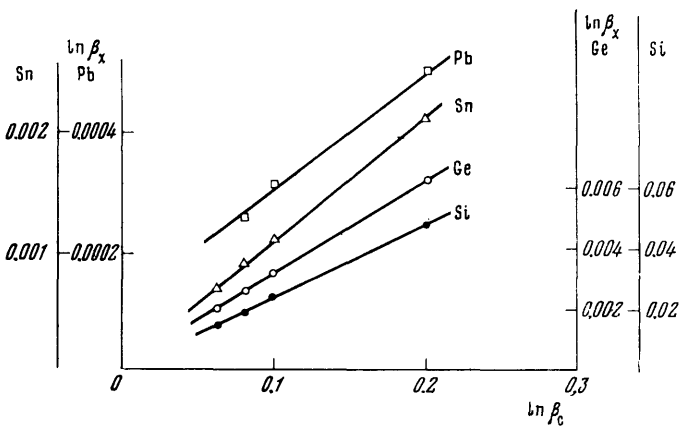


Figure 4. Correlation between the $\ln\beta_X$ for silicon, germanium, tin, and lead tetrahalides and $\ln\beta_C$.

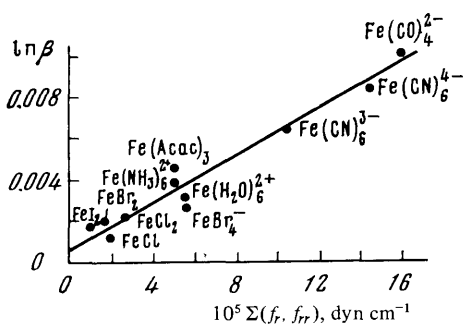


Figure 5. Correlation between $\ln\beta_{Fe}$ and $\Sigma(f_r, f_{rr})$.

Among the numerous other methods for fitting approximate expressions to the sum of valence force constants, we may note the empirical relations of Gordy[106], Guggenheimer[107], Ferreira[108], Varshni[109], and Somayajulu[110], which made it possible to obtain linear correlations between $\ln\beta$ and the internuclear distances, electronegativities, the numbers of valence electrons in the atoms, and other characteristics[97-103] (Figs.8 and 9).

For hydrogen isotope effects, the influences exerted on the H–X bond by other atoms linked to the hydride-forming element are significant. Characteristics such as the electronic charge of the bond, the electron density at the bond, the electronegativity of the substituting group, and the Taft and Hammett constants are fairly closely correlated with $\ln\beta_H$ for the corresponding sets of hydrides[101,102] (Figs.10–12).

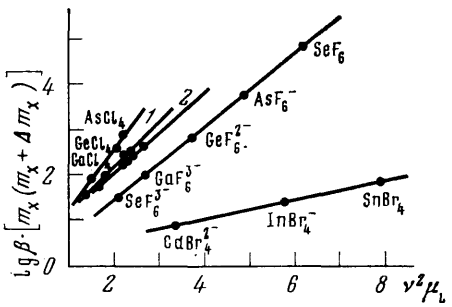


Figure 6. Dependence of $\lg\beta[m_X(m_X + \Delta m_X)]$ on $\nu^2\mu_L$, where ν is the stretching frequency and μ_L the reduced mass $[\mu_L = m_L m_X/(m_L + m_X)]$: 1) cyanides; 2) acetylacetonates.

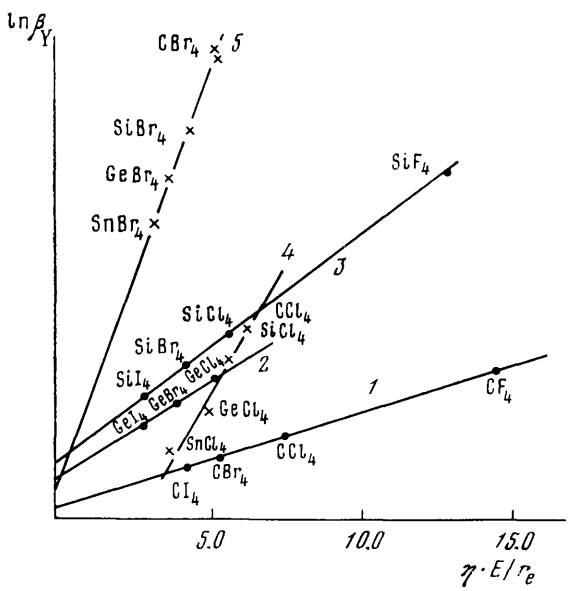


Figure 7. Dependence of $\ln\beta$ on $\eta E/r_e$: 1)–3) for C, Ge, and Si; 4) and 5) for Cl and Br.

2. Phenomenological Relations

This concept includes correlations which can be observed by comparing the isotope effects of one or several elements with generally accepted chemical concepts such as the degree of oxidation of the element, the type of donor atom or ligand,

and the configuration of the coordination sphere of the element involved in isotope substitution. The choice of these features of the chemical compound as the phenomenological equivalent of the intramolecular force field is justified by the possibility of a direct comparison of the isotope effects with a wide variety of chemical data[76,100,111].

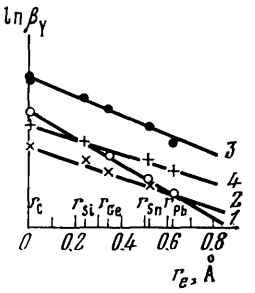


Figure 8. Correlation between $\ln\beta_Y$ and r_e for the tetrahalides XY_4 of Group IV elements: 1) fluorides; 2) chlorides; 3) bromides; 4) iodides.

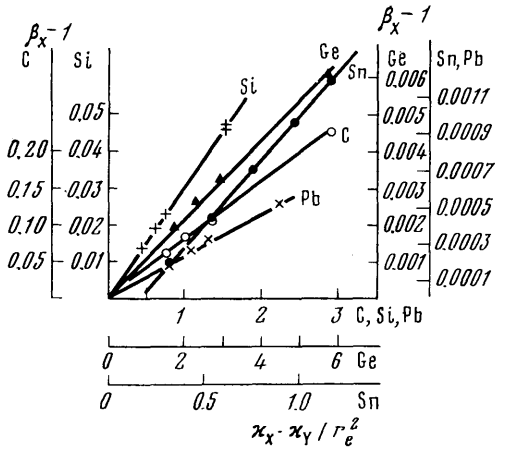


Figure 9. Correlation between $\beta_X - 1$ and the Gordy–Ferreira factor $\kappa_X\kappa_Y/r_e^2$ for the tetrahalides XY_4 of Group IV elements; κ_X and κ_Y = atomic electronegativities; r_e = internuclear distance.

The oxidation state of the element, the type of ligand, and the type of configuration sphere are interrelated discrete parameters. While the others are kept constant, each can vary only within narrow limits. In order to extend the range of values of the given parameter, it is necessary to adjust the isotope effects of different elements to a single scale and to include them in an overall analysis. This is achieved in two ways. Firstly, if one needs to compare the isotope effects of different elements, then one should use effects corresponding to a unit increment in isotopic masses. All the numerical values of $\ln\beta$ and $\ln\alpha$ quoted in this review satisfy this condition. Secondly, if one needs to exclude the influence not only of Δm but also of the atomic mass m of the element involved in isotope substitution, then the quantities $\ln\beta/\Delta\mu$ should be analysed. In conformity with the significance of Eqns. (28) and (29), these quantities can be referred to as the effective force fields in which the atoms in the molecule involved in isotope substitution are located.

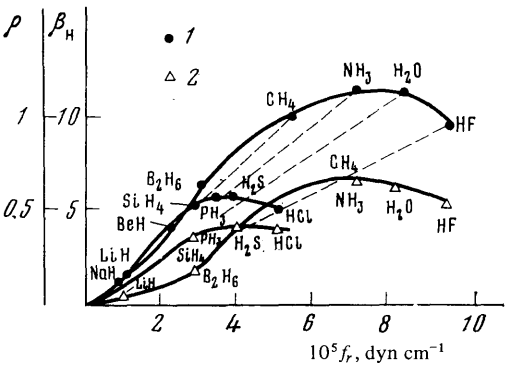


Figure 10. Dependence of β_H (*1*) and electron density ρ (*2*) of the H–X bond on the force constant f_r.

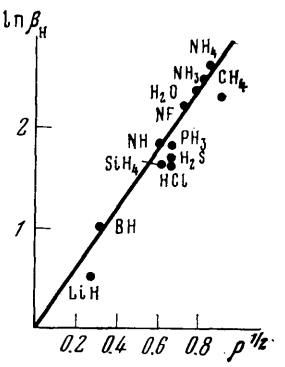


Figure 11. Correlation between $\ln\beta_H$ and the bond electron density ρ.

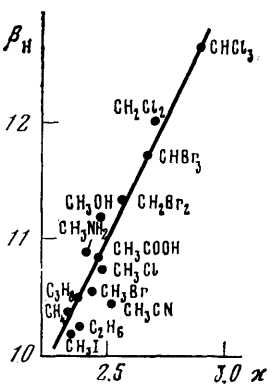


Figure 12. Correlation between β_H and the electronegativity κ of the hydrogen-substituting groups.

The influence of the degree of oxidation of the central atom on its $\ln\beta$ can be most readily followed for the sequence of compounds formed by elements with the same donor atom or ligand. The variation of the effective field $\ln\beta/\Delta\mu$ is simplest for the sequence of isoelectronic-isostructural compounds. Fig. 13 shows that the values of $\ln\beta/\Delta\mu$ are linear functions of the formal oxidation state in the series of tetraoxo-anions and tetra- and hexa-halogeno-complexes of both *p* and *d* elements in the highest oxidation states. For transition metals in isostructural series of compounds the variation of $\ln\beta/\Delta\mu$ with increasing degree of oxidation remains monotonic (Table 4). For σ-donor and (σ−π)-donor ligands, $\ln\beta/\Delta\mu$ increases, while for σ-donor and π-acceptor ligands it diminishes with increasing degree of oxidation.

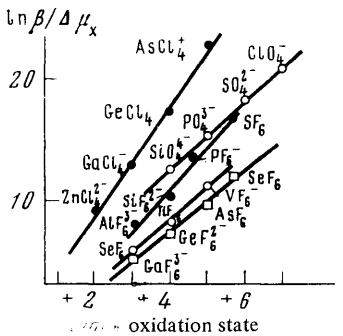


Figure 13. Relation between $\ln\beta_X/\Delta\mu_X$ and the formal oxidation state of the central atom in series of isoelectronic molecules.

Table 4. Relation between $\beta_X - 1$ and the oxidation state of the central atom.

n	β_X-1	*n*	β_X-1	*n*	β_X-1	*n*	β_X-1	*n*	β_X-1	*n*	β_X-1
Isostructural σ-complexes											
	VF_6^n		CrF_6^n		RuF_6^n		ReF_6^n		MnO_4^n		RuO_4^n
−3	0.00550	−3	0.00720	−3	0.00177	−2	0.00065	−3	0.00711	−2	0.00296
−2	0.00860	−2	0.00762	−2	0.00234	−1	0.00087	−2	0.00987	−1	0.00334
−1	0.01066	0	0.01450	0	0.00363	0	0.00129	−1	0.01173	0	0.00396
Isostructural π-complexes											
	$Cr(CN)_6^n$		$Mn(CN)_6^n$		$Fe(CN)_6^n$		$Cr(C_6H_6)_2^n$		$Fe(C_5H_5)_2^n$		
−3	0.00586	−3	0.00583	−3	0.00634	+1	0.00271	+1	0.00313		
−4	0.00678	−4	0.00694	−4	0.00852	0	0.00324	0	0.00506		

The increase of the degree of oxidation of *p* elements is coupled with a change in the number of attached ligands, the type of hybridisation of the valence orbitals, and the configurations of the compounds. The monotonic increase of the effective force fields observed in such sequences (Table 5) must be attributed to the increase of the degree of oxidation, since the configuration can be regarded as derived from the oxidation state and the type of ligand. The monotonic variation of $\ln\beta/\Delta\mu$ for sequences of this type does not imply their simplicity. In these sequences there is a change of both the type of hybridisation and of the number of non-bonding electron pairs. A more flexible and exact equivalent of the concept of the degree of oxidation proves to be the sum of bond orders, which exhibits a closer correlation with $\ln\beta$ (Fig. 14).

Table 5. The values of $\beta_X - 1$ for the fluorides and oxides of Group VI *p* elements.

Compound	β_X-1	Compound	β_X-1	Compound	β_X-1
SF_2	0.00944	SeF_2	0.00174	TeF_2	0.000676
SO	0.00866	SeO	0.00130	TeO	0.000433
SF_3^+	0.019	SeF_3^+	0.0028	TeF_3^+	0.0011
SO_2	0.0243	SeO_2	0.00348	TeO_2	0.00126
SO_3^{2-}	0.0271	SeO_3^{2-}	0.00378	TeO_3^{2-}	0.00145
SF_6	0.0411	SeF_6	0.00718	TeF_6	0.00285
SO_3	0.0430	SeO_3	—	TeO_3	—
SO_4^{2-}	0.0428	SeO_4^{2-}	0.00680	TeO_4^{2-}	0.00177

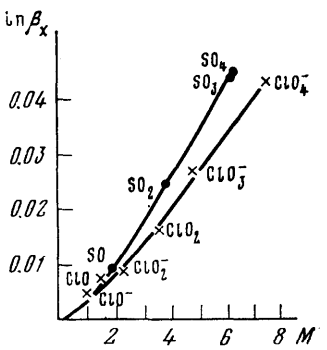


Figure 14. Correlation between $\ln\beta$ of sulphur and chlorine oxides and the sum of bond orders *M*.

The study of the relations between the RPFIF and the nature of the ligands and donor atoms is complicated by the fact that at the present time the values of $\ln\beta$ are known mainly only for compounds with the simplest monatomic ligands. Table 6 shows that, in series of isostructural compounds formed by donor atoms of the elements of a single Group of the Periodic Table, there is a marked decrease of $\ln\beta_X$ with increase of the atomic number of the donor element in the Group. Fairly rigorous relations of the type

$$\ln\beta(XY_n)/\ln\beta(XY_n') = t \simeq \text{const.} \qquad (39)$$

are observed between the values of $\ln\beta_X$ for halides, oxides, and chalcogenides. The values of *t* are then close to the ratios of the electronegativities of the donor elements Y and X. Compounds with different oxidation states of the central atom and ligands belonging to the same Period (F^- and O^{2-}, Cl^- and S^{2-}, Br^- and Se^{2-}) have approximately the same values of the RPFIF of the central atoms.

For octahedral complexes of doubly- and triply-charged metal ions belonging to the first transition Period, the following sequence, corresponding to the variation of $\ln\beta_X$ with the nature of the ligand, apparently holds:

$$CN^->Acac>F^->H_2O\simeq NH_3\geqslant O^{2-}{}_x. \qquad (40)$$

Table 6. Relation between $\beta_X - 1$ and the type of monatomic ligands.

Y	LiY	BeY_2	BY_3	CY_4	PY_3	PY_5	SnY_6^{2-}
F	0,0754	0.1139	0.2435	0.2251	0.0277	0.0465	0.00207
Cl	0.0468	0.0634	0.1364	0.1042	0.0126	0.0219	0.00099
Br	0.0333	0.0486	0.1157	0.0837	0.0109		0.00070
I	0.0217	0.0358	0.0975	0.0649	0.0098		0.00074

Y	CY_2	CY_3^{2-}	PY_4^{3-}	VY_4^{3-}	AsY_4^{3-}	MoY_4^{2-}	WY_4^{2-}
O	0.1888	0.2059	0.03974	0.01253	0.00616	0.00402	0.00121
S	0.1111	0.0985	0.02289	0.00698	0.00298	0.00257	0.00072
Se	0.0938	0.0865	—	—	—	0.00159	0.00047

Overall, there are three factors which determine the dependence of the RPFIF on the nature of the ligand: the occurrence of the donor atom of the ligand in a definite Period, the chemical individuality of the donor atom, and the influence on the donor atom by the remaining atoms of the ligands. The available data for different complex-forming ligands permits the conclusion that the first factor is of greatest importance, while the individuality of the donor atom has less influence and the latter is comparable to the influence of the remaining part of the ligand. There is a satisfactory correspondence between the sequence based on the variation of $\ln\beta$ and the familiar simple sequence of donor elements:

$$C\geqslant N\geqslant O\geqslant F>S\geqslant Cl>Br>I. \qquad (41)$$

The variation of $\ln\beta$ with the degree of oxidation of the element and with the nature of the donor atom or ligand added to it follows the analogous variation of the valence force constants f_r. This correspondence is confirmed by numerous empirical relations between f_r and both phenomenological features of the compound specified above and is caused by the relation between $\ln\beta$ and f_r already discussed.

The relation between the RPFIF and the configurations of the coordination spheres of the element in the compound can be traced only for a few types of configurational transitions. Examples of such transitions are provided by transitions of the following types:

$$CO_2\,(D_{\infty h}) \rightarrow CO_3^{2-}\,(D_{3h});$$
$$BF_3\,(D_{3h}) \rightarrow BF_4^-\,(T_d),$$
$$SiF_4\,(T_d) \rightarrow SiF_6^{2-}\,(O_h).$$

Table 7 shows that in the majority of instances such transtions, associated with an increase in the number of added donor atoms and a change in the type of hybridisation of the electronic orbitals of the atom involved in isotope substitution, are accompanied by a decrease of $\ln\beta$. This can be explained by the marked decrease of f_r in such transitions. However, the configurational transitions caused by the addition of electron-deficient species and by the delocalisation of the nonbonding electron pair of the atom can be accompanied by an appreciable increase of $\ln\beta$. An example of such transitions is $NH_3(C_{3v}) \rightarrow NH_4(T_d)$.[101]

V. SYSTEMATIC TREATMENT OF CHEMICAL ISOTOPE EFFECTS AND THEIR PREDICTION

In both applications of isotope effects—in the separation of stable isotopes and in the employment of such effects as the basis of a research technique—it is necessary to solve the following problems: the determination of the limits of applicability of the corresponding methods and prediction of the systems and situations in which these methods are most effective. In other words, the problems can be formulated in the following way: (a) statistical estimation of the isotope effects for various elements of the Periodic System; (b) the search for a method of rational classification of isotope exchange reactions as the basis for a systematic treatment of isotope effects; (c) the determination of the principles governing the prediction of systems with large isotope effects on the basis of general chemical information. The above problems have been solved[111–117] and the results will be considered briefly in this section.

Table 7. Isotope effects $\beta_X - 1$ in configurational transitions.

Y	$CY_2(D_{\infty h}) \rightarrow CY(D_{3h})$		Y	$BY_3(D_{3h}) \rightarrow BY_4(T_d)$	
O	0.1888	0.2095	OH	0.278	0.247
S	0.1111	0.0985	F	0.2435	0.213
Se	0.0938	0.0865	Cl	0.1364	0.106

Y	$SiY_4(T_d) \rightarrow SiY_6^{2-}(O_h)$		Y	$SnY_4(T_d) \rightarrow SnY_6^{2-}(O_h)$	
F	0.0475	0.0323	F	0.00208	0.00207
Cl	0.0259	0.0085	Cl	0.00119	0.00099
Br			Br	0.000954	0.000996

1. Statistical Estimation of the Isotope Effects of Different Elements

The sets of possible chemical exchange systems of different elements are quantitatively non-equivalent but their number is always at least several thousands. On the other hand, the number of compounds of each element for which the values of the RPFIF are known is almost always small. The sets of systems with calculated isotope separation factors α susceptible to a statistical treatment are also small and for the majority of elements the sets of possible systems are insufficiently representative. The deficiency of information can be compensated by extending the framework of the treatment by combining the systems of different elements in a single set. However, the values of $\ln\beta$ and $\ln\alpha$ depend to the greatest extent on the atomic weight of the element and such combination requires the normalisation of the $\ln\alpha$, i.e. they must be adjusted to a single scale.

For this purpose, the concept of the γ-factor has been introduced; it is defined as the ratio of the absolute value of $\ln\alpha$ for a specific chemical exchange system of a given element to the maximum possible value $\ln\alpha_{max}$ for the same element. α_{max} is numerically equal to the separation factor for a hypothetical system in which the exchange takes place between the compound with the maximum possible value β_{max} and the non-bonded atomic form for which $\beta = 1$:

$$\gamma = |\ln\alpha|/\ln\beta_{max}. \qquad (42)$$

For any element, γ varies in the same range $0 \leq \gamma \leq 1$. The available information about the characteristic features and limits of variation of β is sufficient to create a reference system of maximum values β_{max} for the majority of elements of the Periodic Table. Compounds in which the element exhibits the highest oxidation state, coordinates ligands with donor atoms of elements in the Second Period (C,N,O, and F), and has a nearly saturated coordination sphere have the highest values of β. For a large number of elements, it is possible to indicate directly compounds whose β-factors should be extremely close to the upper limit; for others, the β_{max} were estimated by correlation methods[112]. Comparison of the β_{max} for different elements reveals a periodicity in their variation with increase of the atomic number of the element in the Periodic Table.

Table 8. The γ distribution functions (the probabilities of finding systems in different ranges of γ values).

Type	Characteristic of set	No. of systems	Ranges of γ values						
			0—0.1	0.1—0.2	0.2—0.3	0.3—0.4	0.4—0.5	0.5—0.6	$\gamma_{cp.}$
I	Set taking into account the abundances of different classes	1081	0.573	0.238	0.094	0.063	0.025	0.007	0.126
II	Set not taking into account the abundances of different classes	—	0.381	0.281	0.172	0.091	0.061	0.014	0.171
III	Set of experimentally investigated systems	161	0.410	0.349	0.138	0.058	0.025	0.010	0.150

The separation factors for each element can assume different values within the range $[1; \beta_{max}]$. The frequency of the appearance of larger and smaller values of α can be different. The concept of attainable values of α has the significance of maximum values, the probability of the appearance of which remains acceptably large from the practical point of view. A direct empirical estimate of the probability of the existence of different α is mathematically equivalent to the construction of statistical distribution functions for α.

The conversion of statistical distribution functions for α into statistical distribution functions for γ makes it possible to compare directly the functions for different elements, to estimate the degree of their similarity, and to solve the problem of the possibility of employing average (generalised) distribution functions for γ in order to estimate the attainable values of α for those elements for which direct analysis of the problem is impossible or difficult.

The γ distribution function is determined by the nature of the set of systems for which it is constructed. It is possible to distinguish hypothetical random sets formed by pair combinations of all the compounds with known β-factors; the sets of thermodynamically compatible systems; the sets of systems with a high rate of isotope exchange or a rate satisfactory for practical purposes. The γ distribution functions of the three types have been investigated in the case of eleven elements (H,B,C,N,O,F,Fe,Co,Ni,Zn). It has been established that overall the γ-functions of each type differ little despite the marked chemical individuality of each of the elements enumerated. Hence it follows that the estimation of the attainable values of α for different elements can be achieved with the aid of averaged γ-functions.

However, the set of systems satisfactory in both thermodynamic and kinetic respects can be constructed in different ways. It is possible to investigate the set of all the systems with known values of α in which account is taken of the different abundances of different classes of systems (set I, Table 8). The γ distribution function for such a set will reflect the probability of a random selection or discovery of systems with particular values of γ. One can investigate the γ-functions for each class of systems (see below). The averaging of such functions without taking into account the abundances of the classes leads to γ-functions taking into account the element of specificity in the search for systems (Set II). Finally, one can investigate the γ-function for the set of experimentally investigated systems (set III). Evidently all three types of functions are suitable for the estimation of the attainable values of α.

Table 8 presents the γ distribution functions corresponding to the three specified methods of construction of the initial sets. The probability of obtaining high values of γ is highest for the function which does not take into account the abundance of systems of different classes and is lowest for the function which does take this factor into account. The

Table 9. The values of $\ln \beta_{max}$ at 300 K (the formula of the compound with β_{max} is indicated).

Li_2O 0.117	BeF_2 0.124	BF_3 0.214	CF_4 0.202	NO_3^- 0.150	NO_2^+ 0.115	CF_4 0.0309			
NaF 0.00467	MgF_2 0.0160	AlF_3 0.0257	SiF_4 0.0473	PO_4^{3-} 0.0382	SO_4^{2-} 0.0428	ClO_4^- 0.00406			
KF 0.00121	CaF_2 0.00347	ScF_6^{3-} 0.00704	TiF_6^{2-} 0.00911	VO_4^{3-} 0.0122	CrF_6 0.0133	MnO_4^- 0.0117	$Fe(CO)_4^{2+}$ 0.0104	$Co(CN)_6^{3-}$ 0.00745	NiF_6^{2-} 0.0101
CuF_2 0.00274	ZnF_2 0.00235	GaF_6^{3-} 0.00551	GlF_4 0.00605	AsF_6^- 0.00677	SeF_6 0.00719	BrF_5 0.00449			
RbF 0.000259	SrF_2 0.000661	YF_6^{3-} 0.00223	ZrF_4 0.00302	NbF_6^- 0.00373	MoF_6 0.00429	TcF_6 0.00423	RuF_6 0.00394	RhF_6 0.00385	PdF_6 0.00355
AgF 0.000303	CdF_2 0.000707	InF_6^{3-} 0.00163	SnF_4 0.00220	SbF_6 0.00266	TeF_6 0.00285	IF_6 0.00251			
CsF 0.000102	BaF_2 0.000241	LaF_6 0.000924	HfF_4 0.000980	TaF_6^- 0.00110	WF_6 0.00136	ReF_6 0.00135	OsF_6 0.00129	IrF_6 0.00128	PtF_6 0.00123
AuF 0.000141	HgF_2 0.000269	TlF_6^{3-} 0.000431	PbF_4 0.000493	BiF_4 0.00070	UF_6 0.000642				

function of experimentally investigated systems occupies an intermediate position, which is evidently a consequence of the low specificity of the empirical search for systems to be used in isotope separation. At the same time all three functions are on the whole similar. This shows that their use for the estimation of the attainable values of α is fairly reliable.

Table 9 presents the estimates of the attainable values of α at 300 K, obtained for all the elements in the Periodic Table, with the exception of the lanthanides, actinides, and the noble gases.

2. Classification of Isotope Exchange Reactions

In order to serve as an effective instrument for interpretation and prediction, the classification of chemical exchange systems must cover fairly completely the entire region of equilibrium chemical isotope effects and must constitute a flexible means of combining specific information with general chemical information. The set of features defining the systematic classification must meet these requirements. The choice of the state of oxidation of the element, the type of coordinated ligand, and the configuration of the coordination sphere of the compound as features of this kind is satisfactory in this respect.

Allowance for the three features of each compound implies that each chemical exchange system is described by six features and that in each pair of like features the two can be either identical or different. Hence follows the subdivision of the entire set of isotope exchange reactions into eight classes. Table 10 defines the different classes and presents examples of the corresponding reactions. All the classes can be subdivided into four groups: class I—the class of homomolecular exchange reactions for which the isotope separation factors are mathematically rigorously equal to unity; three "simple" classes (II, III, and IV) in which the number of differing features of the compounds is unity; three classes (V, VI, and VII) with two differing features of the compounds; class VIII, in which the number of differing features of the compounds is a maximum and equal to three. Each class can be subdivided in its turn into subclasses corresponding to a specific combination of both variable and invariant features. However, the available data are insufficient for a detailed investigation of the subclasses and in the main only the classes as a whole are so far susceptible to analysis. Analysis of the experimentally investigated systems does not allow a comparison of the possibilities of different classes, because the vast majority of systems investigated refer to class VII, isolated systems in classes III, IV, VI, VIII have been studied, while classes II and V have not been studied at all.

Table 11. The γ distribution functions for different classes (probabilities of finding systems in different ranges of γ values).

Class	γ_{av}	Ranges of γ values					
		0—0.1	0.1—0.2	0.2—0.3	0.3—0.4	0.4—0.5	0.5—0.6
II	0.174	0.30	0.35	0.22	0.11	0.02	0.00
III	0.079	0.85	0.14	0.00	0.00	0.01	0.00
IV	0.105	0.48	0.30	0.16	0.04	0.05	0.00
V	0.198	0.28	0.38	0.24	0.03	0.07	0.00
VI	0.282	0.08	0.34	0.22	0.12	0.18	0.02
VII	0.124	0.55	0.31	0.09	0.05	0.00	0.00
VIII	0.310	0.16	0.16	0.29	0.24	0.16	0.08

Table 11 illustrates the γ distribution functions for seven classes with $\gamma \neq 0$ obtained as a result of the interpretation of calculated theoretical data[113]. Table 11 shows that the average value γ_{av} for a given class increases with increasing

Table 10. Classification of isotope exchange reactions. Examples of kinetically satisfactory isotope exchange reactions belonging to different classes (290–300 K)[115,116].

Class	System	Kinetic characteristic	α_{theor} ($\Delta m = 1$)	α_{exp} ($\Delta m = 1$)	γ for reaction
Class II Configuration and ligand identical, oxidation states different	$Fe(CN)_6^{3-} + Fe(CN)_6^{4-}$	$k = 3.5 \times 10^2$ litre mol^{-1} s^{-1}	1.00216	—	0.24
	$Mo(CN)_8^{-3} + Mo(CN)_8^{4-}$	$k = 355$ litre mol^{-1} s^{-1}	1.00075	—	0.19
Class III Oxidation state and configuration identical, ligands different	$HDS + H_2O$	HETS = 10 cm	2.20	2.38	0.27
	$Mn(CN)_6^{4-} + Mn(H_2O)_6^{+}$	rapid exchange	1.0032	—	0.21
	$ZnI_4^{2-} + ZnI_3F^{2-}$	very rapid exchange	1.00052	—	0.16
Class IV Oxidation state and ligand identical, configurations different	$NH_3 + NH_4^{+}$	$k = 24.6$ mol s	1.034	1.035	0.25
	$SiF_6^{2-} + SiF_4$	rapid exchange	1.0150	—	0.32
	$HgCl_2 + HgCl_4^{2-}$	rapid exchange	1.00005	—	0.20
Class V Configurations identical, oxidation states and ligands different	$V(H_2O)_6^{2} + V(CN)_6^{3-}$	rapid exchange	1.0012	—	0.08
	$Mn(H_2O)_6^{3+} + Mn(CN)_6^{4-}$	rapid exchange	1.0008	—	0.07
Class VI Ligands identical, configurations and oxidation states different	$NO + NO_3^{-}$	rapid exchange	1.079	—	0.54
	$NO + NO_2$	rapid exchange	1.035	1.028	0.24
Class VII Oxidation states identical, configurations and ligands different	$CO_2 + H_2O$	HETS = 13 cm	1.021	1.021	0.18
	$SO_2 + HSO_3$	rapid exchange		1.010	0.22
	$Zn(H_2O)_6^{2+} + ZnI_4^{2-}$	rapid exchange	1.0007	—	0.30
Class VIII Configurations, oxidation states, and ligands different	Li(amalgam) + $Li(H_2O)_6^{+}$	HETS = 10 cm	1.050	1.055	0.72
	$NO + HNO_3$	HETS = 2–3 cm		1.065	0.43
	Mg (amalgam) + $Mg(H_2O)_6^{2+}$	rapid exchange	1.0105	1.0105	0.43

*HETS = height equivalent to the theoretical stage.

number of differing features. The difference between the influences of individual variable features on γ_{av} can also be clearly traced. The classes of systems with a variable valence state have higher values of γ_{av} than the classes with variable configurations of the coordination spheres, while the classes with different types of ligands have the lowest values of γ_{av} (this is associated with the stepwise nature of the substitution of the ligands and the predominance of the O- and N-donor ligands among those investigated). The most complex class VIII, in which all three features of the contrasted compounds, forming the systems, are different, has the highest value of γ_{av}.

3. Principles of the Prediction of Systems with High Isotope Effects

Both as a means for isotope separation and as the basis for a research technique, chemical isotope effects are more suitable the higher their absolute value. The problem of the prediction therefore usually involves the search for systems with large effects. On the other hand, the principles of the prediction must be formulated as the most rational method for finding such systems on the basis of the entire available information about chemical systems. Direct theoretical calculation and correlation estimates of the values of α are the most reliable means used in such search. However, the computational method of prediction is limited by the small availability of the required initial data. The knowledge of the thermodynamic characteristics of isotope exchange can to some extent compensate for this deficiency and can play the role of the main guiding principle.

However, the broadest base for a rational search and for a comprehensive analysis of systems is provided by the above classification of chemical exchange systems, since it is derived not only from the common causes of the occurrence of isotope effects but also ensures the possibility of employing the most readily available general chemical information.

Isotope effects should be predicted taking into account the specific purpose of the systems sought. In relation to the specific search for chemical exchange systems suitable for isotope separation on the basis of the classification described above, the principle of the selection of systems with high isotope separation factors can be formulated as follows. One of the two compounds of the system should be formed by an element in its highest oxidation state and the ligands coordinated by the element must contain donor atoms belonging to the Second Period (the σ-donor or $\sigma\pi$-donor atoms F, O, and N) and must form an unsaturated coordination sphere. The other compound must contain the given element in the smallest possible oxidation state; the ligands coordinated by this element must contain the elements of higher Periods as donor atoms ($\sigma\pi$-donor ligands with weak π-acceptor properties) and the coordination sphere must be saturated.

This principle conflicts with other requirements. Apart from a high separation factor, the "promising" chemical system must have specific qualities, namely thermodynamic stability, satisfactory kinetics of isotopic exchange, ready separability of the juxtaposed chemical forms between the juxtaposed phases, and simplicity of the interconversion of the juxtaposed chemical forms. Since the thermodynamic classification of chemical exchange systems takes into account the general chemical unity of different classes, it can serve as a basis for a general analysis of the possibilities of different classes, including also the series of specific requirements enumerated.

The prediction of isotope effects in systems which can be fruitful objects of study using the isotope effects themselves constitutes a more difficult problem which awaits solution.

REFERENCES

1. J.C.Lerman, "Environmental and Biological Control of Photosynthesis" (Edited by R.Marchelle), Hague, 1975, p.323.
2. H.Ziegler, C.B.Osmond, W.Stichler, and P.Trunborn, Planta, **128**, 85 (1975).
3. A.A.Ivlev, Uspekhi Sovr.Biol., 81, 84 (1976).
4. Y.Cheung and C.Walsh, Biochemistry, **15**, 3749 (1976).
5. S.Z.Roginskii and S.E.Shnol', "Izotopy v Biokhimii" (Isotopes in Biochemistry), Izd.Akad.Nauk SSSR, Moscow, 1965.
6. E.T.Degens, Symposium, "Organicheskaya Geokhimiya" (Organic Geochemistry), Izd.Nedra, Leningrad, 1974, p.207.
7. E.M.Galimov, "Izotopy Ugleroda v Neftegazovoi Geologii" (Carbon Isotopes in Petroleum–Gas Geology), Izd.Nedra, Moscow, 1973.
8. V.A.Grinenko and L.N.Grinenko, "Geokhimiya Izotopov Sery" (Geochemistry of Sulphur Isotopes), Izd.Nauka, Moscow, 1974.
9. N.A.Eremenko, R.G.Pankina, T.A.Botneva, S.P.Maksimov, V.L.Mekhtieva, and A.A.Ivlev, "Stabil'nye Izotopy v Geokhimii Nefti" (Stable Isotopes in Geochemistry of Petroleum), Izd.Nedra, Moscow, 1974.
10. R.Caplan, Proc.Roy.Soc.B, **189**, 183 (1975).
11. W.Kolodny and S.Epstein, Geochim.Cosm.Acta, **40**, 1195 (1976).
12. L.P.Knowth and S.Epstein, J.Earth Planet.Sci. Lett., **25**, 1 (1975).
13. G.R.Sivens, J.Roy.Soc.(New Zealand), 1, 145 (1971).
14. J.Bigeleisen, M.W.Lee, and F.Mandel, Ann.Rev. Phys.Chem., **24**, 407 (1973).
15. "Isotope Effects in Chemical Processes", Adv.in Chem.Ser., **89**, Amer.Chem.Soc., 1969.
16. P.A.Pock (Editor), "Isotopes and Chemical Principles", Amer.Chem.Soc., New York, 1975.
17. "Proceedings of the International Symposium on Isotope Separation, Amsterdam, 1958".
18. N.M.Zhavoronkov and K.I.Sakodynskii, Zhur.Prikl. Khim., **36**, 2564 (1963).
19. B.N.Laskorin, A.M.Babenko, A.F.Filippov, and E.A.Trubnikov, Uspekhi Khim., **44**, 761 (1975) [Russ.Chem.Rev., No.5 (1975)].
20. E.R.Thornton, Ann.Rev.Phys.Chem., 17, 349 (1966).
21. C.J.Collins and N.S.Bowmen, (Editors), "Isotope Effects in Chemical Reactions", Ann.Chem.Soc. Monograph-167, New York, 1971.
22. P.Krumbiegel, "Isotopieeffecte", Acad.Verlag, Berlin, 1970.
23. T.Ishida, W.Spindel, and J.Bigeleisen, Adv.Chem. Ser., **89**, 192 (1969).
24. M.Wolfsberg, Ann.Rev.Phys.Chem., **20**, 449 (1969).
25. L.Melander, "Isotope Effects on Reaction Rates" (Translated into Russian), Izd.Mir, Moscow, 1964.
26. W.H.Saunders, "Survey of Progress in Chemistry", Acad.Press, New York–London, 1966, Vol.3.
27. E.A.Halevi, Symposium, "Sovremennye Problemy Fizicheskoi Organicheskoi Khimii" (Current Problems in Physical Organic Chemistry) (Translated into Russian), Izd.Mir, Moscow, 1967, p.25.
28. R.E.Weston, Science, **158**, 332 (1967).
29. M.J.Goldstein, Science, **154**, 1616 (1966).

30. I.B.Rabinovich, "Vliyanie Izotopii na Fiziko-Khimicheskie Svoistva Zhidkostei" (The Influence of Isotope Substitution on the Physicochemical Properties of Liquids), Izd.Nauka, Moscow, 1968.
31. Ya.M.Varshavskii and S.E.Vaisberg, Uspekhi Khim., **26**, 1434 (1957).
32. M.Born and R.Oppenheimer, Ann.Phys., **84**, 457 (1927).
33. G.Herzberg, "Molecular Spectra and Molecular Structure" Vol.3, "Electronic Spectra and Electronic Structure of Polyatomic Molecules" (Translated into Russian), Izd.Mir, Moscow, 1969.
34. G.Herzberg, "Molecular Spectra and Molecular Structure", Vol.1, "Spectra of Diatomic Molecules" (Translated into Russian), Izd.Mir, Moscow, 1949.
35. A.Farkas, "Orthohydrogen, Parahydrogen, and Heavy Hydrogen" (Translated into Russian), ONTI, Moscow, 1936.
36. J.Bron, C.F.Chang, and M.Wolfsberg, Z.Naturforsch., **28-A**, 129 (1973).
37. A.S.Friedman and L.Haar, J.Chem.Phys., **22**, 2051 (1954).
38. J.E.Mayer and M.G.Mayer, "Statistical Mechanics" (Translated into Russian), Inostr.Lit., Moscow, 1952.
39. I.N.Godnev, "Vychislenie Termodinamicheskikh Funktsii po Moleculyarnym Dannym" (Calculation of Thermodynamic Functions from Molecular Data), GIITL, Moscow, 1956.
40. H.C.Urey, J.Amer.Chem.Soc., **57**, 321 (1935).
41. R.Halverson, Rev.Mod.Phys., **19**, 87 (1947).
42. G.Herzberg, "Vibrational and Rotational Spectra of Polyatomic Molecules" ["Molecular Spectra and Molecular Structure", Vol.2, "Infrared and Raman Spectra of Polyatomic Molecules"] (Translated into Russian), Izd.Mir, Moscow, 1949.
43. E.B.Wilson, J.C.Decius, and P.C.Cross, "Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra" (Translated into Russian), Inostr.Lit., Moscow, 1960.
44. L.S.Mayants, "Teoriya i Raschet Kolebanii Molekul" (Theory of and Calculations on Molecular Vibrations), Izd.Akad.Nauk SSSR, Moscow, 1960.
45. L.M.Sverdlov, Dokl.Akad.Nauk SSSR, **78**, 5 (1951); **86**, 513 (1952).
46. L.M.Sverdlov, Optika i Spektrosk., **8**, 36 (1960).
47. J.C.Decius and E.B.Wilson, J.Chem.Phys., **19**, 1409 (1951).
48. H.Broderson, J.Mol.Spectroscopy, **3**, 114, 450 (1959).
49. J.Bigeleisen, J.Chem.Phys., **23**, 2264 (1955); **28**, 694 (1958).
50. T.Ishida and J.Bigeleisen, J.Chem.Phys., **64**, 4775 (1976).
51. A.I.Brodskii, Zhur.Fiz.Khim., **9**, 755 (1935).
52. G.Vojta, Ann.Phys., **7**, 397 (1961).
53. G.Vojta, J.Phys.Chem., **217**, 357 (1961).
54. B.T.Darling and D.M.Dennison, Phys.Rev., **57**, 128 (1940).
55. M.Wolfsberg, Adv.Chem., **89**, 185 (1969).
56. M.Wolfsberg, J.Chem.Phys., **50**, 1484 (1969).
57. J.Bron and M.Wolfsberg, J.Chem.Phys., **57**, 2862 (1972).
58. T.Ishida, J.Chem.Phys., **61**, 3009 (1974).
59. G.Vojta, Z.Phys.Chem., **220**, 379 (1962).
60. K.F.Stripp and J.G.Kirkwood, J.Chem.Phys., **19**, 1131 (1951).
61. V.S.Yungman, Zhur.Fiz.Khim., **35**, 319 (1961) [Russ.J.Phys.Chem., No.2 (1961)].
62. H.H.Nielsen, Rev.Mod.Phys., **23**, 90 (1951).
63. R.E.Miller, G.E.Lerov, and D.F.Eggers, J.Chem.Phys., **46**, 2992 (1967).
64. L.I.Kleinman and M.Wolfsberg, J.Chem.Phys., **59**, 2043 (1973).
65. L.I.Kleinman and M.Wolfsberg, J.Chem.Phys., **60**, 4749 (1974).
66. J.Bigeleisen and G.M.Mayer, J.Chem.Phys., **15**, 261 (1947).
67. J.Bigeleisen, J.Chem.Phys., **21**, 1333 (1953).
68. J.Bigeleisen, "Proc.Internat.Symp.on Isotope Separation, Amsterdam, 1958", p.121.
69. J.Bigeleisen and M.Wolfsberg, Adv.Chem.Phys., 1, 15 (1958).
70. E.U.Monse, W.Spindel, and M.G.Stern, Adv.Chem., **89**, 148 (1969).
71. D.A.Denisov, D.A.Knyazev, and N.V.Shafeeva, Zhur.Fiz.Khim., **47**, 2975 (1973) [Russ.J.Phys.Chem., No.12 (1973)].
72. D.A.Knyazev, A.N.Bantysh, and A.A.Ivlev, Zhur.Fiz.Khim., **41**, 1441 (1967) [Russ.J.Phys.Chem., No.6 (1967)].
73. D.A.Knyazev, N.V.Shafeeva, and L.B.Preobrazhenskaya, Trudy Moskov.Khim.-Tekhnol.Inst.im. Mendeleeva, No.56, 97 (1969).
74. D.A.Knjazev, A.A.Ivlev, D.A.Denisov, and L.B.Preobragenskaya, Isotopenpraxis, 6, 471 (1970).
75. L.A.Gribov, "Vvedenie v Teoriyu i Raschet Kolebatel'nykh Spektrov Mnogoatomnykh Molekul" (Introduction to the Theory and Calculation of the Vibrational Spectra of Polyatomic Molecules), Izd. Moskov.Gos.Univ., 1965.
76. M.V.Vol'kenshtein, L.A.Gribov, M.A.El'yashevich, and B.I.Stepanov, "Kolebaniya Molekul" (Molecular Vibrations), Izd.Nauka, Moscow, 1972.
77. S.G.Katal'nikov, A.M.Voloshchuk, and D.A.Knyazev, Kernenergie, **17**, 88 (1974).
78. D.A.Knyazev, A.A.Ivlev, and T.L.Blank, Isotopenpraxis, **14**, 31 (1978).
79. E.M.Galimov, Zhur.Fiz.Khim., **48**, 290 (1974) [Russ.J.Phys.Chem., No.2 (1974)].
80. J.Bigeleisen and T.Ishida, J.Chem.Phys., **48**, 1311 (1968).
81. G.Nemeth, B.Gellai, and G.Jansco, J.Chem.Phys., **54**, 1701 (1971).
82. G.Singh and M.Wolfsberg, J.Chem.Phys., **62**, 4165 (1975).
83. J.Bigeleisen, R.C.Hom, and T.Ishida, J.Chem.Phys., **64**, 3303 (1976).
84. J.Bigeleisen, T.Ishida, and W.Spindel, Proc.Nat. Acad.Sci., 67, 113 (1970).
85. J.Bigeleisen, T.Ishida, and W.Spindel, J.Chem. Phys., **55**, 5021 (1971).
86. J.Bigeleisen and T.Ishida, J.Chem.Phys., **62**, 80 (1975).
87. J.Bigeleisen and P.Goldstein, Z.Naturforsch., **18a**, 205 (1963).
88. J.Bigeleisen and T.Ishida, J.Amer.Chem.Soc., **95**, 6155 (1973).
89. D.A.Knyazev, T.L.Blank, A.A.Ivlev, and A.D.Blank, Dokl.Timiryazev.Sel'skokhoz.Akad., **218**, 208 (1976).
90. D.A.Knyazev, A.A.Ivlev, A.D.Blank, and T.L.Blank, Dokl.Akad.Nauk SSSR, **233**, 126 (1977).
91. A.P.Mishina and I.V.Proskuryakov, "Vysshaya Algebra" (Higher Algebra), GIFL, Moscow, 1962.
92. D.A.Knyazev, T.D.Blank, and S.V.Demin, Izv. Timiryazev, Sel'skokhoz.Akad., No.2, 203 (1977).
93. M.J.Stern, E.U.Monse, and W.Spindel, J.Chem. Phys., **48**, 2908 (1968).

94. W.Spindel, M.J.Stern, and E.U.Monse, J.Chem. Phys., **52**, 2022 (1970).
95. L.M.Mills, "Infrared Spectroscopy and Molecular Structure", Amsterdam, 1963, p.1966.
96. L.H.Jones, J.Chem.Phys., **36**, 1209 (1962).
97. A.M.Rozen and A.I.Mikhailichenko, Dokl.Akad. Nauk SSSR, **148**, 144 (1963); **148**, 1354 (1963).
98. A.M.Rozen and A.I.Mikhailichenko, Atomnaya, Energiya, **18**, 147 (1965).
99. A.M.Rozen and A.I.Mikhailichenko, Zhur.Fiz.Khim., **44**, 1737, 1742 (1970) [Russ.J.Phys.Chem., No.7 (1970)].
100. D.A.Knyazev, A.N.Bantysh, and A.A.Ivlev, Kernenergie, **10**, 113 (1967).
101. D.A.Knyazev, A.N.Bantysh, and A.A.Ivlev, Kernenergie, **10**, 149 (1967).
102. D.A.Knyazev, A.N.Bantysh, and A.A.Ivlev, Zhur.Fiz.Khim., **44**, 2233 (1970) [Russ.J.Phys. Chem., No.9 (1970)].
103. D.A.Knyazev, A.N.Bantysh, and A.A.Ivlev, Zhur.Fiz.Khim., **41**, 1915 (1967) [Russ.J.Phys. Chem., No.8 (1967)].
104. E.R.Lippincott and R.Schroeder, J.Amer.Chem. Soc., 78, 5171 (1956).
105. G.Thyagarajan and R.S.Sarma, J.Mol.Spectroscopy, **31**, 100 (1969).
106. W.Gordy, J.Chem.Phys., **14**, 305 (1946).
107. K.M.Guggenheimer, Discuss.Faraday Soc., **9**, 221 (1950).
108. R.C.Ferreira, Notes de Fisica, 6, 337, 367 (1960).
109. Y.P.Varshni, J.Chem.Phys., **28**, 1081 (1958).
110. G.Somayajulu, J.Chem.Phys., **33**, 1541 (1960).
111. D.A.Knyazev, A.A.Ivlev, and A.N.Bantysh, "Materialy Vsesoyuznoi Konferentsii Posvyashchennoi 20-Letiyu Proizvodstva i Primeneniya Izotopov v SSSR" (Proceedings of the All-Union Conference Devoted to the 20th Anniversary of the Manufacture and Applications of Isotopes in the USSR), Moscow, 1972.
112. D.A.Knyazev, A.A.Ivlev, and A.N.Bantysh, Zhur.Fiz.Khim., **41**, 2200 (1967) [Russ.J.Phys.Chem., No.9 (1967)].
113. D.A.Knjazev, A.A.Ivlev, A.N.Bantys, and E.V.Dobiza, Kernenergie, **11**, 229 (1963).
114. D.A.Knyazev, A.A.Ivlev, G.D.Klinskii, and D.A.Denisov, Zhur.Fiz.Khim., **50**, 2504 (1976) [Russ.J.Phys.Chem., No.10 (1976)].
115. N.M.Zhavoronkov, D.A.Knyazev, and G.D.Klinskii, Zhur.Fiz.Khim., **51**, 1 (1977) [Russ.J.Phys.Chem., No.1 (1977)].
116. N.M.Zhavoronkov, D.A.Knyazev, and G.D.Klinskii, Zhur.Fiz.Khim., **52**, 897 (1978) [Russ.J.Phys.Chem., No.4 (1978)].
117. D.A.Knyazev and G.D.Klinskii, Isotopenpraxis, **14**, 41 (1978).

Kurnakov Institute of General
and Inorganic Chemistry, USSR
Academy of Sciences, Moscow

Timiryazev Moscow Agricultural Academy

Translated from *Uspekhi Khimii*, **49**, 420-447 (1980) U.D.C. 547.45

Saccharinic Acids

R.A.Gakhokidze

Data on the chemistry of saccharinic acids are examined and described systematically. The alkaline degradation of mono-, oligo- and poly-saccharides is discussed, much attention being devoted to the conditions which influence the course of the reaction. It is shown that the nature of the alkali metal cation, the pH of the medium, temperature, and the structure of the carbohydrate play an important role. Data concerning the stabilisation of polysaccharides in alkali are described in detail. The problem of the applications of saccharinic acids is examined.
The bibliography includes 254 references.

CONTENTS

I. Introduction 222
II. The mechanism of the formation of saccharinic acids 223
III. The influence of the nature of the alkali metal cation, pH, and temperature on the formation of saccharinic acids 224
IV. The influence of substituents on the formation of saccharinic acids 225
V. The formation of saccharinic acids by the cleavage of oligo- and poly-saccharides with alkali 227
VI. The properties and applications of saccharinic acids 231

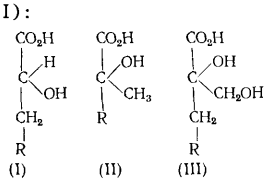
I. INTRODUCTION

The complex and varied reactions of carbohydrates in alkali have long attracted the attention of investigators. However, despite vigorous research, the interconversions and degradation reactions of carbohydrates in alkaline solutions have still been inadequately studied. The conversion of reducing sugars under the influence of aqueous bases includes the following processes[1-3]: mutarotation (anomerisation); epimerisation (the Lobry de Bruyn–van Ekenstein transformation); retroaldol cleavage, the products of which are capable of new reactions; saccharinic rearrangement. The formation of carbocyclic compounds[4-8], the Cannizzaro reaction[9], and intramolecular oxidation–reduction[10] are also possible. The formation of polymeric compounds[11] (probably via aldoxyloses at elevated temperatures[12]) has also been noted. In addition, sugars form complexes (saccharinates) with metal hydroxides[13-19]. Under the influence of alkalies, glycosylamines undergo the Amadori rearrangement[20]. Alkaline agents cause numerous carbohydrate derivatives to undergo intramolecular substitutions, for example the elimination of groups such as alkyl and arenesulphonyloxy-groups, halide ions, or nitrate and sulphate ions with the formation of an epoxy-ring (an intramolecular ether)[21,22] and migration of acyl groups[21], involving isomerisation via intramolecular transesterification. However, sugars are fairly resistant to the action of a base at 5°. Thus 85–90% of a sugar (*D*-glucose, *D*-mannose, and *D*-fructose) remains unchanged after prolonged contact (9 months) with dilute sodium hydroxide[23].

The present review is an attempt to describe the present state of the chemistry of saccharinic acids†. Saccharinic acids, which are formed from reducing carbohydrates under the influence of various alkalies, include all the monobasic hydroxy-acids (deoxyaldonic acids) with the empirical formula $C_nH_{2n}O_n$, which have the same compositions as the corresponding carbohydrates. The first mention of substances of this type dates back to 1838.[28,29] The first such substance investigated was erroneously assumed to be an isomer of saccharose (sucrose)—hence the name saccharinic acids.

† For review of earlier studies, see Refs.24–27.

Saccharinic acids can be synthesised from non-sugar-like compounds[30] and by the oxidation of the corresponding deoxysugars. The Grignard[31] and Fischer–Kiliani (the cyanohydrin method) reactions[32,33] have also been used to synthesise saccharinic acids and their derivatives. However, the present review deals with the problems of the formation of saccharinic acids from reducing carbohydrates in an alkaline medium in the absence of oxygen. In an alkaline medium in the presence of oxygen carbohydrates undergo both oxidation and alkaline degradation with formation of a complex mixture of products#. According to their carbon skeleton, saccharinic acids belong to three types: 3-deoxyaldonic (metasaccharinic) acids (I), 2-*C*-methylaldonic (saccharinic) acids (II), and 2-*C*-(hydroxymethyl)-3-deoxyaldonic (isosaccharinic) acids (III):



The structure of saccharinic acids has been reviewed[26]. Later the configuration of α-*D*-glucoisosaccharinic acid[36-38] and its lactone[39] was established by X-ray diffraction; both proved to be *erythro*-compounds. It has been shown by chemical methods[40] that α-*D*-glucosaccharinic acid has the *ribo*-configuration. The γ-lactone of α-*D*-glucosaccharinic acid (2-*C*-methyl-*D*-ribonic acid) and hamamelose (2-*C*-hydroxymethyl-*D*-ribose), whose structure has been established by an independent method, have the same absolute configurations, which has been confirmed by the transformation of each compound into 5-deoxy-2-*C*-methyl-*D*-ribitol[41]. Branched saccharinic acids[42] and di- and tri-deoxysaccharinic acids[43,44] have been detected in the conversion products of polymeric carbohydrates in alkali. Despite the fact that saccharinic

After the oxidation of *D*-glucose and cellobiose with oxygen in a highly alkaline medium, 13 and 19 monobasic acids were isolated respectively[34]. The isolation of 21 organic acids from the products of the oxidation of cellobiose by molecular oxygen in an alkaline medium has been reported[35].

acids are known to form in highly alkaline solutions, metasaccharinic acids and their sulphur-containing derivatives have been obtained by treating carbohydrates with neutral[45-48] or acid sulphite solutions (pH 4.4–6.0; 135 °C).[49-51]

The saccharinic rearrangement of a carbohydrate is undoubtedly of wider importance in nature than has been thought hitherto. Saccharinic acids have been found in plants[52,53]; they are apparently formed from monosaccharides in weakly alkaline media and probably give rise to deoxysugars with straight and branched carbon skeletons as a result of the reduction of the carboxy-group. However, deoxidation of sugars can also take place via reductive reactions of the alcoholic groups.

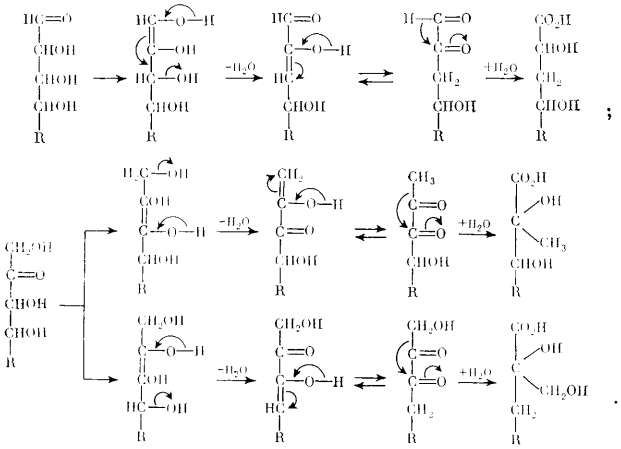
The application of gas chromatography[54-63], mass spectrometry[64-67], and spectrophotometry[68,69], as well as ion-exchange[70,71] and thin-layer[72] chromatography make it possible to determine saccharinic acids rapidly in the complex mixture obtained on alkaline degradation of carbohydrates.

II. THE MECHANISM OF THE FORMATION OF SACCHARINIC ACIDS

Numerous mechanisms have been proposed for the formation of saccharinic acids from reducing sugars. In order to account for the formation of saccharinic acids, Nef[11,73] proposed schemes according to which monoses are converted initially into biradicals in consequence of the elimination of water from an alcoholic group; the migration of hydrogen atoms from another, adjacent alcoholic group to a carbon atom involved in a saturated bond leads to the formation of an aldehydo-ketonic or diketonic form, which undergoes the benzilic acid rearrangement to saccharinic acids. However, this mechanism is complex and the formation of biradicals at a particular site in the chain is doubtful.

Other workers[74,75] modified Nef's scheme, postulating the formation of enediol oxides as intermediates in the isomerisation of carbohydrates. These substances are converted into diketones, which undergo the benzilic acid rearrangement. However, the formation of unsaturated epoxide structures is regarded as unlikely at the present time. It has been suggested[76] that saccharinic acids are formed via a mechanism involving the pinacol rearrangement via alcoholic epoxide forms. The formation of saccharinic acids via the recombination of carbohydrate fragments has been discussed[77,78].

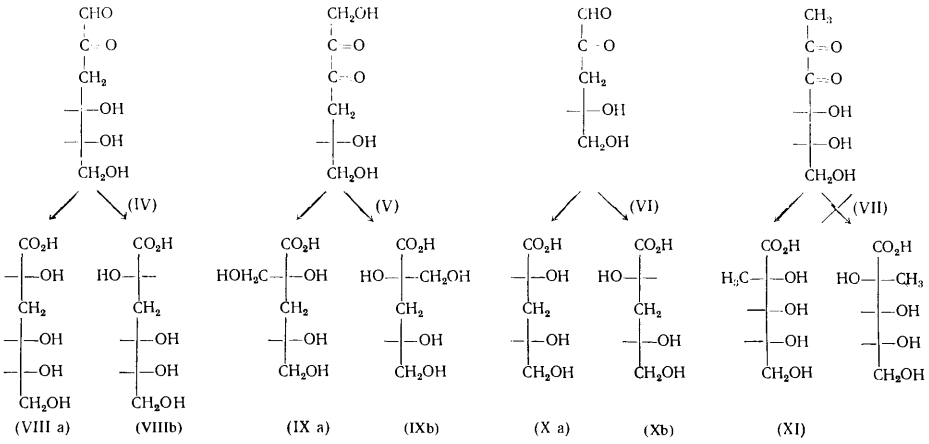
The ionic mechanism put forward by Isbell[79], who treats Nef's hypothesis from the standpoint of electronic ideas, has gained the widest currency at the present time. According to Isbell, the mechanism of the formation of saccharinic acid involves the following stages: (a) the formation and ionisation of the enediol; (b) β-elimination of a hydroxy- or alkoxy-group; (c) rearrangement to an α-dicarbonyl intermediate; (d) benzilic acid rearrangement with formation of saccharinic acid. Accordingly, the formation of saccharinic acids can be represented by the following reactions:



The postulated intermediate dicarbonyl compounds, involved in the formation of saccharinic acids, have been synthesised or isolated after the alkaline treatment of appropriately substituted sugars§. Their rapid conversion into saccharinic acids under the influence of lime water supports the Nef—Isbell mechanism. The proposed mechanism has been partly confirmed in experiments using labelled compounds[67,70,82,83].

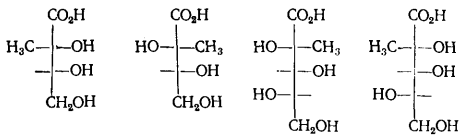
Two possible saccharinic acids are obtained from the intermediates (IV) and (V)—α- and β-*D*-glucosaccharinic acids (VIIIa, VIIIb) and α- and β-*D*-glucoisosaccharinic acids (IXa, IXb) respectively. Similarly in an alkaline medium compound (VI) gives rise to metasaccharinic acids with five carbon atoms (Xa, Xb).[84] However, treatment of compound (VII) with alkali yields only α-*D*-glucosaccharinic acid (XI)[54] (see Scheme 1).

Scheme 1



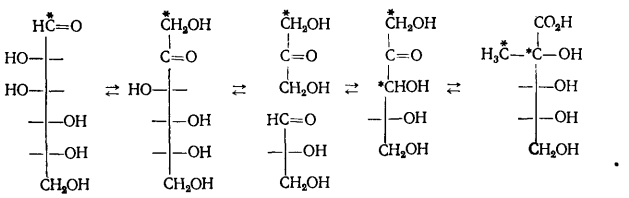
§ For details of the dicarbonyl derivatives of carbohydrates, see Theander[80] and Anet[81].

Since only compound (VII) has an asymmetric carbon atom adjoining the carbonyl group, it has been suggested[54] that the stereospecificity depends on the asymmetry of compound (VII), while compounds (IV) and (V) should give rise to two isomeric acids. Indeed treatment with alkali converts *D-arabino*-2-hexosulose (*D*-glucosone) preferentially into *D*-mannonic acid[85]. However, treatment of *D*-xylose[57] and *L*-sorbose[33] with calcium hydroxide yields respectively α- and β-*D*-xylosaccharinic acids (XIIa, XIIb) and α- and β-*L*-galactosaccharinic acids (XIIIa, XIIIb):

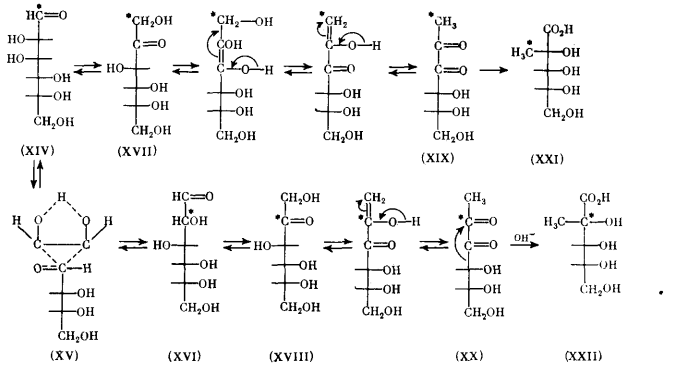


(XIIa) (XIIb) (XIIIa) (XIIIb)

It has been shown with the aid of labelled hexoses[82,83] that different acids arise via different mechanisms. Treatment of *D*-[1-^{14}C] galactose with $Ca(OH)_2$ yielded α-*D*-galactometasaccharinic acid. It was found that 95% of the initial activity was located in the carboxy-group, which is fully consistent with the Nef–Isbell mechanism. Under the same conditions, α-*D*-glucoisosaccharinic acid, in which 94% of the initial activity was contained in $C_{(2)}$, was obtained from [1-^{14}C] lactose; this is also fully consistent with the Nef–Isbell mechanism. However, treatment of *D*-[1-^{14}C] mannose with calcium hydroxide led to the formation of α-*D*-glucosaccharinic acid containing 39% of the initial activity in the CH_3 group and 57% is $C_{(2)}$. In contrast to these observations, the Nef–Isbell mechanism predicts that the radioactivity should appear wholly in the CH_3 group. To account for this phenomenon, it has been suggested[86] that *D*-mannose undergoes rapid retroaldol decomposition under the reaction conditions and that labelled [1,3-^{14}C] hexose is reformed from the resulting dihydroxyacetone and *D*-glyceraldehyde and undergoes a further rearrangement with formation of [2,2'-^{14}C] saccharinic acid.



However, this hypothesis was rejected by Sowden and coworkers[26,82]. They believe that the recombination of trioses should lead to a uniform distribution of the radioactivity in the ketohexose between $C_{(1)}$ abd $C_{(2)}$. According to Isbell's scheme, this would lead to α-*D*-glucosaccharinic acid in which the $C_{(2)}$ atom and the carbon atom in CH_3 would be equally radioactive. The isomerisation of *D*-[1,^{14}C] mannose (XIV) to *D*-[2-^{14}C] glucose (XVI) as a result of the intramolecular rupture of the bond between $C_{(2)}$ and $C_{(3)}$ in the intermediate (XV) has been suggested[87]. *D*-[1-^{14}C] fructose (XVII) and *D*-[2-^{14}C] fructose (XVIII) can give rise, via the Isbell and intramolecular mechanisms respectively, to α-*D*-glucosaccharinic acid with the radioactivity in the methyl group [compound (XXI)] and at $C_{(2)}$ [compound (XXII)]:



(XIV) (XVII) (XIX) (XXI)

(XV) (XVI) (XVIII) (XX) (XXII)

However, the hypothesis of the migration of the methyl and [CH_2OH–CHOH–CHOH] groups respectively in the dicarbonyl intermediates (XIX) and (XX) does not take into account the experimental results, and the formation of α-*D*-glucosaccharinic acid with a reduced radioactivity (2%) in the carboxy-group when the methyl group migrates in compound (XX) weakens this hypothesis. Furthermore, *D*-fructose, prepared from *D*-[1-^{14}C] mannose under conditions analogous to those used to obtain α-*D*-glucosaccharinic acid, contained 98% of the radioactivity in $C_{(1)}$.[23]

According to another mechanism[23], α-*D*-glucosaccharinic acid can be formed from a hexose via a 3-deoxydicarbonyl intermediate. In fact this product gives rise to metasaccharinic acids only[81,88,89]. Thus the problem of the mechanism of the formation of *D*-glucosaccharinic acid remains virtually open.

The formation of saccharinic acids with four, five, and six carbon atoms from *D*-xylose and *D*-fructose[56], as well as the detection of α-*D*-glucosaccharinic acid in the products of the interaction of $Ca(OH)_2$ with glycerose[90] show that the reaction proceeds via a mechanism involving fragmentation and recombination together with direct isomerisation.

III. THE INFLUENCE OF THE NATURE OF THE ALKALI METAL CATION, pH, AND TEMPERATURE ON THE FORMATION OF SACCHARINIC ACIDS

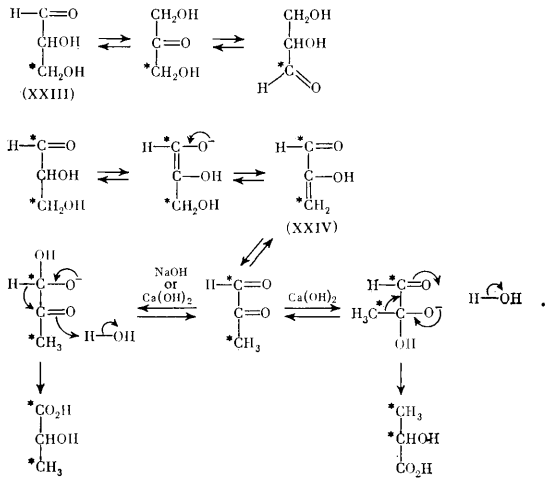
Early studies by Kiliani and Nef[26] showed that glucose is converted into glucosaccharinic acids under the influence of calcium hydroxide, while treatment of the sugar with sodium hydroxide leads mainly to metasaccharinic acid and insignificant amounts of isosaccharinic acid¶. An analogous result was obtained when *D*-fructose was treated with a concentrated solution of sodium hydroxide; *D*-glucosaccharinic acid was not detected, but it was the main product on treatment of *D*-fructose with $Ca(OH)_2$.[56] After treating *D*-xylose with $Ca(OH)_2$, α- and β-*D*-xylosaccharinic acids together with other acids were isolated[56]. Consequently the influence of

¶ *D*-[1-^{14}C]galactose and *D*-[1-^{14}C] mannose isomerise on treatment with $Ca(OH)_2$ to α-*D*-galactometasaccharinic acid and α-*D*-glucosaccharinic acid respectively[82]. It has been shown[91] that the yields of *D*-glucometasaccharinic and α-*D*-glucosaccharinic acids become comparable at high calcium ion concentrations.

the nature of the cation on the mechanism of the formation of saccharinic acid is evident and can be attributed to the kinetic effect[92]†.

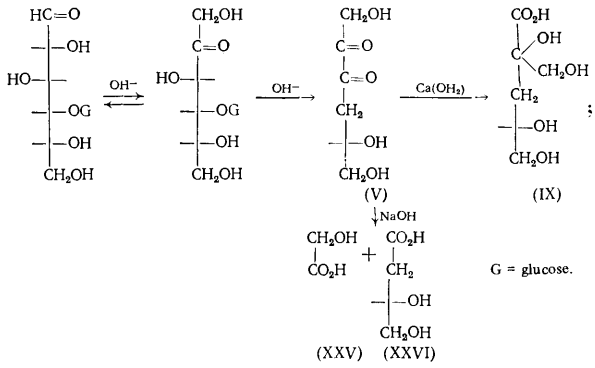
It has been shown[90] that *D*-[3-^{14}C]glycerose (XXIII) isomerises in 1.68 *N* NaOH at 25 °C to lactic acid, where the radioactivity is distributed only between the $C_{(1)}$ and $C_{(3)}$ atoms. An analogous result was obtained on treating *D*-[1-^{14}C]glucose with 3 *N* NaOH at 25 °C.[97] In contrast to this, *D*-[2-^{14}C]glycerose isomerises in saturated lime water at 25 °C to lactic acid with 37, 13 and 50% of the initial radioactivity in the $C_{(1)}$, $C_{(2)}$, and $C_{(3)}$ atoms respectively[90].

Evidently the epimerisation glycerose ⇆ 1,3-dihydroxypropanone is faster in an alkaline medium than the saccharinic rearrangement. In an alkaline medium a hydoxide ion adds to the aldehyde carbonyl of the α-dicarbonyl intermediate [methylglyoxal (XXIV)]. In the presence of $Ca(OH)_2$ the hydroxide ion attacks the ketone carbonyl group in (XXIV), which can probably be accounted for by the stabilisation of the transition state as a result of interaction with the divalent calcium ion and subsequent migration of the methyl group. *D,L*-Lactic acid is the main product of the alkaline degradation of 1-O-substituted fructose[86] and 6-O-substituted sugars—6-O-methyl-*D*-glucose[98] and melibiose)6-O-α-*D*-galactopyranosyl-*D*-glucose).[99,100]



The intermediate in the formation of isosaccharinic acids postulated by the Nef–Isbell theory, namely 4-deoxy-*D*-glycerohexose-2,3-diulose (V), was isolated[110] on treating maltose with sodium hydroxide; treatment with calcium hydroxide yielded only traces of compound (V). Compound (V), isolated on treatment with an aqueous solution of calcium hydroxide, was converted almost quantitatively into *D*-glucoisosaccharinic acid. The α-diketo-group in the sugar molecule is also subjected to extremely vigorous attack by alkalies, which leads to the dissociation of the carbon–carbon bond. Calcium ions catalyse the benzilic acid rearrangement of diulose to saccharinic acids, i.e. (V) → (IX), while sodium ions promote cleavage into fragments (Scheme 2).

Scheme 2



It has been shown[102] that treatment of 4-O-substituted *D*-glucose with sodium hydroxide results in the formation of large amounts of fragmentation products—glycolic acid (XXV) and *D*-3,4-dihydroxybutyric acid (XXVI). The formation of formic and lactic acids in concentrated sodium hydroxide solution is accelerated on raising the temperature. The temperature dependence of the relative amounts of acids obtained when hydrocellulose is acted upon by NaOH has been demonstrated[58].

A change in the pH of the reaction medium has a considerable influence on the formation of saccharinic acids as a function of the concentration of the alkali and sugar. For example, *D*-glucose gives rise to a greater amount of acid at low hydroxide concentrations than at high concentrations[91]. The main products of the alkaline degradation of cellobiose with sodium hydroxide are isosaccharinic acids together with small amounts of 2-deoxytetronic, 3-deoxypentonic, and 3,4-dideoxypentonic acids[43,103,104], while on treatment of cellobiose with bicarbonate the latter predominate[43].

IV. THE INFLUENCE OF SUBSTITUENTS ON THE FORMATION OF SACCHARINIC ACIDS

1. The Influence of the 1-O-Substituent

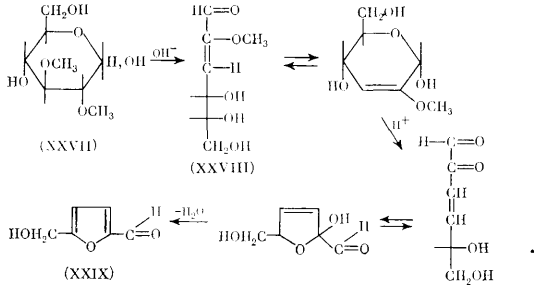
Acetal-O-substituted carbohydrates (alkyl glycosides[105–108], sucrose[109], and trehalose[109]) are usually stable in alkaline solutions free from oxygen and undergo alkaline hydrolysis only under severe conditions, for example, on treatment with a 10% NaOH solution for several hours at 170 °C. However, the glycosides derived from phenols, enols, and alcohols substituted by an electronegative group in the β-position are sensitive to the action of alkalies[110].

1-O-Substituted ketoses are converted into the usual saccharinic acids. For example, treatment of 1-O-methyl-*D*-fructose with lime water gives rise to the formation of α-*D*-glucosaccharinic acid with a higher yield (together with *D,L*-lactic acid) than that obtained from *D*-fructose[86]. When *D*-fructose 1,6-diphosphate is acted upon by alkali (0.46 *N* NaOH at 100 °C, 15 min), α-*D*-glucosaccharinic acid 6-phosphate is formed[111], while alkaline degradation of *D*-glucose 6-phosphate leads to the formation of the 6-phosphate of *D*-glucometasaccharinic acid[112].

† Many reactions of sugars depend on the nature of the cation of the alkali. For example, in the Lobry de Bruyn–van Ekenstein reaction divalent metal hydroxides are somewhat more effective (at comparable concentrations) than sodium or potassium hydroxide. The calcium ion has a stronger influence than the barium ion[93,94]. In methylation with dimethyl sulphate sodium hydroxide is more effective than potassium hydroxide[93]. The tendency towards the formation of an alkoxide in the reaction of cellulose with alkali increases in the sequence LiOH < NaOH < KOH < RbOH < CsOH < organic quaternary bases[96].

2. The Influence of the 2-O-Substituent

2-O-Substituted aldoses are relatively stable in alkaline solutions and do not give rise to saccharinic acids[113-115]. The absorption spectrum of 2,3-di-O-methyl-*D*-glucose (XXVII) in an alkaline solution corresponds to the 1,2-unsaturated carbonyl derivative (XXVIII), which is readily converted into 5-hydroxymethylfurfural (XXIX) under acid conditions[115].



(XXVII) (XXVIII) (XXIX)

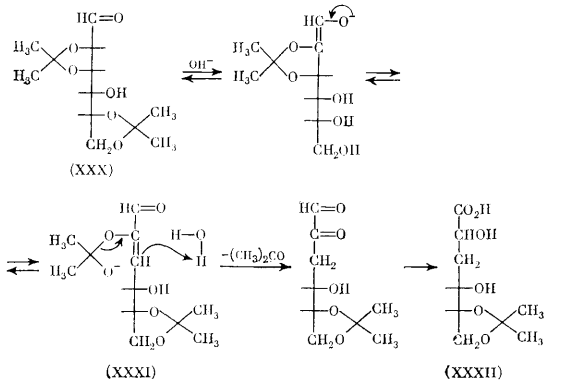
Substitution at $C_{(2)}$ prevents the formation of saccharinic acid as a result of the inability of the carbohydrate residue at CO_2 to ionise. However, it has been shown for xylans isolated from wood and containing 4-O-methyl-α-*D*-glucopyranosyluronic acid residues at $C_{(2)}$,[116] 2-O-*D*-xylopyranosyl-*L*-arabinose[113], 2-O-(4-O-methyl-α-*D*-glucuronopyranosyl)-*D*-xylose[117], and 4-O-β-*D*-glucopyranosyl)-2-O-methyl-β-*D*-glucose (2-O-methylcellobiose)[118] that the 2-O-substituent does not inhibit the degradation process at high temperatures. In 1 *M* NaOH (in the absence of oxygen) 2,3,4-tri-O-methyl-*D*-glucose decomposes fully after 5 h at 100 °C. Formic, acetic, lactic, glycolic, and glyceric acids were isolated from the reaction mixture. Under analogous conditions, 2-O-methylcellobiose is fully converted after 4 h. Apart from the products obtained from 2,3,4-tri-O-methyl-*D*-glucose, *D*-glucose and saccharinic acids were detected in the reaction products[118]. In both cases the 4-O-substituted compound (XXVIII) was identified. The main product of the conversion of 2-deoxy-*D*-*arabino*-hexose under the influence of alkali is 3,6-anhydro-2-deoxy-*D*-*arabino*-hexose[119].

3. The Influence of the 3-O-Substituent

Alkaline degradation of 3-O-substituted sugars, namely 3-O-methyl-*D*-glucose[120], 3-O-methyl-*D*-fructose[120], 3-O-ethyl-*D*-glucose[121], 3-O-n-propyl-*D*-glucose[121], 3-O-n-butyl-*D*-glucose[121], 3-O-benzyl-*D*-glucose[121], 3-O-methane-sulphonyl-*D*-glucose[121], and 3-O-toluene-*p*-sulphonyl-*D*-glucose[121], leads to the preferential formation of α- and β-*D*-glucometasaccharinic acids: the degradation proceeds more readily in lime water than in a solution of sodium hydroxide of the same normaility[120]. The conversion of 3,6-anhydro-*D*-glucose in lime water[122] leads to the formation of mainly *D*-glucometasaccharinic acid (apart from traces of lactic, glyceric, and 2-deoxypentonic acids, which are obtained in sodium hydroxide solutions). The main product of the alkaline degradation of 3-O-methyl-*D*-xylose with calcium hydroxide[123] is 3-deoxy-*threo*-pentonic acid, but a small amount of 3-deoxy-*erythro*-pentonic acid was also detected. Glycosyl phosphates and other non-reducing phosphates are resistant to the action of alkalies. However, compounds such as glycerose 3-phosphate, *D*-ribose 3-phosphate, and *D*-glucose 3-phosphate readily undergo β-elimination with formation of *D,L*-lactic, *D*-glucometasaccharinic, and 3-deoxypentonic acids[124].

3, 6-Di-O-methyl-*D*-glucose[98] and 6-O-β-*D*-glucopyranosyl-3-O-methyl-*D*-glucose[125] are converted into 6-O-methyl-*D*-glucometasaccharinic and 6-O-β-*D*-glucopyranosyl-*D*-glucometasaccharinic acids under the influence of $Ca(OH)_2$ at room temperature. Alkaline degradation of 3-O-methyl-*D*-glucose 6-(dihydrogen phosphate) leads to the formation of the 6-(dihydrogen phosphates) of *D*-glucometasaccharinic acids[126], while the conversion of *D*-arabinose 3,5-(hydrogen phosphate) or *D*-xylose 3,5-(hydrogen phosphate) results in the formation of a mixture of 3-deoxy-5-phospho-*D*-*erythro*-pentonic and 3-deoxy-5-phospho-*D*-*threo*-pentonic acids[127].

2-O-Substituted aldoses are stable in relation to the action of alkali, but 2,3; 5,6-di-O-isopropylidene-*D*-mannose (XXX) is converted under the influence of calcium hydroxide[128] into 5,6-O-isopropylidene-*D*-glucometasaccharinic acids (XXXII), since β-elimination leads to the removal of the 2,3-O-isopropylidene group#.



(XXX) (XXXI) (XXXII)

4. The Influence of the 4-O-Substituent

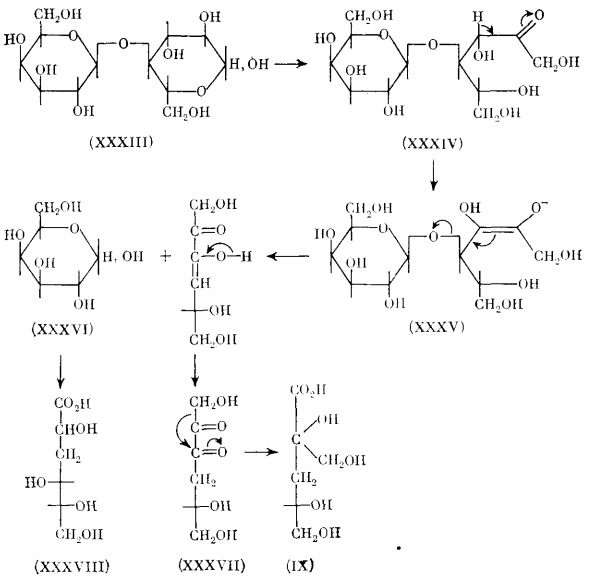
The alkaline degradation of 4-O-substituted sugars leads to the formation of isosaccharinic acids. For example, the main products of the degradation of 4-O-methyl-*D*-glucose[54,102,129,130], 4-O-methyl-*D*-fructose[129], and 4,6-O-benzylidene-*D*-glucose[128] are *D*-glucoisosaccharinic acids. Treatment of 4,6-di-O-methyl-*D*-glucose with alkali[98] results in the formation of 5-O-methyl-α-*D*-glucoisosaccharinic acid. Treatment of *D*-glucose 4,6-(hydrogen phosphate) with alkali leads to the formation of a mixture of 2-*C*-(hydroxymethyl)-3-deoxy-5-phospho-*D*-*erythro*-pentonic and the corresponding *threo*-pentonic acids (5-phospho-*D*-glucoisosaccharinic acids).[127] 4-O-Methyl-*D*-xylose is converted into *D*-xyloisosaccharinic acids in alkali.[131]

The formation of saccharinic acids from 4-O-substituted sugars takes place more slowly than from 3-O-substituted sugars. 4-O-Substituted ketoses decompose at a higher rate than the related aldoses, which is consistent with the Nef–Isbell mechanism. However, lactose and lactulose are converted more slowly than maltose or maltulose. Cellobiose decomposes at approximately the same rate as lactose.

Compound (XXX) remains unchanged at 25 °C in saturated lime water free from oxygen as a result of the inability of the initial anion (XXXI) to be converted into an α-diketone and subsequently into compound (XXXII). However, at 100 °C dissociation takes place with formation of compound (XXXII).

5. The Influence of the 6-O-Substituent

Substitution at $C_{(6)}$ activates attack by alkali on the hydroxy-groups at $C_{(3)}$ or $C_{(4)}$. For example, 3,6- and 4,6-di-O-methyl-*D*-glucoses decompose faster in lime water than the corresponding 3- and 4-O-methyl-*D*-glucoses. When *D*-glucose is treated with calcium hydroxide, the product is mainly α-*D*-glucosaccharinic acid (together with a small amount of *D*-glucoisosaccharinic acids), while analogous treatment of 6-O-substituted *D*-glucose leads to the formation of α- and β-*D*-glucometasaccharinic acids. It has been shown[98,99] that the main products of the conversion of 6-O-substituted sugars are *D*,*L*-lactic acid and 6-O-substituted metasaccharinic acid.



V. THE FORMATION OF SACCHARINIC ACIDS BY THE CLEAVAGE OF OLIGO- AND POLY-SACCHARIDES WITH ALKALI

Treatment of polysaccharides with alkalies has been described in detail in a number of reviews[110,132-137]. This section deals with the formation of saccharinic acids in the absence of oxygen. Alkaline degradation of polysaccharides proceeds under these conditions with formation of definite types of saccharinic acids characteristic of the bonds present in the polysaccharide, and chain branching has a specific influence on the cleavage process.

1. Glycans with (1→4)-Linkages

(*a*) *Lactose and Lactulose.* It has been known for a long time that reducing disaccharides with (1 → 4)-bonds are cleaved by lime water with formation of α-*D*-isosaccharinic acid. Thus early investigations[138] showed that alkaline degradation of lactose leads to the formation of succinic acid, formic acid, and a crystalline lactone, which has been identified[139] as α-*D*-glucosaccharinolactone. Approximately 20% of this lactone is formed from lactose on treatment with $Ca(OH)_2$. Apart from this, *D*-galactose[140,141], formaldehyde[142], and other saccharinic acids were detected in the reaction products. The presence of a small amount of β-*D*-glucoisosaccharinic acid has also been demonstrated[11,54,129,143-146]. α-*D*-Galactometasaccharinic acid was first detected as a product of prolonged treatment of lactose with lime water at room temperature[147]. It was later shown that it can be obtained by treating *D*-galactose[26] or melibiose[99] with solutions of sodium and calcium hydroxides. Crystalline lactulose (4-O-β-*D*-galactopyranosyl-*D*-fructose) was isolated from the products obtained on treating lactose with alkali[138]. At the very beginning of the process lactose (XXXIII) is slowly converted into the corresponding lactulose (XXXIV). Lactulose is then converted at a higher rate, via postulated intermediates, (XXXV) → (XXXVII), into a mixture of α- and β-*D*-glucoisosaccharinic acids (IX) and *D*-galactose (XXXVI), which is converted in its turn into α- and β-*D*-galactometasaccharinic acids (XXXVII).[144]

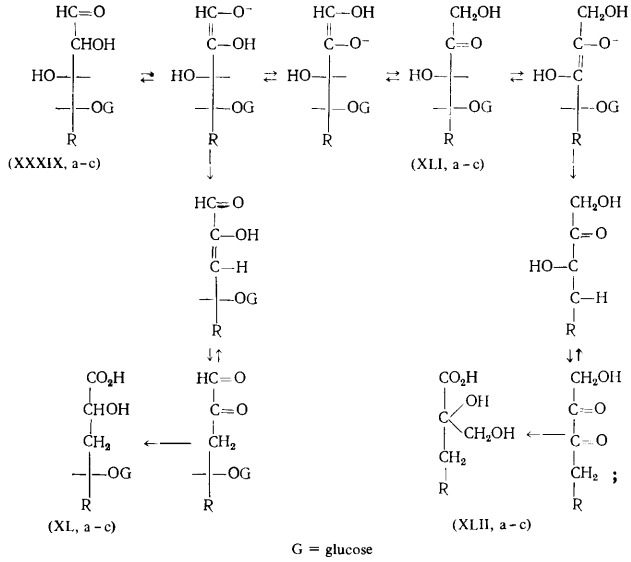
(*b*) *Maltose and Maltulose.* When maltose[54,144] or maltulose[144] are treated with $Ca(OH)_2$ at 25 °C a mixture of α- and β-*D*-glucoisosaccharinic acids is formed. Alkaline degradation of maltose should proceed via maltulose, like the degradation of lactose. However, maltulose decomposes so fast in an alkaline medium, compared with lactulose, that its detection is virtually impossible.

(*c*) *Cello-, manno-, and xylo-oligosaccharides.* It has been established[148] that α-*D*-glucoisosaccharinic acid is the main product of the degradation of cellobiose by $Ca(OH)_2$. Apart from isosaccharinic acid, cellobiulose, *D*-glucose, and *D*-fructose are formed. In NaOH solution other acid products are detected together with isosaccharinic acid. It has been shown[149] that, under the influence of 1 *M* NaOH, cellobiose gives rise to the epimeric 4-O-β-*D*-glucopyranosyl-*D*-mannose (glucosylmannose), cellobiulose, *D*-glucose, *D*-fructose, and *D*-mannose. When cellobiose was treated with 0.04 *N* $Ba(OH)_2$ at 25° and 50 °C, a considerable amount of *D*-glucosaccharinic acid and *D*-glucose was detected[150,151], apart from small amounts of glyceric, 3,4-dihydroxybutyric, and *D*-arabinonic acid. In the presence of oxygen the oxidation reaction involving the formation of aidonic acids predominates[150,152,153]. Cellobiulose[148] reacts with $Ca(OH)_2$ to form cellobiose, *D*-fructose, *D*-glucose, and α-*D*-glucoisosaccharinic acid. Alkaline degradation of cellotetraose[148] and partly hydrolysed cellulose[132] leads to the formation of the same *D*-glucoisosaccharinic acid.

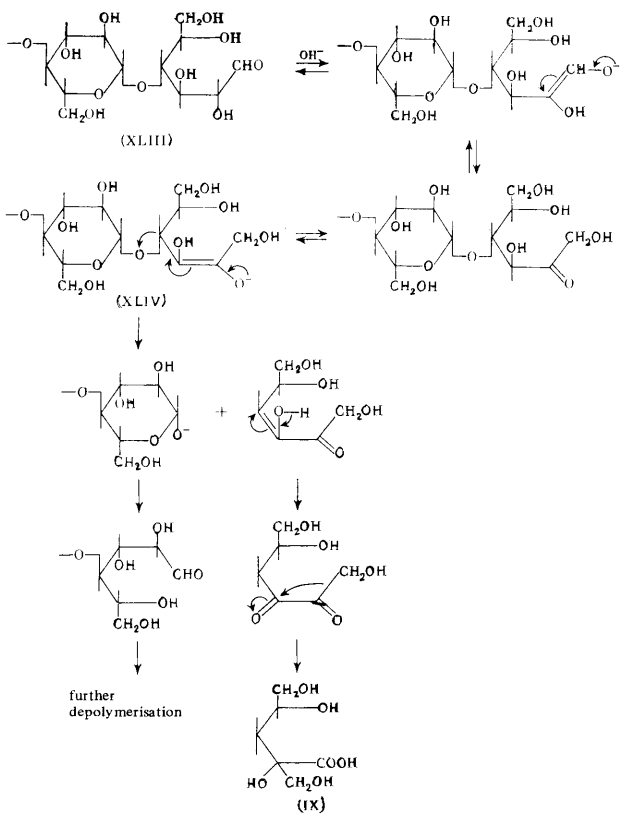
Xylobiose (4-O-β-*D*-xylopyranosyl-*D*-xylose)[154,155] (XXXIXc) undergoes an analogous degradation under the influence of alkali, probably via xylobiulose (4-O-β-*D*-xylopyranosyl-*D*-xylose) (XLIc) and intermediates with formation of 2-*C*-(hydroxy methyl)-2,4-dihydroxybutyric acid (XLIIc). Compound (XLIIc) is formed similarly from xylotriose[156]. By investigating the kinetics of the degradation of the xylotetraose molecule from the reducing end, it has been established[157] that the overall rate of degradation is largely determined by the rate of conversion of the anion derived from the reducing end of the xylose unit into a xylulose unit. In the second stage of the degradation reaction, which determines the overall rate, the terminal group of xylulose rearranges with dissociation of the glycosidic linkage. This reaction stage is slower for cellotetraose than for xylotetraose and the rate is

independent of the number of xylose units in the oligomer. On treatment with bases, isosaccharinic acids (XLII, a-c) and O-glycosylsaccharinic acids (XL,a-c) respectively are formed from cellobiose (XXXIXa), 4-O-β-*D*-mannopyranosyl-*D*-mannose (XXXIXb), and 4-O-β-*D*-xylopyranosyl-*D*-xylose (XXXIXc). O-Glycosylsaccharinic acids hydrolyse to form metasaccharinic acids[158] (Scheme 3):

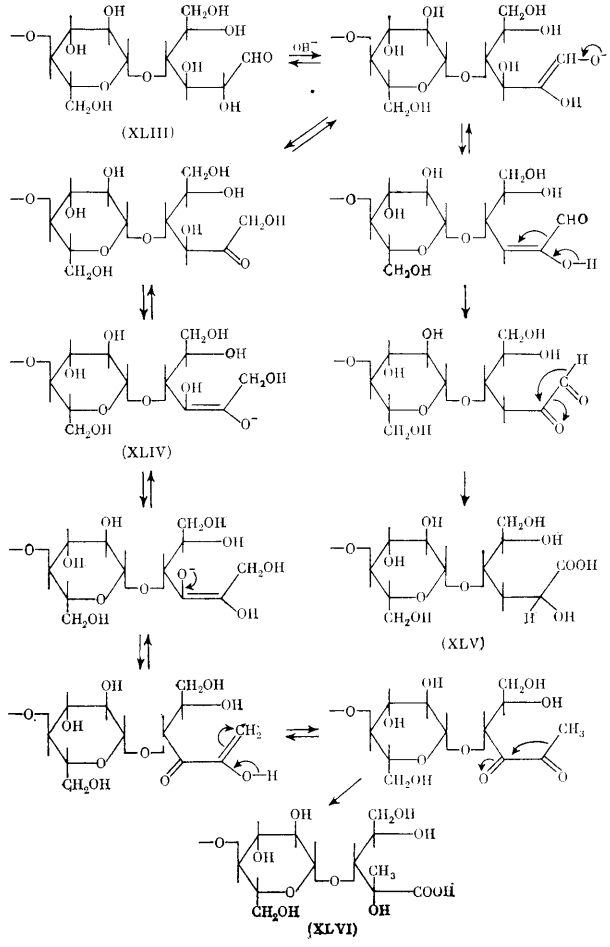
Scheme 3



(*d*) *Cellulose.* Isosaccharinic acid (IX) is the main product of the degradation of cellulose (XLIII) by alkalies[102,159-161] (the "peeling" process).



Alkaline degradation of cellulose and other polysaccharides usually does not go to completion. The termination of the "peeling" process is due to the conversion of the reducing monosaccharide terminal units into non-reducing saccharinic acids[159,162]. Machell and coworkers[163,164] subjected alkali-stabilised hydrocellulose to acid hydrolysis and isolated *D*-glucometasaccharinic acids, whose formation on treatment with alkali may be a consequence of the β-elimination of the hydroxygroup at the $C_{(3)}$ atom in terminal *D*-glucose and subsequent rearrangement of the resulting enol. *D*-Glucometasaccharinic acids have also been isolated from the hydrolysate of sulphate cellulose from pine, demonstrating the occurrence of the stabilisation reaction during sulphate digestion[165]. Small amounts of α-*D*-glucosaccharinic acid have also been detected[163]. However, the formation of the usual stable saccharinic end units (XLV) is difficult, since the intermediate enol (XLIV), produced in the course of the formation of the metasaccharinic terminal units, (XLIII) → (XLVI), can readily undergo transformations via the alternative mechanism (XLIII) → (IX):



Hydrocellulose derived from cotton cellulose subjected to alkaline treatment at 170 °C included α- and β-*D*-glucometasaccharinic and 2-*C*-methylglyceric acids and a smaller amount of α-*D*-glucosaccharinic acid[166]. 2-*C*-Methylglyceric acid has also been detected in the products of the hydrolysis of unbleached eucalyptus and pine celluloses[167].

The stabilisation reaction ("inhibition" process) is usually slower than the degradation reaction ("peeling" process) from the reducing end owing to the influence of the 4-O-substituent. It has been shown[168] that the activation energy

for the degradation of cellulose under the influence of a 5% NaOH solution is 24 kcal mol^{-1}, while the activation energy for the stabilisation reaction is 34 kcal mol^{-1}, the rate of stabilisation increasing with increase of temperature. Above 150 °C glucosidic linkages are hydrolysed with formation of new reducing end groups, which promote further degradation via the "peeling" mechanism[169]. It has been shown[170] that the rate of hydrolysis of the glucosidic linkages in cotton cellulose is directly proportional to the concentration of hydroxide ions and the activation energy is 35.9 kcal $mole^{-1}$. Hydrocellulose undergoes degradation faster and the sensitivity of the pre-hydrolysed wood celluloses to alkali increases during alkaline digestion[171]. With decrease of the degree of polymerisation, the rate of degradation of hydrocellulose increases[162,172].

Much attention has been devoted in recent years to the problem of the formation of saccharinic acids from wood polysaccharides during sulphate digestion. As was to be expected, the main products (50%) of the sulphate digestion of pine cellulose are *D*-glucoisosaccharinic acids[104]. Lactic acid (20%) and insignificant amounts of glycolic, 2-hydroxybutyric, 3-hydroxypropionic, 2,5-dihydroxyvaleric, *D*-xyloisosaccharinic, and 3-deoxypentonic acids were also detected. *D*-Xyloisosaccharinic and *D*-glucoisosaccharinic acids predominate in the sulphate digestion of birchwood[104].

The main products of the conversion of hydrocellulose[175], cotton cellulose[177], and cellobiose[150,186] under the influence of alkalies in the absence of oxygen are isosaccharinic acids, while treatment with atmospheric oxygen in an alkaline medium leads to the oxidation of the terminal aldehyde group to aldonic (mainly arabinonic, mannonic, and erythronic) acids. The oxidative stabilisation of cellulose, glucomannan, and xylan takes place with the intermediate formation of glucosone (*D-arabino*-hexosulose) and xylosone (*D-threo*-pentosulose) structures and their conversion into aldonic acid residues[85,181,182,187].

Alkaline degradation of cellulose is of enormous theoretical and practical importance. In the first place it must be taken into account in the isolation of cellulose from plant materials (alkaline digestion, refining) and chemical processing of cellulose (manufacture of viscose fibre, ethers, xanthates, and certain partly substituted cellulose derivatives for technical purposes, mercerisation of textile materials) in an alkaline medium. Since the degradation of cellulose from the reducing end, which occurs inevitably to some extent under these conditions, leads to a considerable loss of cellulose in the form of low-molecular-weight substances (for example, in the manufacture of cellulose its yield reaches only 20–45% depending on the manufacturing method used), the reduction of losses of this kind to a minimum is an important task for the paper and textile industries. A decrease of these losses can be achieved, in principle, in different ways: by modifying the reducing end groups of cellulose with formation of structural end units resistant to the action of alkalies (by glucosidation and reduction or oxidation of hemiacetal groups) or by decreasing the degree of degradation of cellulose from the reducing end as a result of the acceleration of the stabilisation reaction[136].

The resistance of polysaccharides to the action of alkalies can be increased by the catalytic hydrogenation[188] and reduction with sodium tetrahydroborate[131,159,162,180,188–197] of the terminal aldehyde groups to primary alcoholic groups, by the oxidation of the reducing groups to aldonic acids with chlorite (sodium chlorite or chlorous acid)[198–201], polysulphide (usually sodium polysulphide)[165,176,188,201–207], bisulphite (sodium bisulphite or a mixture of sodium bisulphite and sulphite)[208], and a copper ammine solution[209], by glycosidation (treatment of the polysaccharide with an alcoholic solution of hydrogen chloride[210] or methylation with the aid of dimethyl sulphate and alkali and subsequent treatment with metnyl iodide and silver oxide[131]), by thermal dehydration in an inert medium at 175–220 °C (this probably leads to the formation of an intramolecular anhydride incorporating a glycosidic hydroxyl)[211], and by the conversion of the reducing end groups into mercapto-groups under the influence of hydrogen sulphide in the presence of aqueous sodium carbonate[212].

At the same time there are indications that the degradation of cellulose[158,172] and model compounds[213] can be limited by accelerating the stabilisation reaction with the aid of alkaline earth metal ions (Ca^{2+}, Sr^{2+}, Ba^{2+}). Magnesium[175,187,214–217] and lanthanum[184,218] compounds proved to be the most effective. The role of inhibitors has not been established accurately. It has not yet been fully demonstrated that bivalent cations stabilise the intermediate enol as a result of complex formation[121,219,220] or influence the benzilic rearrangement[102]. Iron, cobalt, copper, and manganese salts have an appreciable catalytic effect on the rate of degradation[35,184,217], while the introduction of lignin, xylan, and glucose intensifies the catalysis by heavy metals[217]. The influence of a multiplicity of reagents has been investigated in order to increase the resistance of polysaccharides to the action of alkalies[221–223].

(*e*) *Amylose.* Amylose is an alkali-sensitive component of starch. In dilute alkaline solutions in the absence of oxygen amylose is poorly cleaved and degradation of potato amylose (degree of polymerisation 415) ceases after the elimination of 230 glucose units from each chain[224]. On treatment of amylose with oxygen-free 1 *N* and 0.5 *N* NaOH at 100 °C, stepwise depolymerisation takes place vigorously. The degradation proceeds with formation of *D*-glucoisosaccharinic, formic, and lactic acids, while the stabilisation reaction leads to the formation of alkali-resistant amylose with a *D*-glucometasaccharinic end-group[225,226].

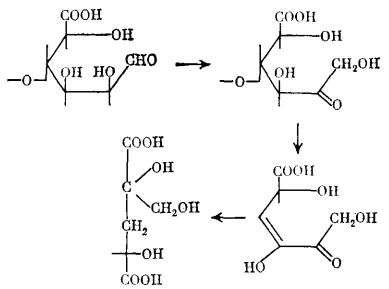
In contrast to amylose, the second fraction of starch (amylopectin) is relatively resistant to the action of alkalies and undergoes only insignificant degradation on treatment with 1 *N* NaOH in the absence of oxygen at room temperature[227], which is apparently due to its highly branched structure. A kinetic study of the degradation of amylose has been made[228]. At 100 °C an increase of the concentration of alkali to 0.1 *N* entails an increase of the rate of degradation. Higher concentrations of alkali do not affect the rate of degradation, while the rate of the stabilisation reaction increases on raising the concentration of alkali to 1.5 *N*. The activation energies for the degradation and stabilisation reactions in 1.25 *N* NaOH are 21.1 and 19.3 kcal mol^{-1} respectively[228].

(*f*) *Xylan.* The xylan from corn cobs is fairly resistant to the action of 1 *N* NaOH at 100 °C [156]§, while its oxidative alkaline degradation leads to large amounts of 3-deoxy-2-*C*-hydroxymethyltetronic acid (xyloisosaccharinic acids)[178]. However, when arabinoxylan from rye flour is treated with an oxygen-free dilute aqueous solution of sodium hydroxide, 3-deoxy-2-*C*-hydroxymethyltetronic and other acids are formed at room temperature[131]. Alkaline degradation of birch xylan in the absence and presence of oxygen leads to the formation of approximately equal amounts of xyloisosaccharinic

§ It has been shown[178] that the molecule of the xylan from corn cobs contains *L*-arabinoduranose residues as well as glucuronic acid and its 4-O-methyl derivative and that the latter add to the main chain via (1 → 2)-linkages. The branching of the $C_{(2)}$ atom in the main chain, joined by (1 → 4)-linkages, should arrest the degradation process.

acid[183]. It has been shown[131] that the inhibition of the degradation is caused by the conversion of the reducing end groups into non-reducing xylometasaccharinic units. After preliminary reduction with tetrahydroborate[131,188], xylans become resistant to the action of alkali and the formation of acids or a decrease of the molecular weight is not observed.

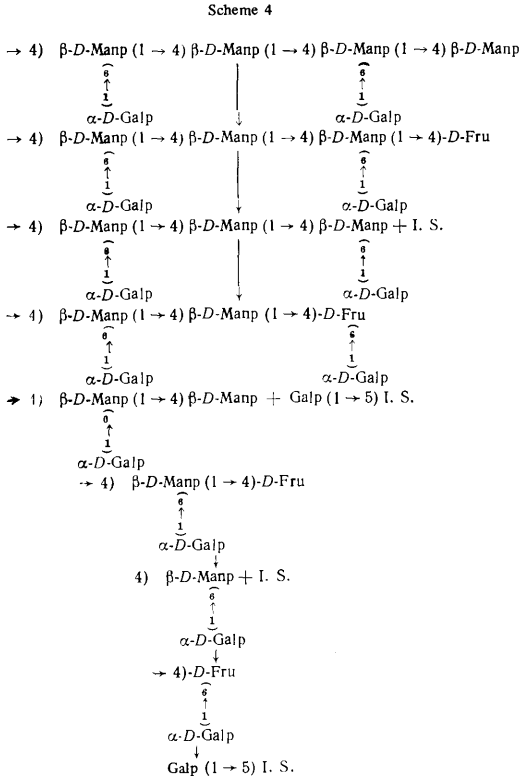
(*g*) *Alginic acid.* The main products of the degradation of alginic acid (heteroglucuronoglycan consisting of *D*-mannuronic and *D*-guluronic acid residues) salts and esters under the influence of alkalies are 3-deoxy-2-*C*-hydroxymethyl-*D*-*erythro*(*threo*)-pentaric acids (dibasic isosaccharinic acids with six carbon atoms) (XLVII) [229]:



3-Deoxy-2-*C*-hydroxymethylpentaric acids (with the *threo*-isomer predominating) are formed also when 4-O-methyl-*D*-glucuronic acid is treated with alkali[230]. The ready isomerisation of 4-O-methyl-*D*-glucuronic acid to the corresponding hexulose in an alkaline medium[231] supports the proposed mechanism.

(*h*) *Guaran.* The alkaline degradation of guaran [a polysaccharide with a main chain consisting of β-(1 → 4)-*D*-mannopyranose residues, to the alternate members of which α-*D*-galactopyranose residues are added via the $C_{(6)}$ atoms] leads to the formation of *D*-glucoisosaccharinic[54,145] and 5-O-α-*D*-galactopyranosyl-*D*-glucoisosaccharinic acids[145]. It has been suggested that the degradation reaction proceeds via the β-alkoxycarbonyl mechanism. The initially reducing terminal mannose residue is converted under the influence of alkali into a fructose residue, which is eliminated in the form of the enol of a dicarbonyl compound; under the reaction conditions, the enol immediately undergoes a subsequent rearrangement to isosaccharinic acid. The formation of *D*-glucoisosaccharinic acid and 5-O-α-*D*-galacto-pyranosyl-*D*-glucoisosaccharinic acid is determined by the structure of guaran. The detection of *D*-galactose and equal amounts of *D*-glucoisosaccharinic and 5-O-α-*D*-galactopyranosyl-*D*-glucoisosaccharinic acids in the reaction products is consistent with the proposed mechanism (see Scheme 4).

Scheme 4



2. Glycans with (1 → 3)-Linkages

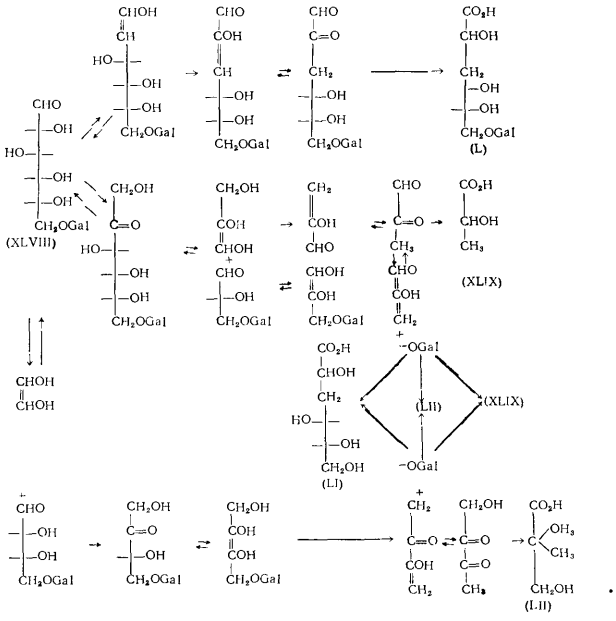
Laminaribiose (3-O-β-*D*-glucopyranosyl-*D*-glucose)[232], turanose (3-O-α-*D*-glucopyranosyl-*D*-fructose)[232], and laminarin[148,233] are degraded by alkalies with the formation of *D*-glucometasaccharinic acids. When 48% of the initial laminarin has been degraded, the process ceases and then restarts after partial hydrolysis of the residue. The termination of the degradation process may be due to a structural feature of the chain. In fact, it has been shown recently[234] that laminarin contains chains with terminal non-reducing mannitol units. The decomposition of laricinan and pachyman[233] takes place in exactly the same way under these conditions with formation of metasaccharinic acids. It may be that the presence of branches is also the cause of the incomplete degradation of these polysaccharides. The results of kinetic studies on the alkaline degradation of (1 → 3)-glucans have been published[233].

3. Glycans with (1 → 6)-Linkages

When melibiose (6-O-α-*D*-galactopyranosyl-*D*-glucose) (XLVIII) is treated with calcium hydroxide, the products are[99] *D*,*L*-lactic acid (XLIX), *D*-galactose, 6-O-α-*D*-galactopyranosyl-*D*-glucometasaccharinic acid (L) and the corresponding isosaccharinic acid. Treatment of melibiose with barium hydroxide[235] led to the formation, apart from the above compounds, of considerable amounts of 3-deoxy-*D*-xylohexonic and 3-deoxy-*D*-lyxohexonic acids (α- and β-*D*-galactometasaccharinic acids) (LI) and 2-*C*-methylglyceric acid (LII). 6-O-α-*D*-Galactopyranosyl-*D*-glucosaccharinic acids are formed via the Isbell mechanism and the glycosidic linkage remains unaffected; the rupture of the glycosidic linkage in melibiose is accompanied by the formation of compounds (XLIX), (LI), and (LII). The cleavage of the $C_{(3)}$–$C_{(4)}$ linkage in the

reducing *D*-glucose unit of the disaccharide leads to the formation of a triose, which rearranges to *D,L*-lactic acid after the elimination of *D*-galactose. The rupture of the $C_{(2)}-C_{(3)}$ bond should lead to the formation of a 4-O-substituted tetrose, which can be cleaved with formation of 2-*C*-methylglyceric acid (LII). The *D*-galactose eliminated in this process can undergo subsequent rearrangement with formation of *D*-galactometasaccharinic acids (LI) (Scheme 5).

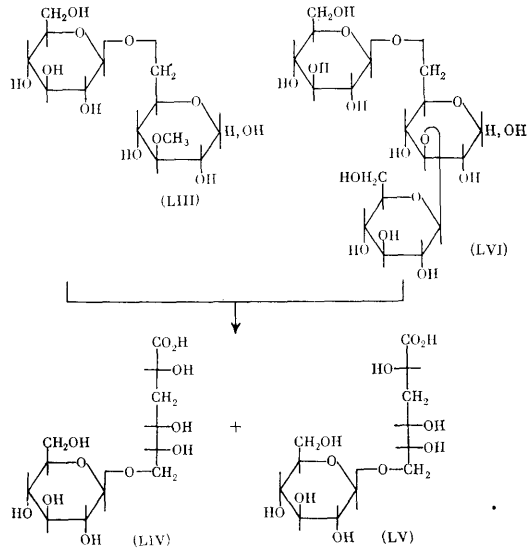
Scheme 5



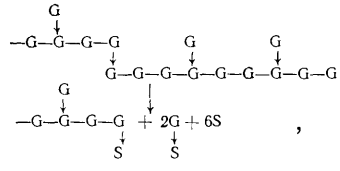
According to this scheme, compound (LII) and pyruvic acid (precursor of lactic acid), labelled at $C_{(4)}$ and $C_{(3)}$ respectively , should be formed from *D*-glucose-6-*t*. In fact, the radioactivities of *D*-glucose-6-*t* (LII) and pyruvic acid were almost identical (to within 5%)[235].

2-*C*-Methylglyceric acid is a product of the successive chain degradation of isomaltose oligosaccharides (isomaltose, isomaltotriose, and isomaltotetraose) under the influence of $Ba(OH)_2$. Apart from 2-*C*-methylglyceric acid, considerable amounts of stabilisation products, in particular 6-O-substituted 3-deoxy-*D*-hexonic acids, are formed[235].

As shown above, substitution at $C_{(6)}$ tends to increase the rates of degradation of 3-O- and 4-O-substituted sugars with retention of the 6-O-substituent. When 6-O-β-*D*-glucopyranosyl-3-O-glucose (LIII) is acted upon by lime water at room temperature, O-glycosylmetasaccharinic acids are formed; 6-O-β-*D*-glucopyranosyl-α-*D*-glucometasaccharinic acid (3-deoxy-6-O-β-*D*-glucopyranosyl-*D-ribo*-hexonic acid) (LIV) and 6-O-β-*D*-glucopyranosyl-β-*D*-glucometasaccharinic acid (3-deoxy-6-β-*D*-glucopyranosyl-*D-arabino*-hexonic acid) (LV) [125]. The acids were characterised by reduction to substituted 3-deoxyhexoses. The same 6-O-glucosylmetasaccharinic acids are formed[236] on treatment of the trisaccharide 3-O-β-6-β-di-*D*-glucopyranosyl-*D*-glucose (LVI) with 0.05 *N* $Ba(OH)_2$:



Compounds (LIII) and (LVI) are models of the (1 → 3)-linked β-*D*-glucan from *Sclerotium rolfsii* containing β-*D*-glucopyranosyl substituents at each third glucose residue of the main (1 → 6)-linked chain[237]. The degradation of this polysaccharide by NaOH in the absence of oxygen at 56 °C leads to compounds (LIV) and (LV)[125]:



where G = β-*D*-glucopyranose, S = *D*-glucometasaccharinic acid residue, a line indicates a (1 → 3)-linkage, and an arrow indicates a (1 → 6)-linkage.

It has been shown[238] that dextran is cleaved on treatment by 1 *N* NaOH at 60 °C with formation of a stable acid dextran containing 1 unit of *D*-glucometasaccharinic acid for each dextran chain. Hydrolysis of the acid dextran leads to α- and β-*D*-glucometasaccharinic acids.

Alkaline degradation of oxidised celluloses and the influence of the supermolecular structure of cellulose on its alkaline degradation are discussed in a review[137].

VI. THE PROPERTIES AND APPLICATIONS OF SACCHARINIC ACIDS

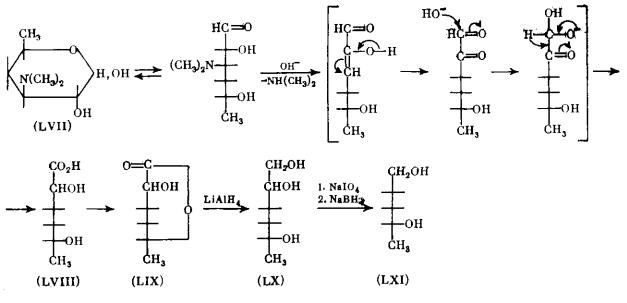
1. The Formation of Saccharinic Acids as an Analytical Method for the Investigation of the Structures of Polysaccharides and Certain Carbohydrate Derivatives

The study of the influence of alkalies on model, partly substituted, monosaccharides, oligosaccharides, and polysaccharides with known structures has shown that in broad outline it is possible to predict which reaction products should be formed when the main polysaccharide chains are acted upon by alkali. Thus polysaccharides with (1 → 2)-linkages are resistant to dilute alkali at 25 °C. Polysaccharides with (1 → 3)-linkages are cleaved by alkali in the absence of oxygen with formation of metasaccharinates and those with (1 → 4)-linkages

are cleaved with formation of isosaccharinates. Polysaccharides with (1 → 5)-linkages are stable, while those with (1 → 6)-linkages exhibit a relative resistance to dilute alkali at 25 °C; they give rise to 6-O-glycosylmetasaccharinate, 2-*C*-methylglycerate, and lactate at a higher temperature and an increased concentration of alkali. Polysaccharides with (2 → 1)-linkages, containing ketose units (for example, inulin), are cleaved by dilute alkali with formation of the usual saccharinates.

In the presence of chain branching the alkaline degradation and the nature of the substances formed can frequently yield information concerning the types of bonds in the initial monosaccharide. Thus the branch at the $C_{(6)}$ atom will be split off and, depending on the type of bonds in the main chain, the product will have stable iso- or meta-saccharinate end groups. The branches at $C_{(4)}$ in main chains joined by (1 → 5)- or (1 → 6)-linkages are not cleaved owing to the resistance of the main chains to the action of alkali. When the branches at $C_{(4)}$ in chains joined by (1 → 3)-linkages as well as branches at $C_{(3)}$ are split off, a stable metasaccharinate terminal unit is formed from the residue in the main chain to which the branch had been attached. This unit will be located at the branch ($C_{(4)}$) in the former case and in the main chain in the latter ($C_{(3)}$). The main chain does not undergo further degradation, but the eliminated branches decompose via a pathway which depends on the type of bonds in the branch. The branches at the $C_{(2)}$ atom in the main chain joined by (1 → 3)-linkages should be split off and should terminate in a 2,3-unsaturated monosaccharide unit, resistant to alkali, formed from the monosaccharide residue of the main chain to which the branch was attached. The branches at the $C_{(2)}$ atom in the main chain, joined by (1 → 4)-linkages, should arrest the degradation process. Thus the use of the saccharinic rearrangement as an analytical method in combination with other procedures makes it possible to obtain extremely valuable information about the structure of polysaccharides.

The saccharinic acid method is particularly useful for the establishment of the structures of mono-O-substituted reducing sugars. This method has been used successfully[239] to determine the absolute configuration in the 5-position of desosamine—an important carbohydrate component of the macrolide antibiotics erythromycin, methymycin, narbomycin, oleandomycin, and picromycin. Alkaline degradation of desosamine (3,4,6-trideoxy-3-dimethylaminohexose) (LVII) led to *erythro* + *threo*-2,5-dihydroxyhexonic acid (LVIII). The δ-lactone of this acid (LIX) gave rise to the hexanetriol (LX) after reduction with lithium tetrahydroaluminate. Oxidation of the hexanetriol with sodium periodate followed by reduction with sodium tetrahydroborate led to pentane-1,4-diol (LXI) whose molecule retains only one asymmetric centre, corresponding to the fifth carbon atom of desosamine. Since the absolute configuration of the pentanediol (LXI) corresponds to that of *D*-glyceraldehyde, it follows that desosamine belongs to the *D*-series.

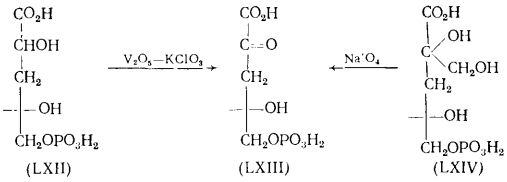


2. Syntheses of Deoxysugars via Saccharinic Acids

Saccharinic acids are particularly useful for the synthesis of deoxysugars and branched sugar derivatives. When γ-lactones of α- and β-*D*-glucometasaccharinic acids are reduced. 3-deoxy-*D*-*ribo*-hexose and 3-deoxy-*D*-*arabino*-hexose are formed respectively[32]. The reduction of the γ-lactones of α- and β-*D*-glucoisosaccharinic acids leads to 3-deoxy-2-*C*-hydroxymethyl-*D*-*erythro*-aldopentose and 3-deoxy-2-*C*-hydroxymethyl-*D*-*threo*-aldopentose respectively. It has been shown[56] that the reduction of both γ-lactones with sodium tetrahydroborate proceeds more effectively than with sodium amalgam. The reduction of the lactone of α-*D*-glucoisosaccharinic acid had been investigated previously[240]. 2-*C*-Methyl-*D*-ribose has been obtained by the reduction of the lactone of α-*D*-glucosaccharinic acid with sodium amalgam[56]¶.

2-Deoxy-*D*-xylose has been obtained by the Ruff cleavage from *D*-galactometasaccharinic acids[241]. Numerous studies[242,244] have been devoted to the conversion of *D*-glucometasaccharinic acid salts into 2-deoxy-*D*-*erythro*-pentose (2-deoxy-*D*-ribose) by the same method. Synthesis via metasaccharinic acids has also been used to obtain 2-deoxy-*D*-*erythro*-tetroses and 2-deoxy-*D*-*threo*-tetroses from *D*-arabinose and *D*-xylose respectively[245].

3-Deoxy-2-oxo-*D*-*threo*-hexonic acid has been obtained from α-*D*-galactometasaccharinic acid[246]. Selective oxidation of a mixture of the 5-phosphates of 3-deoxy-*D*-*erythro*-pentonic and 3-deoxy-*D*-*threo*-pentonic acids (LXII) at the $C_{(2)}$ atom with potassium chlorate and vanadium pentoxide yielded the 5-phosphates of 3-deoxy-2-oxo-*D*-glyceropentonic acid (LXIII). The latter has been obtained also by the periodate oxidation of a mixture of the 5-phosphates of 3-deoxy-2-*C*-hydroxymethyl-*D*-*erythro*- and -*D*-*threo*-pentonic acids (LXIV)[247]:



The 6-phosphates of 3-deoxy-2-oxo-*D*-*erythro*- and *D*-*threo*-hexonic acids have been obtained from the 6-phosphates of *D*-glucometasaccharinic and *D*-galactometasaccharinic acids respectively[248]. The formation of a cyclic enol by oxidising the 6-phosphates of *D*-glucometasaccharinic acid with potassium chlorate in the presence of vanadium pentoxide has been studied[249]. The γ-lactone of α-*D*-glucosaccharinic acid has been used as the initial compound in the synthesis of nucleosides containing branched sugars[250-252].

Certain properties of saccharinic acids have been described in a review[26]. It was shown subsequently[56,145] that α- and β-*D*-glucoisosaccharinic acids are resistant to alkaline solutions up to 125 °C and are not interconverted under these conditions. α-*D*-Glucosaccharinic acid is also not isomerised on treatment with alkali or on heating[56], while the lactones of α- and β-*D*-glucometasaccharinic acids are interconverted via epimerisation[49,120,166,253]. A similar transformation has been observed by Nef[11] for the lactones of *D*-galactometasaccharinic acids. Acids which do not contain hydrogen atoms at $C_{(2)}$ do not undergo this transformation.

¶ The corresponding polyrols can also be obtained by the reduction of saccharinic acids with tetrahydroborate[56].

The γ-lactones of saccharinic acids are more stable in aqueous solutions than the lactones of aldonic acids and remain unchanged for several days. Like normal aliphatic esters and lactones, the lactones of deoxy- and 2-*C*-methylaldonic acids are extremely resistant to non-catalysed hydrolysis[254].

REFERENCES

1. N.K.Kochetkov, A.F.Bochkov, B.A.Dmitriev, A.I.Usov, O.S.Chizhov, and V.N.Shibaev, "Khimiya Uglevodov" (The Chemistry of Carbohydrates), Izd.Khimiya, Moscow, 1967, p.97.
2. W.Pigman and E.F.L.J.Anet, in "The Carbohydrates", Acad.Press, New York, 1972, Vol.1A, Chapter 4.
3. L.Hough and A.C.Richardson, in "Rodd's Chemistry of Carbon Compounds", Amsterdam–London–New York, 1967, Vol.1, Part F, p.251.
4. T.Enkvist, Finska Kemists.Medd., 71, 105 (1962).
5. E.Shaw, J.H.Tatum, and R.E.Berry, J.Agric Food Chem., **16**, 979 (1968).
6. H.Kato, M.Mizushima, T.Kurata, and M.Fujimaki, Agric Biol.Chem., **37**, 2677 (1973).
7. R.Koetz and H.Neukom, Carbohydr.Res., **42**, 365 (1975).
8. I.Forsskahl, T.Popoff, and O.Theaner, Carbohydr. Res., **48**, 13 (1976).
9. V.F.Kazimirova and S.N.Danilov, Zhur.Obshch. Khim., **33**, 1424 (1963).
10. R.A.Gakhokidze, Zhur.Obshch.Khim., **46**, 1620 (1976).
11. J.U.Nef, Annalen, **376**, 1 (1960).
12. F.Shafizadeh and Y.Z.Iai, Carbohydr.Res., 7 263 (1975).
13. A.Herzfeld, Annalen, **220**, 214 (1883).
14. J.E.Mackenzie and J.P.Quin, J.Chem.Soc., 951 (1929).
15. E.G.V.Percival, J.Chem.Soc., 1160 (1934).
16. N.Roy and A.K.Mitra, Carbohydr.Res., **24**, 175 (1972).
17. N.Roy and A.K.Mitra, Carbohydr.Res., **24**, 180 (1972).
18. S.P.Moulik and A.K.Mitra, Carbohydr.Res., 28, 371 (1973).
19. S.P.Moulik and D.P.Kahn, Carbohydr.Res., **41**, 93 (1975).
20. J.E.Hodge, Adv.Carbohydr.Chem., **10**, 169 (1955).
21. J.M.Sugihara, Adv.Carbohydr.Chem., **8**, 1 (1953).
22. R.S.Tipson, Adv.Carbohydr.Chem., **8**, 107 (1953).
23. H.S.Isbell, H.L.Frush, R.Schaffer, C.W.R.Wade, and R.A.Peterson, Nat.Bur.Stand.Tech.Note, **274**, 36 (1965).
24. W.L.Evans, Chem.Rev., **6**, 281 (1929).
25. W.L.Evans, Chem.Rev., **31**, 537 (1942).
26. J.C.Sowden, Adv.Carbohydr.Chem., **12**, 35 (1957).
27. J.Staněk, M.Černy, et al. "The Monosaccharides". Acad.Press, New York, 1963.
28. E.Peligot, Compt.rend., **7**, 106 (1838).
29. G.J.Mulder, J.prakt.Chem., **21**, 203 (1840).
30. J.D.Crum, Adv.Carbohydrate Chem., **13**, 169 (1958).
31. A.M.Gakhokidze, Zhur.Obshch.Khim., **11**, 109 (1941).
32. H.B.Wood, Jr., and H.G.Fletcher, Jr., J.Org. Chem., **26**, 1969 (1961).
33. A.Ishizu, K.Yoshida, and N.Yamazaki, Carbohydr. Res., **23**, 23 (1972).
34. O.Samuelson and L.Thede, Acta Chem.Scand., **22**, 1913 (1966).
35. R.Malinen and E.Sjöström, Paperi ja Puu, **54**, 451 (1972).
36. M. von Glehn and P.-E.Warner, Chem.Comm., 291 (1967).
37. R.Norrestam, P.-E.Werner, and M.von Glehn, Acta Chem.Scand., 22, 1395 (1968).
38. P.-E.Werner, R.Norrestam, and C.Rönnquist, Acta Cryst., **B25**, 714 (1969).
39. D.L.Hughes, J.Trotter, and J.Howard, J.Chem. Soc., B,983 (1970).
40. J.C.Sowden and D.S.Strobach, J.Amer.Chem.Soc., **82**, 3707 (1960).
41. A.B.Foster, T.D.Inch, J.Lehman, and J.M.Weber, J.Chem.Soc., 948 (1964).
42. G.Petersson, Carbohydr.Res., **43**, 1 (1975).
43. L.Löwendahl and O.Samuelson, Acta Chem.Scand., **B30**, 691 (1976).
44. L.Löwendahl, G.Petersson, and O.Samuelson, Cellul. Chem.Technol., **10**, 471 (1976).
45. S.Ylner, Acta Chem.Scand., **10**, 1251 (1956).
46. R.H.Cordingly, TAPPI, **42**, 654 (1959).
47. D.L.Ingles, Chem.Ind.(London), 1312 (1961).
48. U.Schmidt, Holzforschung, **55**, 79 (1961).
49. B.Lindberg and O.Theander, Svensk Papperstidn., **65**, 509 (1962).
50. B.Lindberg, J.Tanaka, and O.Theander, Acta. Chem.Scand., **18**, 1164 (1964).
51. H.-L.Hardell and O.Theander, Acta Chem.Scand., **25**, 877 (1971).
52. S.V.Soldatenkov and T.A.Mazurova, Biokhimiya, 21, 6 (1956).
53. S.V.Soldatenkov, "Biokhimiya Organicheskikh Kislot Rastenii" (Biochemistry of Organic Acids in Plants), Izd.Leningrad.Univ., 1971, p.50.
54. A.A.J.Feast, B.Lindberg, and O.Theander, Acta Chem.Scand., **19**, 1127 (1965).
55. D.Monzie-Guillemet and P.Monzie, Tech.Rech.Papet., **4**, 74 (1966).
56. A.Ishizu, B.Lindberg, and O.Theander, Carbohydr. Res., **5**, 329 (1967).
57. A.Ishizu, B.Lindberg, and O.Theander, Acta Chem. Scand., **21**, 424 (1967).
58. B.Alfredson and O.Samuelson, Svensk Papperstidn., 71, 679 (1968).
59. J.J.M.Rowe and K.B.Gibney et al., J.Amer.Chem. Soc., **90**, 1924 (1968).
60. V.Alfredson and O.Samuelson, Svensk Papperstidn.. **72**, 361 (1969).
61. M.S.Feather and J.F.Harris, Carbohydr.Res., **15**, 304 (1970).
62. W.Droge, V.Lehmann, O.Luderitz, and O.Westphal, Europ.J.Biochem., **14**, 175 (1970).
63. G.Petersson, Carbohydr.Res., **33**, 47 (1974).
64. G.Petersson, Tetrahedron, **26**, 3413 (1970).
65. G.Petersson, Org.Mass.Spectrom., **6**, 577 (1972).
66. G.O.Aspinall and Sze Chan Tam, Carbohydr. Res., **38**, 71 (1974).
67. R.F.Burns and P.J.Somers, Carbohydr.Res., **31**, 289 (1973).
68. S.A.Barker, A.R.Law, P.J.Somers, and M.Stacey, Carbohydr.Res., **3**, 435 (1967).

69. A.M.Y.Ko and P.J.Somers, Carbohydr.Res., **33**, 281 (1974).
70. R.F.Burns and P.J.Somers, Carbohydr.Res., **31**, 301 (1973).
71. K.Larsson, L.Olsson, and O.Samuelson, Carbonhydr. Res., **38**, 1 (1974).
72. S.A.Barker, J.M.Edwards, P.J.Somers, and A.Repas, Carbohydr.Res., **6**, 341 (1968).
73. J.U.Nef, Annalen, **357**, 214 (1907).
74. W.L.Evans, R.H.Edgar, and G.P.Hoff, J.Amer. Chem.Soc., **48**, 2665 (1926).
75. M.P.Benoy and W.L.Evans, J.Amer.Chem.Soc., **48**, 2675 (1926).
76. H.Ohle, Ergeb.Physiol., **33**, 694 (1931).
77. H.Kiliani and S.Kleemann, Ber., **17**, 1302 (1884).
78. A.Windaus, Chem.Z., **29**, 564 (1904).
79. H.S.Isbell, J.Res.Nat.Bur.Stand., **32**, 45 (1944).
80. O.Theander, Adv.Carbohydr.Chem., **17**, 223 (1962).
81. E.F.L.J.Anet, Carbohydr.Chem., 19, 181 (1964).
82. J.C.Sowden, M.G.Blair, and D.J.Kuenne, J.Amer. Chem.Soc., **79**, 6450 (1957).
83. J.C.Sowden and D.J.Kuenne, J.Amer.Chem.Soc., **75**, 2788 (1953).
84. H.P.Humphries and O.Theander, Acta Chem.Scand., **25**, 883 (1971).
85. B.Lindberg and O.Theander, Acta Chem.Scand., **22**, 1782 (1968).
86. J.Kenner and G.N.Richards, J.Chem.Soc., 1784 (1954).
87. R.U.Lemieux, in "Molecular Rearrangements", Part 2, (Edited by P.de Mayo), Intersci.Publ. New York, 1964, p.744.
88. G.Machell and G.N.Richards, J.Chem.Soc., 1938 (1960).
89. R.M.Rowell and J.Green, Carbohydr.Res., 15, 197 (1970).
90. J.C.Sowden and E.K.Pohlen, J.Amer.Chem.Soc., **80**, 242 (1958).
91. W.M.Corbett and A.M.Liddle, J.Chem.Soc., 531 (1961).
92. M.S.Feather and J.F.Harris, Adv.Carbohydr.Chem., **28**, 161 (1973).
93. J.C.Sowden and R.Schaffer, J.Amer.Chem.Soc., **74**, 499 (1952).
94. J.C.Speck Jr., Adv.Carbohydr.Chem., 13, 63 (1958).
95. H.A.Hampton, W.N.Haworth, and E.L.Hirst, J.Chem.Soc., 1739 (1929).
96. S.V.Bleshchinskii and S.F.Lozitskaya, Trudy Khim. Inst.Kirgiz.Fil.Akad.Nauk SSSR, **4**, 73 (1951).
97. M.Gibbs, J.Amer.Chem.Soc., **72**, 3964 (1950).
98. J.Kenner and G.N.Richards, J.Chem.Soc., 2916 (1956).
99. W.M.Corbett and J.N.Kenner, J.Chem.Soc., 3281 (1954).
100. R.F.Burns and P.J.Somers, Carbohydr.Res., **31**, 191 (1973).
101. G.Machell and G.N.Richards, J.Chem.Soc., 1932 (1960).
102. G.Machell and G.N.Richards, J.Chem.Soc., 1924 (1960).
103. J.W.Green, J.Amer.Chem.Soc., **78**, 1894 (1956).
104. R.Malinen and E.Sjöström, Paperi Puu, **57**, 728 (1975).
105. E.Fischer, Ber., **26**, 2400 (1893).
106. E.Fischer and L.Beensch, Ber., **27**, 2478 (1894).
107. E.Fischer and B.Helferich, Annalen, **383**, 68 (1911).
108. B.Indberg, Svensk Papperstidn., 59, 531 (1956).
109. C.S.Hudson, J.Amer.Chem.Soc., 38, 1566 (1916).
110. C.E.Ballou, Adv.Carbohydr.Chem., 9, 59 (1954).
111. J.B.Lee, J.Org.Chem., **28**, 2473 (1963).
112. C.Degani and M.Halmann, J.Amer.Chem.Soc., **90**, 1313 (1968).
113. R.L.Whistler and W.M.Corbett, J.Amer.Chem.Soc., **77**, 3822 (1955).
114. R.L.Whistler and W.M.Corbett, J.Amer.Chem.Soc., **77**, 6328 (1955).
115. J.Kenner and G.N.Richards, J.Chem.Soc., 2921 (1956).
116. J.K.Hamilton, Pure Appl.Chem., 5, 197 (1962).
117. R.Aurell, N.Hartler, and G.Persson, Acta Chem. Scand., **17**, 545 (1963).
118. B.Lindberg and O.Theander, Acta Chem.Scand., **20**, 206 (1966).
119. R.J.Ferrier, W.G.Overend, and A.E.Ryan, J. Chem.Soc., 1488 (1962).
120. J.Kenner and G.N.Richards, J.Chem.Soc., 278 (1954).
121. J.Kenner and G.N.Richards, J.Chem.Soc., 3019 (1957).
122. W.M.Corbett and J.Kenner, J.Chem.Soc., 927 (1957).
123. W.M.Corbett, G.N.Richards, and R.L.Whistler, J.Chem.Soc., 11 (1957).
124. D.M.Brown, F.Hayes, and A.R.Todd, Ber., **90**, 936 (1957).
125. G.O.Aspinall et.al. Canad.J.Chem., **53**, 2171 (1975).
126. S.Lewak aand L.Szabo, J.Chem.Soc., 3975 (1963).
127. W.Jachymczyk, L.Menager, and L.Szabo, Tetrahedron, **21**, 2049 (1965).
128. W.M.Corbett, J.Kenner, and G.N.Richards, J. Chem.Soc., 1709 (1955).
129. J.Kenner and G.N.Richards, J.Chem.Soc., 1810 (1955).
130. M.Sten and T.Mustola, Cellul.Chem.Technol., 7, 359 (1973).
131. G.O.Aspinall, C.T.Greenwood, and R.J.Sturgeon, J.Chem.Soc., 3667 (1961).
132. R.L.Whistler, J.N.BeMiller, Adv.Carbohydr.Chem., **13**, 289 (1958).
133. J.Honeyman (Editor), "Recent Advances in the Chemistry of Cellulose and Starch, Intersci.Publ. New York, 1959.
134. N.S.Mayat and O.P.Golova, Uspekhi Khim., **28**, 1114 (1959).
135. A.Meller, Holzforschung, **14**, 78, 129 (1960).
136. G.N.Richards, in "Cellulose and Cellulose Derivatives", Wiley Intersci., New York, 1971, p.1007.
137. O.P.Golova and N.I.Nosova, Uspekhi Khim., **42**, 743 (1973)[Russ.Chem.Rev., No.4 (1973)].
138. J.R.Clamp, L.Hough, et al., Adv.Carbohydr. Chem., **16**, 159 (1961).
139. H.Kiliani, Ber., **42**, 3903 (1909).
140. J.U.Nef, Annalen, **357**, 301 (1907).
141. T.M.Lowry and G.L.Wilson, Trans.Faraday Soc., **24**, 683 (1928).
142. G.Klein, Biochem.Z., **169**, 132 (1926).
143. W.M.Corbett and J.Kenner, J.Chem.Soc., 2245 (1953).
144. W.M.Corbett and J.Kenner, J.Chem.Soc., 1789 (1954).
145. R.L.Whistler and J.N.BeMiller, J.Org.Chem., **26**, 2886 (1961).
146. R.J.Whistler and D.G.Medcalf, J.Org.Chem., **27**, 3560 (1962).
147. H.Kiliani, Ber., **16**, 2625 (1883).
148. W.M.Corbett and J.Kenner, J.Chem.Soc., 1431 (1955).

149. D.J.MacLaurin and J.W.Green, Canad J.Chem., **47**, 3957 (1969).
150. R.M.Rowell, P.J.Somers, S.A.Barker, and M.Stacey, Carbohydr.Res., **11**, 17 (1969).
151. R.M.Rowell, Pulp.Paper Mag.Can., **72**, 74 (1971).
152. O.Samuelson and L.Thede, Acta Chem.Scand., **22**, 1913 (1968).
153. R.Malinen and E.Sjöström, Paperi ja Puu, **54**, 451 (1972).
154. G.O.Aspinall, M.E.Carter, and M.Los, J.Chem. Soc., 4807 (1956).
155. G.O.Aspinall, M.E.Carter, and M.Los, Chem.Ind. (London), 1553 (1955).
156. R.L.Whistler and W.M.Corbett, J.Amer.Chem.Soc., 78, 1003 (1956).
157. M.H.Johansson and O.Samuelson, Chem.Scripta, **9**, 151 (1976).
158. B.Lindberg, O.Theander, and J.-E.Uddegard, Svensk Papperstidn., **69**, 360 (1966).
159. H.Richtzenhain and B.A.Abrahamsson, Svensk Papperstidn., **57**, 538 (1954).
160. J.W.Green, TAPPI, **39**, 472 (1956).
161. G.N.Richards and H.H.Sephton, J.Chem.Soc., 4492 (1957).
162. H.Richtzenhain, B.O.Lindberg, B.A.Abrahamsson, and K.Holmberg, Svensk Papperstidn., **57**, 363 (1954).
163. G.Machell and G.N.Richards, J.Chem.Soc., 4500 (1957).
164. G.Machell, G.N.Richards, and H.H.Sephton, Chem. Ind.(London), 467 (1957).
165. B.Alfredson, O.Samuelson, and B.Sandstig, Svensk Papperstidn., **66**, 703 (1963).
166. M.H.Johansson and O.Samuelson, Carbohydr.Res., **34**, 33 (1974).
167. P.F.Nelson and O.Samuelson, Svensk Papperstidn., 71, 325 (1968).
168. D.W.Hass, B.F.Hrutfiord, and K.V.Sarkanen, J. Apl.Polymer Sci., **11**, 587 (1967).
169. A.Meller, Holzforschung, **14**, 81 (1960).
170. Y.-Z.Lai and K.V.Sarkanen, Cellulose Chem. Technol., 1, 517 (1967).
171. G.Centola, F.Pancirolli, and G.Ceragioli, Chimica e Industria, **87**, 345 (1955).
172. R.L.Colbran and G.F.Davidson, J.Textile Inst., **52**, T140 (1961).
173. R.Malinen and E.Sjöström, Paperi ja Puu, **57**, 101 (1975).
174. D.Monzie-Guillemet, H.Roux, and P.Monzie, Tech. Rech.Papet., **7**, 37 (1966).
175. O.Samuelson and L.Stolpe, TAPPI, **52**, 1709 (1969).
176. L.Jansen and O.Samuelson, Svensk Papperstidn., **72**, 216 (1969).
177. H.Kolmodin and O.Samuelson, Svensk Papperstidn., **73**, 93 (1970).
178. H.Kolmodin and O.Samuelson, Svensk Papperstidn., **74**, 310 (1971).
179. S.M.Aronovic, E.P.Crowell, D.M.Whalen, and B.B.Vurnett, TAPPI, **54**, 1693 (1971).
180. R.Malinen, E.Sjöström, and J.Ylijoki, Paperi ja Puu, **55**, 5 (1972).
181. H.Kolmodin and O.Samuelson, Svensk Papperstidn., **75**, 369 (1972).
182. R.Malinen and E.Sjöström, Paperi ja Puu, **55**, 547 (1973).
183. H.Kolmodin and O.Samuelson, Svensk Papperstidn., **76**, 71 (1973).
184. M.Manouchehri and O.Samuelson, Svensk Papperstidn., **76**, 486 (1973).
185. R.Malinen, Paperi ja Puu, **57**, 193 (1975).
186. R.M.Rowell, Pulp.Paper.Mag.Can., **72**, T236 (1971).
187. O.Samuelson, Papier, **24**, 671 (1970).
188. J.-A.Hansson and N.Hartler, Svensk Papperstidn., **71**, 669 (1968).
189. E.Dryselius, B.Lindberg, and O.Theander, Acta Chem.Scand., **11**, 663 (1957).
190. J.L.Minor, L.E.Kihle, and N.Sanyer, TAPPI, **52**, 2178 (1969).
191. R.M.Rowell and J.Green, TAPPI, **55**, 1326 (1972)
192. A.Meller, TAPPI, **38**, 682 (1955).
193. F.S.Head, J.Text.Ind., **46**, T58 (1965).
194. N.Hartler, Svensk Papperstidn., **65**, 513 (1962).
195. A.Meller, TAPPI, **46**, 317 (1963).
196. A.Meller and E.L.Ritman, TAPPI, **47**, 55 (1964).
197. R.L.Casebier and J.K.Hamilton, TAPPI, **50**, 441 (1967).
198. A.Meller, TAPPI, 38, 682 (1955).
199. A.Meller, TAPPI, **39**, 722 (1956).
200. W.K.Wilson and A.A.Podgett, TAPPI, **38**, 292 (1955).
201. I.Szabo and O.Teder, Svensk Papperstidn., **72**, 68 (1969).
202. O.Samuelson and N.Hartler, Svensk Kem.Tidskr., **62**, 197 (1950).
203. E.Venemark, Svensk Papperstidn., **67**, 157 (1964).
204. S.A.Rydholm, "Pulping Processes", Interscience, New York, 1965, p.642.
205. P.H.Abenius et al., Svensk Papperstidn., **70**, 612 (1967).
206. A.Teder, Svensk Papperstidn., **71**, 149 (1968).
207. P.Ahlgren, A.Ishizu, I.Szabo, and O.Theander, Svensk Papperstidn., **71**, 355 (1968).
208. A.Meller, Svensk Papperstidn., **65**, 307 (1962).
209. A.Meller, TAPPI, **45**, 481 (1962).
210. R.E.Reeves, W.M.Schwartz, and J.E.Giddens, J.Amer.Chem.Soc., **68**, 1383 (1962).
211. A.Meller, Svensk Papperstidn., **65**, 629 (1962).
212. A.R.Procter and R.H.Wiekenhamp, J.Polymer. Sci., Part C, **28**, 1 (1969).
213. G.Machell and G.N.Richards, TAPPI, **41**, 12 (1958).
214. A.Robert, P.Perolle, A.Viallet, and C.M.Barret, Bull.ATIP, **18**, 151 (1964).
215. O.Samuelson and L.Stolpe, Svensk Papperstidn., **74**, 662 (1969).
216. O.Samuelson and L.Stolpe, Svensk Papperstidn., **74**, 545 (1971).
217. B.Ericsson, B.Lindgren, and O.Theander, Svensk Papperstidn., **74**, 757 (1971).
218. O.Samuelson and L.Stolpe, Svensk Papperstidn., **77**, 16 (1974).
219. J.Defaye and A.Gadelle, Pulp.Paper Mag.Can., **75**, T394 (1974).
220. J.Defaye, H.Driguez, and A.Gadelle, Carbohydr. Res., **38**, C4 (1974).
221. D.W.Clayton and L.M.Marricini, Svensk Papperstidn., **69**, 311 (1966).
222. M.Ya.Zarubin and D.V.Tishchenko, Zhur.Prikl. Khim., **35**, 2724 (1962).
223. G.Chirkin and D.V.Tishchenko, Zhur.Prikl.Khim., **35**, 153 (1962).
224. R.T.Bottle and G.A.Gilbert, Chem.Ind.(London), 1201 (1954).
225. J.Kenner and G.N.Richards, Chem.Ind.(London), 1483 (1954).
226. G.Machell and G.N.Richards, J.Chem.Soc., 1199 (1958).
227. C.J.Stacey, J.F.Foster, and S.N.Erlander, Macromol Chem., **17**, 181 (1956).

228. Y.-Z.Lai and K.V.Sarkanen, J.Polymer Sci., **C28**, 15 (1969).
229. R.L.Whistler and J.N.BeMiller, J.Amer.Chem.Soc., **82**, 457 (1960).
230. L.Löwendahl, G.Peterson, and O.Samuelson, Carbohydr.Res., **43**, 355 (1975).
231. K.Larsson and O.Samuelson, Carbohydr.Res., **31**, 81 (1978).
232. W.M.Corbett and J.Kenner, J.Chem.Soc., 3274 (1954).
233. R.A.Young and K.V.Sarkanen et al., Carbohydr. Res., **21**, 111 (1972).
234. T.E.Nelson and B.A.Lewis, Carbohydr.Res., **33**, 63 (1974).
235. R.F.Burns and P.J.Somers, Carbohydr.Res., **31**, 191 (1973).
236. A.Klemer and K.Homborg, Ber., **96**, 631 (1963).
237. T.E.Nelson, J.Johnson, E.Jantzen, and S.Kirkwood, J.Biol.Chem., **244**, 5972 (1969).
238. T.Bremner, J.S.G.Cox, and G.F.Moss, Carbohydr. Res., **11**, 77 (1969).
239. C.H.Bolton, A.B.Foster, M.Stacey, and J.M.Webber, J.Chem.Soc., 4831 (1961).
240. P.Schorigin and N.N.Makarowa-Semlianskaia, Ber., **66**, 387 (1933).
241. H.Kiliani and P.Loeffler, Ber., **38**, 2667 (1905).
242. G.N.Richards, J.Chem.Soc., 3639 (1954).
243. J.C.Sowden, J.Amer.Chem.Soc., **76**, 3541 (1954).
244. H.W.Diehl and H.G.Fletcher, Arch.Biochem. Biophys., **78**, 386 (1958).
245. H.Venner, Ber., **90**, 121 (1951).
246. I.De Ley and M.Doudoroff, J.Biol.Chem., **227**, 745 (1957).
247. F.Trigalo and L.Szabo, J.Chem.Soc.,Perkin Trans.I, 604 (1975).
248. F.Trigalo , W.Jachymczyk, J.C.Young, and L.Szabo, J.Chem.Soc., Perkin Trans.I, 593 (1975).
249. F.Trigalo and L.Szabo, J.Chem.Soc.,Perkin Trans.I, 598 (1975).
250. E.Walton, S.R.Jenkins, R.F.Nutt, M.Zimmermann, and F.W.Holley, J.Amer.Chem.Soc., **88**, 4524 (1966).
251. S.R.Jenkins, B.Arison, E.Walton, J.Org.Chem., 33, 2490 (1968).
252. J.J.Novak, I.Smejkal, and F.Sorm, Tetrahedron Letters, 1627 (1969).
253. B.Alfredson and O.Samuelson, Svensk Papperstidn., **65**, 690 (1962).
254. F.Shafizadeh, Adv.Carbohydr.Chem., **13**, 9 (1958).

Faculty of Chemistry,
Tbilisi State University

Translated from *Uspekhi Khimii*, 49, 449 - 469 (1980) U.D.C. 542.953 : (547.235 + 547.556)

The Formation of the Azoxy-group in Reactions Involving Anions with Nitrogen - Nitrogen Bonds

V.N.Yandovskii, B.V.Gidaspov, and I.V.Tselinskii

The methods for the formation of azoxy-compounds by substitution reactions with participation of anions having nitrogen - nitrogen bonds are examined. Attention is concentrated on the alkylation reactions of alkanediazotates, nitrosohydroxylamines, and nitroamines as well as substitution reactions involving the distal nitrogen atom in azoxy-compounds. The literature up to 1976 inclusive is covered.
The bibliography includes 194 references.

CONTENTS

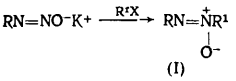
I. Introduction 237
II. Alkylation of alkanediazotates 237
III. Alkylation (acylation) of *N*-nitrosohydroxylamines 238
IV. Substitution reactions involving the distal nitrogen atom in azoxy-compounds 240
V. Nucleophilic substitution reactions involving *N*-nitroamines and *N*-nitroamides 242
VI. Conclusion 244

I. INTRODUCTION

The chemistry of azoxy-compounds is now attracting considerable interest as shown by the publication of several monographs and reviews in the last ten years[1-9]. The vigorous growth of research in this field has led to the discovery of new methods for the introduction of the azoxy-group into organic compounds and has imparted a new significance to the studies by Bamberger, Hantzsch, Angeli, and others carried out at the beginning of the XXth century. In a previous review[10] we examined the methods for the formation of the azoxy-group by the oxidation of compounds with nitrogen–nitrogen bonds[10]. This review deals with the formation of the azoxy-group in substitution reactions with participation of ambident anions having nitrogen–nigrogen bonds.

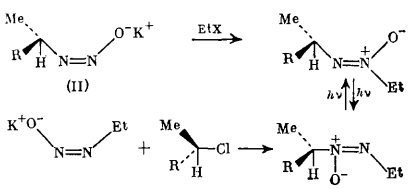
II. ALKYLATION OF ALKANEDIAZOTATES

A convenient method for the synthesis of azoxyalkanes, consisting in the alkylation of alkanediazotates, has been developed by Moss and coworkers[11-16]:



(I)

Azoxyalkanes, particularly those containing asymmetric substituents (I, $R \neq R^1$) were previously described in isolated instances only, but have now become more available. The method of synthesis described is unsuitable for compounds (I) where R and (or) R^1 = aryl or t-alkyl, but it does have many advantages, as noted by Moss et al. [12], and makes it possible to vary the groups R and R^1, which can be primary and (or) secondary alkyl or arylalkyl groups. The synthesis by this method is specific, and it leads to a single structural iosmer. The method makes it possible to obtain optically active azoxyalkanes, since the alkylation stage is not accompanied by the loss of chirality in the R and R^1 groups[12,13,15,16] (see also McGahren and Kunstmann[17]):



(II)

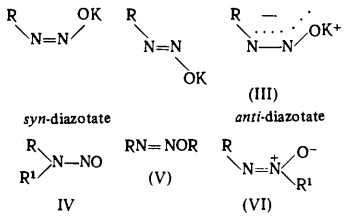
Evidently the configuration of the centre in the distal position remains unchanged, but there is a complete inversion at the carbon atom of the reagent[13,15,16].

The retention of the chiral centre in the diazotate (II) in the alkylation reaction has been used in a 12-stage synthesis of the dihydro-derivative of elaiomycin—an antiobiotic and carcinogen, which is encountered in nature and which contains the azoxy-group[15]. The photochemical interconversions of the distal and proximal isomers into their equilibrium mixture without loss of asymmetry at C* constitute an additional confirmation of the possibilities of the new method of synthesis of azoxyalkanes, which makes it possible to obtain a chiral centre in R and (or) R^1.[13]

The possibility of using allyl halides for the alkylation of diazotates indicates yet another interesting aspect of their practical application, since "functional" alkylating agents can be introduced into the reaction[14].

Alkanediazotates, which are the key compounds in the new synthesis, usually occur merely as intermediates in the nitrosative deamination of alkylamines and alkylhydrazines[16,18,19], in the alkaline cleavage of *N*-alkyl-*N*-nitroso-urethanes[20-30], etc. but can also be isolated in a pure state[20-27]. Moss[31] modified somewhat the procedure for the decomposition of urethanes, usually employed for the synthesis of diazoalkanes, and carried out the reaction with potassium t-butoxide in an inert solvent. Diazotates are then obtained in the form of solid salts and are believed to have the *syn*-configuration[16]. Other methods, for example, the alkaline nitrosation of hydrazines, give rise to the more stable *anti*-diazotates, but the *syn* → *anti* conversion is greatly hindered[16,27]. The N–N (1.32 Å) and N–O (1.29 Å) bond lengths in *syn*-methanediazotate are intermediate between the values for single and double bonds, so that the compound is best represented by

the mesomeric anion (III).[16,32] The presence of *p* electrons at $N_{(2)}$ is responsible for the formation of nitrosoamines (IV), diazoethers (V), or ethoxy-compounds (VI) in the alkylation of the anion:



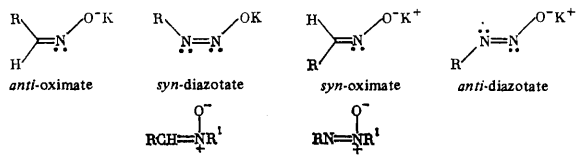
syn-diazotate (III) *anti*-diazotate

IV (V) (VI)

The yield of azoxyalkanes varies from 30 to 60% and is little affected by the solvent. In alkylation in hexamethylphosphoramide, a polar aprotic solvent which causes the dissociation of the salt, an appreciable proportion of the alkanediazotate remains in the form of the anion. The high electron density at the oxygen atom and its appreciable steric accessibility compared with the $N_{(1)}$ atom cause the yield of the nitrosoamine to be small and make the yield of the *O*-alkylation product up to 50%. In a less polar solvent (95 : 5 ether–hexamethylphosphoramide mixture) a considerable proportion of the alkanediazotate is present in the form of ion pairs, the $O_{(3)}$ atom is blocked by the counter-ion, and the nitrosoamine (IV) predominates over the diazoether (V) among the side products[16]. Arylation of the alkanediazotate (III, $R = CH_3$) gives rise exclusively to compound (IV), i.e. takes place at the $N_{(1)}$ atom[21].

It is of interest to compare all these data with the alkylation of arenediazotates. The latter are known to exist in the more stable form of isodiazotates[33–39] (equivalent to the *anti*-configuration of alkanediazotates) and calculation of the electron density in the anion shows that the site of attack is the key nitrogen atom and the oxygen atom[39]. Experimental data[39,40], indicating the predominant formation of *O*-alkylation products in dimethylformamide (DMF) and dimethyl sulphoxide (DMSO), are fully consistent with the calculations. Thus the ambident anion reacts in the usual way, at the first and third atoms[39,40], and azoxy-compounds are not formed in this case.

The unusual behaviour of alkanediazotates, manifested by the possibility of alkylation in the 2-position of the ambident anion, is associated with the presence of the electron pair at $N_{(2)}$. This situation is not unique in the series of nitrogen-containing functional groups and has a direct analogy in the alkylation of the oximate anion. In both cases the 2- and 3-positions in the ambident anion are alkylated preferentially. Whereas alkylation at $C_{(1)}$ is not observed in the oximate anion[41–43], $N_{(1)}$-alkylation does occur to a slight extent in the *syn*-alkanediazotate owing to the presence of an electron pair at the key nitrogen atom[12,16]:



anti-oximate *syn*-diazotate *syn*-oximate *anti*-diazotate

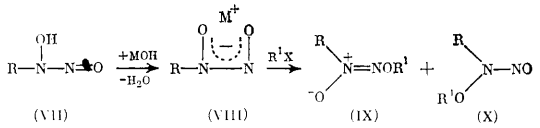
The *anti*-oximate anion, which is sterically equivalent to *syn*-diazotate†, is alkylated preferentially at the nitrogen atom[41–43,45–51], giving rise to a nitrone, i.e. the ambident anion is alkylated in both cases in the 2-position (but with different selectivities). The *syn*-oximate anion, which is sterically equivalent to the *anti*-diazotate and to the anion derived from ketoximes, gives preferentially $O_{(3)}$-alkylation products[41–43], i.e. in both cases the ambident anion is alkylated preferentially at the oxygen atom and nitrones or, correspondingly, azoxy-compounds[52] are not formed. The influence of the geometry of the diazo-bond on the regio- and stereo-specificity of the alkylation of alkanediazotates has been recently discussed[52].

The intramolecular interaction of propargyl[30,53,54], allene[55], and epoxy-groups[56,57] with the *syn*-diazotate ion, obtained by the decomposition of "functional" urethanes, proceeds in the same way as *O*-alkylation.

The formation of an azoxy-compound in the decomposition of cyclopropane-bisdiazotate, which constitutes an intramolecular *N*-cyclopropylation reaction, has been reported[58]. However, the multiplicity of pathways leading to the decomposition of the initial product hinders interpretation.

III. ALKYLATION (ACYLATION) OF *N*-NITROSOHYDROXYLAMINES

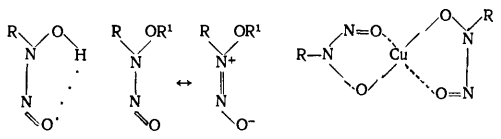
The alkylation of *N*-nitrosohydroxylamines (VII) and their salts (VIII) constitutes yet another group of reactions leading to the formation of azoxy-compounds (IX).[59–78]. The side products in this process are apparently alkoxynitrosoamines (X):



(VII) (VIII) (IX) (X)

The key compounds for this reaction—the acids (VII) and the salts (VIII)—constitute an interesting class of compounds; the problem of their structure has been discussed in earlier studies by Bamberger[62,63,79], Hantzsch[67,80,81], Traube[65,81–83], Gomberg[84], Angeli[85–87]#, and Thiele[88]. A recent review[78] is a first attempt at a systematic account of the relevant data (see also Bamberger and Baudisch[79], and Marvel, where methods for the preparation of cupferrons are summarised[89]). The acids (VII) are unstable in a free state, while their salts are more stable; for example, the ammonium salt of phenylnitrosohydroxylamine (cupferron) is a familiar analytical reagent[90,91].

O,*N*-Disubstituted nitrosohydroxylamines (X) exist preferentially and the free acids (VII) exclusively in the *trans*-configuration[92], whose additional stabilisation in the case of the acids (VII) is caused by the intramolecular hydrogen bond[92]. The salts of nitrosohydroxylamines, which are represented as the chelates (VIII) and (XI), have an analogous configuration[78,90,93]:



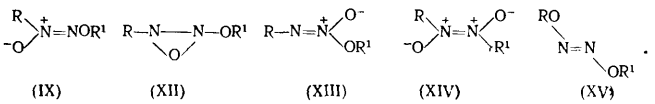
(VII) (X) (XI)

† The effective size of the free electron pair in space is even smaller than the size of bound hydrogen[44].

Angeli represented arylnitrosohydroxylamines by the formula $ArN(O) = NOH$ and regarded them as the oximes of nitro-compounds or as the oxides of diazohydrates[79,85–87].

The geometry of the salts and their stability are apparently associated with the formation of a 6-electron system, the principle of the structure of which has already been used to account for the geometry, thermal stability, and reactivity of the ketoxime dianions[94] and has been extrapolated to other "*U*-type" molecules–tosylhydrazone dianions[94,95] and *cis*-difluoro-olefins[94,96].

The salts of *N*-nitrosohydroxylamines are readily alkylated and, as shown for the first time[60,61] in relation to the benzylation of *N*-benzyl-*N*-nitrosohydroxylamines, can give rise to two reaction products—(IX) and (X) (R = R^1 = CH_2Ph). The structure of the latter compound was adopted immediately and was not questioned subsequently, since in the general case it can be obtained by specific synthesis—the nitrosation of alkoxyamines[61–63,77,78,97]. The structure of the first product (which is more stable), represented by formulae (IX),[63] (XII),[62] (XIII),[67] and (XIV),[70] has been the subject of a prolonged controversy. Wright and coworkers[70] seemingly demonstrated by all the available evidence that the first alkylation products exist in form (IX), but the fact that these compounds (R = alkyl or aryl; R^1 = alkyl) evolve methane on treatment with methylmagnesium chloride led them into a blind alley§. Wright and coworkers[70] then attributed formula (XIV) to the alkylation products and at the same time threw doubt on the structure of the dimers of nitroso-compounds:



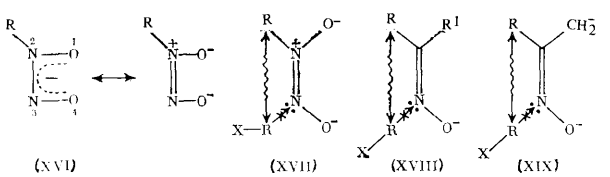
(IX) (XII) (XIII) (XIV) (XV)

Freeman[73] and Stevens[74] corrected this error and later Smith[59] and Woodward and Wintner[75,76] confirmed that the product has structure (IX). Bearing in mind that the structure of the dimers of nitroso-compounds was not immediately adopted and that the hyponitrites (XV) are isomeric with compounds (IX) and that the spectroscopic characteristics of their salts (XV, R = R^1 = Na) are close to those of nitrosohydroxylamines salts[98,99], the difficulties in the determination of the structure become understandable.

The alkoxydiazene oxides (IX) are isolated by the usual preparative methods—distillation, crystallisation, and chromatography. The products of the methylation of the Traube salt (VIII, R = $CH_2N_2O_2Na$, M = Na) as well as other alkoxydiazene oxides constitute surprising examples of stability[65,76–78]. Their high stability can be used for their purification by heating with sulphuric acid or alkali[77].

The geometry of compound (IX) has not been established, but Lamberton and Yusuf[77] clearly noted the formation of a single stereoisomer in the ethylation of *N*-nitrosomethylhydroxylamine.

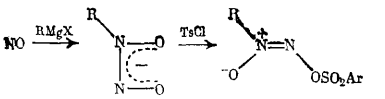
The anion (XVI) has three potential nucleophilic centres susceptible to attack—both oxygen atoms and the $N_{(3)}$ atom. In reality only the first possibility is realised:



(XVI) (XVII) (XVIII) (XIX)

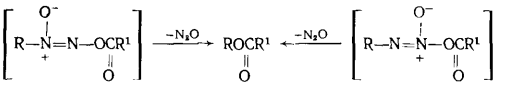
§ Subsequently Stevens[74] explained this finding.

We believe that the general considerations concerning the alkylation of the oximate and diazotate anions, described above, are applicable in this case too. As the reagent approaches the nitrogen atom of nitrosohydroxylamine, a structure, analogous to the two non-realisable structures conceivable in the alkylation of the ketoximate anion (XVIII) and the dianion (XIX), is produced. In all three cases the nitrogen atom is sterically blocked, so that the oxygen atom (see Section II above) and the carbon atom are attacked in the alkylation of compounds (XVIII) and (XIX) respectively[94]; in compound (XVI) alkylation proceeds via both oxygen atoms. It is of interest that the electron pair of the nitrogen atom of the anion (XVI) is blocked also for other electrophilic reactions. Thus its tosylation takes place at the $O_{(4)}$ atom with formation of compound (XX)[74] in which the *cis*-orientations of the oxygen atoms are retained[100]:



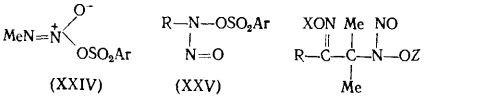
(XVI) (XX)

Compounds of type (XX) are of interest as starting materials for the synthesis of azoxy-compounds by substitution using various nucleophiles (carbanions and alkoxides) (see below) and are frequently obtained as a result of a single-stage reaction[74]. The tosyl derivatives (XX) are more stable than other acyl derivatives of *N*-nitrosohydroxylamines. For example, the alkali metal salts (VIII) evolve N_2O and give rise to the esters (XXI) on treatment with aroyl halides, since the intermediates (XXII) readily decompose[101]:



(XXII) (XXI) (XXIII)

It is of interest that both the diazene $N_{(2)}$-oxides (XXII) and the diazene $N_{(1)}$-oxides (XXIII)[101–104] behave similarly and that the position of the oxygen atom does not influence the formation of esters[101]. On the other hand, the tosyl derivatives (XX) and (XXIV) have sharply different stabilities; thus the attempt to tosylate the silver salt of methylnitroamine gives rise solely to methyl tosylate as a result of the decomposition of the intermediate (XXIV):[105]



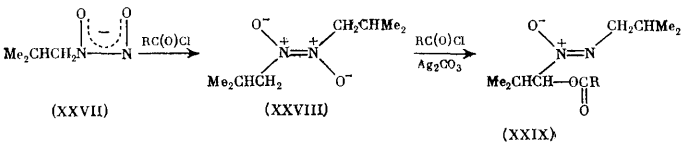
(XXIV) (XXV) (XXVI)

(a) R=Ph, X=MeCO, $Z=SO_2Ar$;
(b) R=Z=Me, X=H

Nor is it possible to obtain the tosyl derivative (XXV) by the nitrosation of the corresponding hydroxylamine[105], which confirms the validity of the choice, made for the first time by Stevens,[74], between the alternative structures (XX) and (XXV) in favour of (XX). In a recent study White et al.[100] explained some of the properties of compounds of type (XX). In contrast to these data, structure (XXVIa) has been attributed to the product of the tosylation of N-[1-acetoxymino-2-methyl-1-phenyl-(2-propyl)] hydroxylamine[106]. The anomalous course of the reaction may be due to the specific properties of the initial compound, so that the alkylation of its homologue (XXVI, R = Me, X = Z = H) with dimethyl

sulphate leads to the formation of compound (XXVIb),[106] which again conflicts with the analogous reaction of cupferron[70] or *N*-t-alkyl-*N*-nitrosohydroxylamines[105].

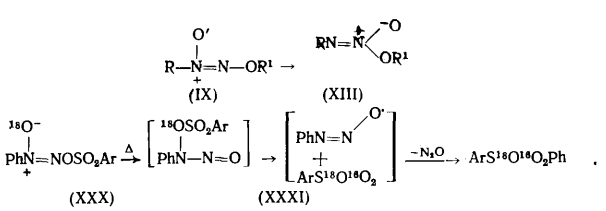
The prolonged controversies which have accompanied each new step in the development of the chemistry of nitrosohydroxylamines can be accounted for by the weak theoretical ideas concerning the state of the bonds in the initial anion (VIII) or structures of type (IX). Evidently its further development promises to have many unexpected features. For example, it has been observed quite recently that the 3,5-dinitrobenzoylation of salts of *N*-isobutyl-*N*-nitrosohydroxylamine (XXVII) gives rise to compound (XXIX),[107] whose formation is difficult to account for by the mechanism involving the acylation of the $O_{(1)}$ atom[108] or the $O_{(4)}$ atom[101] in the initial anion. It has been shown that in the general case compounds (XXIX, RCO = acetyl, 3,5-dinitrobenzoyl, or 3-nitro-1-naphthoyl) are products of the acylation of the nitroso-dimers (XXVIII), which is usually accompanied by reactions of *N*-nitrosohydroxylamines[107]:



(XXVII) (XXVIII) (XXIX)

Acylating deoxygenation of compounds (XXVIII) constitutes a new type of rearrangements, related to the generalised Polonovskii reaction[109].

The alkylation of nitrosohydroxylamines gives rise to azoxy-compounds (IX), which are isomeric with the products of the alkylation of primary nitroamines (XIII). The possibility of the migration of oxygen from $N_{(1)}$ to $N_{(2)}$ has not been investigated by the intermediates in this migration [oxadiaziridines (XII)] have been erroneously regarded by Bamberger[62] as possible products of the alkylation of nitrosohydroxylamines. We may note, incidentally, that the double bond in diazoethers is not azoxidised under the influence of peracids[70]:

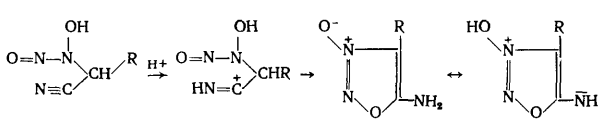


(IX) (XIII)

(XXX) (XXXI)

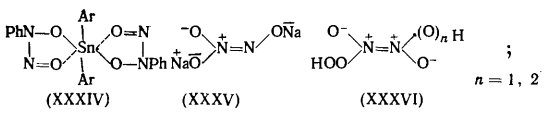
Another variety of isomeric transformations, namely in the pair of compounds (IX) and (X), has not been investigated, but it has been shown in relation to the thermal decomposition of the derivatives (XXX) labelled at the oxygen atom[110] that the tosyl group migrates to the *N*-oxide oxygen with formation of compound (XXXI). According to the mechanism presented above, its further decomposition gives rise to the phenyltosylate (Ar = *p*-tosyl) in which the label is uniformly distributed between the three oxygen atoms in the sulpho-group[110].

Nitrosohydroxylamines (XXXII) can also undergo intramolecular alkylation processes, giving rise to the sydnones (XXXIII):[141]



(XXXII) (XXXIII)

The interaction of diaryltin dichlorides with cupferron leads to chlorine-substitution products instead of the expected complexes suitable for the quantitative precipitation of the metal. According to a brief communication[112], the substance obtained has the structure (XXXIV), which has been demonstrated by infrared spectroscopy:

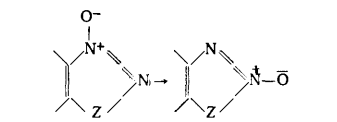


(XXXIV) (XXXV) (XXXVI) $n = 1, 2$

Organic derivatives of the Angeli salt (XXXV) and other oxyhyponitrites (XXXVI) have not been investigated at all[113]. When an attempt is made at a direct alkylation of (XXXV) by primary alkyl halides, the products are aldoximes and the reaction proceeds without the intermediate formation of the nitroxyl NOH.[114] It is also significant that in ethanol the nitrogen atom is alkylated and that the contribution of this process usually diminishes (relative to *O*-alkylation) on passing from alcohol to water[114].

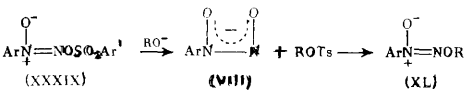
IV. SUBSTITUTION REACTIONS INVOLVING THE DISTAL NITROGEN ATOM IN AZOXY-COMPOUNDS

Numerous substitution, addition, and degradation reactions of azoxy-compounds with retention of the azoxy-group are known. In the present section we shall confine ourselves to the consideration of processes involving direct substitution at the $-N=N(O)$ group. Reactions of this type include the photochemical reactions of aliphatic and aliphatic-aromatic azoxy-compounds as a result of the migration of the oxygen atom. They were considered in our previous review[10] and have been studied only in recent years. Analogous migration of oxygen from $N_{(1)}$ to $N_{(2)}$, induced photochemically, has been observed in heterocycles: triazole oxides (XXXVII)[115–117] and thiadiazole oxides (XXXVIII)[118–120]:



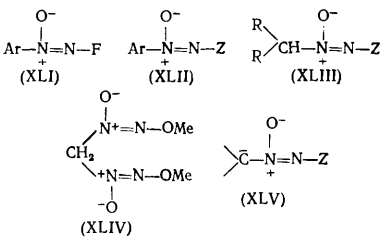
(XXXVII): Z = NR (XXXVIII): Z = S

Examples of migrations of this kind are few; reactions involving substitution at the distal nitrogen atom of the azoxy-group are more familiar. The formation of alkoxydiazene oxides (XL) in the reaction of alkoxides with tosyl derivatives (XXXIX) is fully consistent with this behaviour[74]. However, in reality the anion of nitrosohydroxylamine (VIII), liberated as a result of the substitution at the sulphur atom, is alkylated:



(XXXIX) (VIII) (XL)

The reaction of compounds (XXXIX)[74,121], (XL, R = Me),[70] and (XLI)[122] with organomagnesium reagents (Ar^1MgX, AlkMgX), which leads to the exchange of the OSO_2Ar^1, OMe, and F groups for a hydrocarbon group, giving rise to yet another possibility for the synthesis of the azoxy-compounds (XLII, Z = aryl or alkyl), takes place quite differently; however, the tosyl group in azoxysulphones (XLII, $Z = SO_2Ar^1$)[123] is not exchanged for the aryl group in Ar^1MgX:[124]

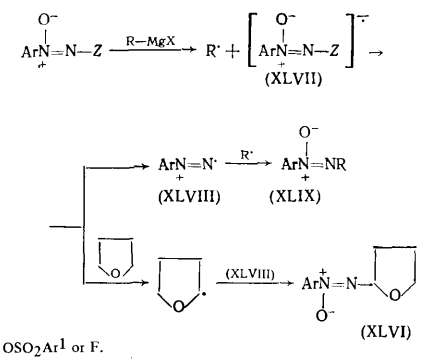


(XLI) (XLII) (XLIII) (XLIV) (XLV)

The attempt to substitute a group Z for a hydrocarbon group in aliphatic diazene oxides (XLIII, $Z = OSO_2Ar^1$ [74] or F[121,122]) was unsuccessful owing to the exchange of the proton in the α-position. For the same reason, the substitution of the alkoxy-group in bis(nitrosohydroxylamine)methane (XLIV) also fails, since the CH_2 group is metallated in the first place[70,76]. The stability of the anion having the general formula (XLV), where Z = Me, MeO, etc., has been used in a number of synthetic investigations[14,76].

Despite the fact that the distal group in the diazene oxides (XXXIX)–(XLI) can be exchanged for the alkyl (aryl) group in organomagnesium reagents, direct substitution at the nitrogen atom is not observed in reactions with other nucleophiles; for example, compounds (XLI) do not change under the influence of MeCOOH, MeONa, or Et_2NH.[121,122] Furthermore, in the reactions of compounds (XXXIX) and (XLI) with organomagnesium reagents in tetrahydrofuran (THF), compounds (XLVI) are formed as side products, evidently as a result of radical substitution[121]. (The α-position in THF is activated for radical substitutions of this kind; see, for example, Refs.125 and 126).

This finding and also the fact that, among the nucleophiles investigated, only Grignard reagents led to substitution at the nitrogen atom while other reagents proved to be inert or led to exchange at the sulphur atom or to metallation indicate the validity of the mechanism proposed by Stevens[121]:



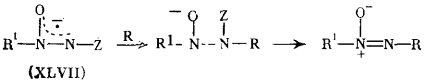
(XLVII) (XLVIII) (XLIX) (XLVI)

Z = OSO_2Ar^1 or F.

It is based on electron transfer to the azoxy-group with formation of the radical-anion (XLVII), which is converted into the azoxy-radical (XLVIII). The latter combines with the primary (R·) or secondary () radical, giving rise to compounds (XLIX) and (XLVI) respectively. Whereas the first stage, one-electron transfer from the organometallic compound to the azoxy-group, has aroused no doubts hitherto and has been adequately confirmed in the literature[127–129], the attempt to detect radical (XLVIII) by EPR has failed[121].

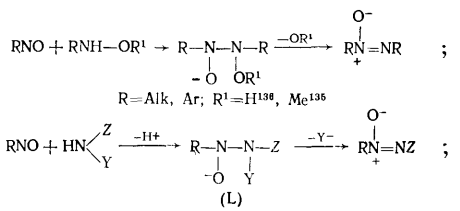
The azoxy-radical, with the unpaired electron at the nitrogen atom, is identical with the diazenyl radical, the possibility of the formation of which has been studied vigorously. Nevertheless many substitution reactions at the N–N bond can be accounted for on the basis of the addition–elimination mechanism[130–132] without resorting to ideas involving a discrete diazenyl radical.

Similar considerations are apparently applicable also to the substitution reactions with organomagnesium reagents involving the distal nitrogen atom of the azoxy-group, considered in this review. The final products of such reactions arise as a result of the pairing of the species (XLVII) with the primary or secondary radical present in the medium and subsequent elimination of the anionic fragment¶:



(XLVII)

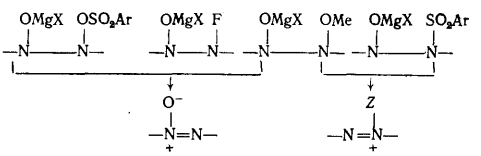
In this interpretation the substitution reaction is put in the same class with the already known processes involving the formation of the azoxy-group via the coupling of N-centred radicals†:



R = Alk or Ar; Z = Y = F[122] or Cl[137]; Y = Cl, Z = SO_2Ar[123]; Z = Y = Cl, H = Alk or Ar[138].

The formation of azoxysulphones[123] and not azoxychloro-derivatives by the condensation of nitroso-compounds with chloramine-T indicates the preferential rupture of the N–Cl bond compared with N–SO_2Ar in the intermediate (L, Y = Cl, Z = SO_2AR). It is also remarkable how much more difficult are the conditions for the elimination of the sulphinate group, for example in the Carpino reaction[139–141] compared with the analogous elimination of the sulphonate group, for example, in the amination of nitrogen-containing bases by hydroxylamine-*O*-

All the foregoing considerations illustrate the idea that the stabilisation of the intermediate (L) by the elimination of the anion (in the form of OMgX or Y) is apparently determined by the ease of dissociation of the N–O and N–Y bonds and the stability of the leaving anion:

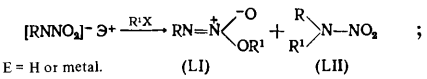


¶ The coupling of R· with the O-centred radical-anion leads to deoxygenation to a first approximation. Such a process is well known for the reaction of azoxyarens with organomagnesium reagents[70,133,134].

† Another mechanism of these reactions involves nucleophilic addition to the N = O double bond (see, for example, Taylor et al.[135]).

V. NUCLEOPHILIC SUBSTITUTION REACTIONS INVOLVING *N*-NITROAMINES AND *N*-NITROAMIDES

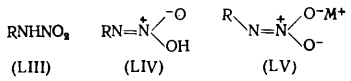
The alkylation of primary nitroamines, nitroamides, and their salts leads to the corresponding 1-alkoxydiazene 1-oxides (LI). The ratio of the *O*-alkylation [compound LI)] and *N*-alkylation [compound (LII)] products differs within very wide limits depending on the nature of the substituting group (R = alkyl, aryl, or SO_2AR), the alkylating agent, the metal cation (sodium, potassium, or silver), and the solvent:



E = H or metal. (LI) (LII)

Reactions in which primary nitroamines add to multiple bonds and many other nucleophilic substitution processes involving their anions also lead to a mixture of products (LI) and (LII). The chemistry of nitroamines has been considered in a number of reviews[144–150] and sections devoted to the alkylation of primary nitroamines are contained in a number of monographs[145,146,148,149]. However, since the publication of the last monograph, numerous experimental facts have accumulated, which have to be surveyed.

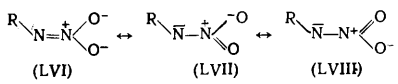
The structure of primary nitroamines and their salts has been the subject of theoretical disputes at the end of the XIXth and the beginning of the XXth century. The principal topic of these disputes has been the following question: do nitroamines exist in the form of true nitro-compounds (LIII) or do they have the structure of isonitroamines (LIV)# (for the history of the development of the relevant views, see Wright[147]):



(LIII) (LIV) (LV)

It has been shown recently that the N–N and N–O bond orders in methylnitroamine are to some extent equalised, which is accompanied by partial localisation of the negative charge at the oxygen atoms. However, primary nitroamines in the non-ionised state have the true nitroamine structure. It has been shown[152] that the ionisation of methylnitroamine entails an increase of the N–N bond force constant and a decrease of the N–O bond force constant, which corresponds to the isonitroamine structure being preferred for its salts, the metal cation being located in the *cis*-position relative to the alkyl group [structure (LV)].

Although the static distribution of charges in alkali metal salts of nitroamines is described by structure (LV), the reactivity of the corresponding anion is determined by the presence of three reaction centres—both oxygen atoms and the amino-nitrogen atom. The localisation of the electron pair at the central nitrogen atom is impossible in any of the main mesomeric structures (LVI)–(LVIII) and the central atom is consequently not susceptible to electrophilic attack:



(LVI) (LVII) (LVIII)

In a number of early studies, *N*-nitrosohydroxylamines were referred to as "isonitroamines", which introduced an additional confusion into this problem (See, for example, Traube[151]).

Nitroamines and their anions are typical examples of ambident (1,3) nucleophiles and many features of their individual behaviour can be accounted for on the basis of the general characteristics of the behaviour of such reagents. For example, it is well known that the reaction of silver salts of nitroamines gives rise to *O*-alkylation products, while alkali metal (potassium and sodium) salts give rise preferentially to *N*,*N*-dialkylnitroamines[145,146,148,149]. This conclusion is based both on studies carried out at the end of the XIXth and the beginning of the XXth century[153–159] and on more modern data[77,160–172]. Unfortunately in the majority of these investigations accurate ratios of the *O*- and *N*-alkylation products are not quoted. The available data are compiled in Table 1, which clearly illustrates the quantitative aspect of the relation.

Table 1. The ratios of the products of the *O*- and *N*-alkylation of $RNHNO_2$ and its salts.

No.	R/[$RNNO_2$]$^-$	Cation	Alkylating agent R^1/R^1X	Ratio* of products of *O*- and *N*-alkylation	Refs.
1	Isopropyl	K	MeI	0.15	162
2	Isopropyl	Ag	MeI	12.5	162
3	Neopentyl	Ag	MeI	12.5	162
4	Methyl	Na	$PhCH_2Cl$	0.25	167
5	Methyl	Na	*p*-$BrPhCH_2Cl$	0.14	167
6	Ethyl	Na	*p*-$BrPhCH_2Cl$	0.4	167
7	Methyl	Na	*p*-$CNPhCH_2Cl$	0.18	167
8	Ethyl	Na	*p*-$CNPhCH_2Cl$	0.4	167
9	Methyl	Li	$FcCH_2CH_2I$**	***	171
10	Methyl	Li	$FcCH_2X$**	***	170
11	n-Butyl	Na	n-BuI	0.75	160
12	Isopropyl	Na	iso-*o*-PrI	1.8	161
13	n-Octyl	Na	n-$C_8H_{17}I$	2.50****	161
14	Isopropyl	H	Me_2SO_4	1.2	162
15	Methyl	Na	$EtOCH_2Cl$	1.0	167

* The alkylation of alkali metal (Li, Na, K) salts was carried out in alcohol (MeOH, EtOH), that of silver salts was carried out in ether, and the alkylation with dimethylsulphate was carried out in water.

** Fc = ferrocenyl.

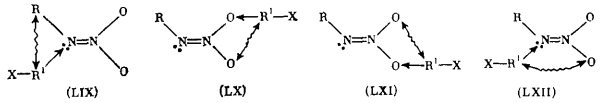
*** Only *N*-alkylation takes place.

**** The result is apparently distorted by partial decomposition on distillation.

The different modes of alkylation, depending on the metal cation, can be explained in terms of the general rule for the alkylation of ambifunctional nucleophiles; a polar electrophile combines primarily with the atom of the nucleophilic substrate having the highest electron density[173]. Such a centre in the nitroamine anion is the oxygen atom, which is attacked in the presence of a strong electrophilic catalyst (silver), which polarises the R^1–X bond[174]. Similarly other polar compounds [Me_2SO_4 and $EtOCH_2Cl$ (Nos. 14 and 15, Table 1)] give rise to a high percentage of the *O*-isomer.

Electrophiles with a small positive charge or electrically neutral electrophiles react preferentially with the atom of the ambifunctional system which is most readily polarised[173]. Such a centre in a nitroamine is the amino-nitrogen atom, which reacts preferentially, in relation to oxygen, with R^1–X (in the absence of silver ions) or adds to the multiple bond. Thus the condensation of alkylnitroamines with epoxyethane[175] and an activated double bond[146,148,168,176] as well as the aminomethylation of nitroamines[146,148,177] proceed exclusively at the nitrogen atom.

Another important feature is the increase of the amount of the *O*-isomer with increase of the bulk of the alkyl group. Comparison of Nos.1 and 12 in Table 1 shows that the methylation of isopropylnitroamine results in the formation of the *N*,*N*-isomer, while isopropylation gives preferentially the *O*,*N*-isomer. The progressive increase in the bulk of the group in both the alkylating agent and in the initial nitroamine (Nos.5–8 and 11–13) has a similar influence. Evidently the steric hindrance to the approach of the alkylating agent in structure (LIX) is manifested to a greater extent than in compounds (LX) or (LXI):

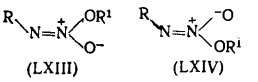


(LIX) (LX) (LXI) (LXII)

In conformity with the hypothesis put forward previously in the interpretation of the alkylation of diazotates (see Section II) (see also the earlier review[10]), the steric interactions with the vicinal group in structure (LXII) are less important than the steric interactions with the geminal group. It is also evident that, when R and R^1 are cumbersome groups, a situation may arise where the approach of the reagent to either the nitrogen atom [structure (LIX)] or to the oxygen atoms [structures (LX) and (LXI)] is impossible. Thus the failure of a reported attempt at the cyclohexylation of the sodium salt of cyclohexylnitroamines[161] was apparently caused by the high steric constant (−0.79)[178] for the cyclohexyl group.

It follows from the inspection of formulae (LX) and (LXI) that they are non-equivalent. The steric hindrance of the approach of the reagent in compound (LXI) is smaller, since in the case of compound (LX) the interactions with group R are superimposed (see the footnote in Section II). This non-equivalence of the oxygen atoms in the limiting structure (LVI) has been confirmed in practice by the preferential formation of the *trans*-isomers in the alkylation of the silver salts of nitroamines.

The possibility of the existence of geometrical isomers of 1-alkoxydiazene 1-oxides (LI) was already suggested by Umbgrove and Franchimont[159] and was demonstrated experimentally in later studies[77,165]. Analysis of kinetic data for the alkaline hydrolysis of the products of the reaction of silver salts of alkylnitroamines led the authors[77,165] to the conclusion that compounds (LI), which had been believed for a long time to be chemical individuals, are in reality mixtures of the *cis*-isomer (LXIII) and the *trans*-isomer (LXIV). The latter are more resistant to the action of acids, alkalies, and light and can be obtained in a pure form.



(LXIII) (LXIV)

The content of the *cis*-isomer was estimated on the basis of the kinetics of the decomposition of "crude" reaction mixtures, (see Table 2).

Evidently the *trans*-isomers predominate quantitatively in the mixtures of products; a general tendency towards a decrease of the content of the *cis*-isomer with increase of the bulk of the groups R and R^1 is also evident. This tendency was confirmed in another investigation. For example, in the methylation of $RNHNO_2$ by diazomethane both the total amount of the *O*-isomer and its content of the *trans*-isomer increase in the sequence R = Me < Et < iso-Pr < t-Bu.[179]

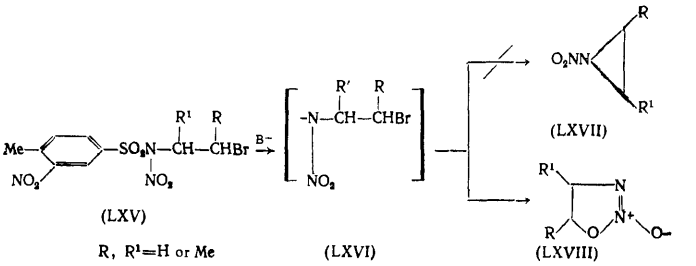
The estimate of the content of the *cis*-isomer in mixtures is not always objective, since its amount depends strongly on the action of light on the silver salt, the reaction time, the excess of the alkylating agent, etc.[77] It has been shown recently that the reaction of dicyclohexylcarbodiimide with ethyl nitroamine leads to the exclusive formation of the *trans*-isomer of the *O*,*N*-diethylnitroamine. This method has been proposed as a promising procedure for the synthesis of the pure product[166].

Table 2. The content of the *cis*-isomer (LXIII) in the reaction of silver salts of alkylnitroamines with alkyl iodides (according to the data of Lamberton and Newton[165]).

$R/RNHNO_2$	R^1/R^1I	Content of *cis*-isomer, %	$R/RNHNO_2$	R^1/R^1I	Content of *cis*-isomer, %
Methyl	Ethyl	15—20	Isopropyl	Methyl	20
Methyl	Isopropyl	15—20	Propyl	Methyl	10
Ethyl	Methyl	30	t-Butyl	Methyl	—

The silver salt of methylnitroamine reacts with methyl iodide, giving rise to a mixture of the *cis*- and *trans*-isomers of *O*,*N*-dimethylnitroamine[169], although it had been postulated earlier that the pure *trans*-isomer was produced in an analogous reaction[165].

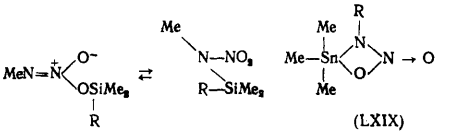
The intramolecular alkylation of nitroamine anions has also been investigated. When alkylnitrosulphonamides (LXV) are acted upon by alkali, the anion (LXVI) is displaced and, as a result of intramolecular alkylation, can give rise to both the *N*-alkyl derivative (LXVII) and the *O*,*N*-alkyl derivative (LXVIII):



(LXV) (LXVI) (LXVII) (LXVIII)

R, R^1=H or Me

In reality the second possibility is realised and it has been shown in relation to the isomeric compounds (LXV, R = H, R^1 = Me) and (LXV, R = Me, R^1 = H) that nitroaziridine (LXVII) is neither the final nor the intermediate product of this reaction[180]. Silylation of methylnitroamine or its silver salt leads to an equilibrium mixture of the *O*- and *N*-derivatives, the content of the *O*-isomer increasing with increasing temperature and in the sequence R = H < Me < iso-Pr ≪ t-Bu.[181,182]



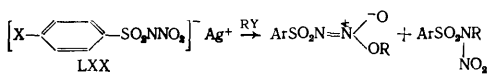
(LXIX)

In contrast to the unstable silyl derivatives, trialkylstannylation of nitroamines or their silver salt leads to stable *N*-derivatives (LXIX).[183] It has been suggested that tin is

coordinated to the oxygen atom of the nitro-group. This conclusion concerning the preferential *N*-stannylation conflicts with the results of the silylation of nitroamine salts[181,182]. Nevertheless, the possibility of *O*-stannylation has been rejected[183] on the basis of the analysis of the infrared spectra of the products.

We have already mentioned the alkylation of nitroamines by diazomethane. Degner and Pechmann[184] showed for the first time that the interaction of methylnitroamine with diazomethane leads to the exclusive formation of the *N*-methylation product, although it was found later that the mixture of products nevertheless contains also the *O*-methylation product[179]. The reaction with isopropylnitroamine gave a mixture of *N*- and *O*-methylation products in proportions of 7 : 3,[162] while other workers[185] ethylated triethylenetetranitroamine with diazoethane and obtained only the *N*-ethyl derivative. Despite certain discrepancies, one may conclude that the *N*-alkylation reaction predominates, but this requires certain comments. If it is assumed that the alkylating species is R^+ or the extremely unstable ion MeN_2^+, then preferential *O*-alkylation is to be expected. A mechanism involving the intermediate formation of a complex of MeN_2^+ with the nitroamine anion has been proposed[146]; this complex subsequently decomposes with evolution of nitrogen. The mechanism is apparently based on the familiar hypothesis by Smith[186] that the combination of diazomethane with a proton and the subsequent attack on methyldiazonium involve the same centre, since, in consequence of its rapid decomposition, the MeN_2^+ cation does not leave the sphere of action of the atom in the substrate. The prospect of testing for prototropic equilibria with the aid of diazomethane is attractive, but unfortunately this possibility is not confirmed in practice[186]. Phenylnitroamine, which has more pronounced acid properties than methylnitroamine, gives rise to the *O*-methylation product on interaction with diazomethane.

The anions of alkylnitroamides (LXX) also exhibit a dual reactivity. Like the anions of primary nitroamines, they can be attacked at the N or the O atom. The reactions of the silver salts of the nitroamides of arenesulphonic acids with alkyl halides give rise to *O*- and *N*-alkylation products[187,188]:



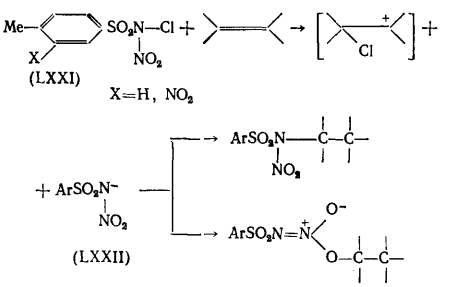
LXX

It has been shown[187] that the ratio of the *O*- and *N*-alkylation products for compound (LXX, X = Me, R = benzyl) is 3.5. Luk'yanov et al.[188] studied in detail the influence of various factors on the ratio of the products of the *O* and *N*-alkylation of compound (LXX). They found that the decrease of solvent polarity in the sequence DMF > acetonitrile > diglyme > ethyl acetate > ether > hexane and the increase of the effective volume of group R in the alkylating agent from the methyl group to the isopropyl group entail an increase of the fraction of the *O*-alkylated product. The latter also increases on passing from alkyl iodides to alkyl bromides.

The salts (LXX, X = Me) form trimethylsilyl and diethylboryl derivatives exclusively via the oxygen atom[189]. The trimethylsilyl group is rigidly bound to the oxygen atom and reversible migration to the nitrogen atom is not observed. Both trimethylsilyl and diethylboryl derivatives are readily hydrolysed and, on raising the temperature slightly, decompose with evolution of N_2O.[189]

Primary *N*-nitroamides have stronger acid properties than nitroamines, but, like the latter, they are alkylated by compounds with small rings (oxirans, aziridines) exclusively at the nitrogen atom[190].

N-Chloro-*N*-nitroamides of arenesulphonic acids (LXXI) add to olefins with formation of *O*- and *N*-alkulation products whose ratio (N/O) increases in the range from 2.0 (cyclohexene, X = H) to 1.4 (styrene, X = H).[191]



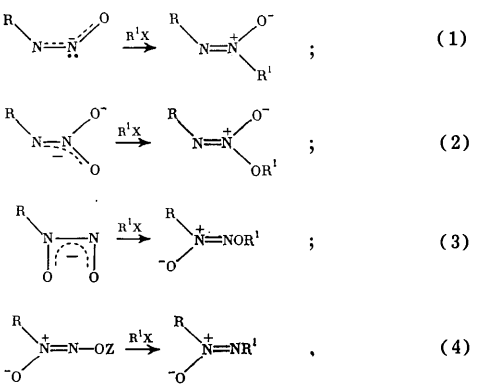
(LXXI)

(LXXII)

Luk'yanov et al.[191] proposed a mechanism involving the primary attack by the positively charged halogen on the double bond with subsequent alkylation of the anion (LXXII). If the intermediate existence of the cation is postulated, the *O*-alkylation product should be formed. In reality mainly the nitrogen atom is attacked. A situation analogous to that in the methylation of the *N*-nitroamines by diazomethane arises[146]. The formation of a cationic intermediate may be postulated, but alkylation proceeds contrary to the Kornblum rule. Additional studies will help to resolve these problems.

VI. CONCLUSION

Generalising the data described, one may note that the alkylation of ambident anions with nitrogen–nitrogen bonds can be divided into reactions of two types. Alkanediazotates of primary *N*-nitroamines give rise to azoxy-compounds with the proximal fixation of the *N*-oxide oxygen atom in relation to the incoming group; *N*-nitrosohydroxylamines and 1-alkoxy-(fluoro, toluenesulphonato)-diazene 2-oxides give rise to isomers with the distal fixation of the oxygen.



(1)

(2)

(3)

(4)

All these reactions represent new methods for the synthesis of azoxy-compounds. For example, reaction (1) was described for the first time in 1969[11] and reaction (4) was

described in 1964[74]§. Reactions involving the alklation of primary nitroamines or *N*-nitrosohydroxylamines were elucidated only after studies by Lamberton (1955–1961), Woodward, Freeman, and Stevens (1963–1969). Whereas the competitive alkylation of the O and C atoms has been investigated in comparative detail in relation to the enolate anions or nitroso-compounds[148,173,193,194] (at least in terms of the volume of factual data obtained), the analogous processes for the O–N or O–O atoms have been studied much less. The number of experimental studies whose main aim was preparative synthesis of the final products in the field indicated has been small; there are also difficulties in structural aspects (see, for example, Section III). Many characteristics of reactions (1)–(4) are therefore still obscure. There are no systematic data concerning the influence of the solvent, the metal cation, the salt concentration in solution, etc. on the alkylation processes. The significant role attributed to the study of the influence of these factors on the activity of ambident anions in recent years makes it probable that studies on these lines will be published in the immediate future.

REFERENCES

1. K.H.Schundehutte, "Houben-Weyl Methoden der Organischen Chemie", Georg Thieme Verlag, Stuttgart, 1965, Vol.10/3, p.745.
2. E.Enders, "Houben-Weyl Methoden der Organischen Chemie", Georg Thieme Verlag, Stuttgart, 1965, Vol.10/3, p.467.
3. E.Muller, "Houben-Weyl Methoden der Organischen Chemie", Georg Thieme Verlag, Stuttgart, 1967, Vol.10/2, p.757.
4. E.Buncel, in "Mechanisms of Molecular Migrations" (Edited by B.S.Thyagarajan), Intersci.Publ., New York, 1968, Vol.1, p.61.
5. S.R.Sandler and W.Karo, "Organic Functional Group Preparations" Acad.Press, New York, 1971, Vol.2, p.343.
6. S.Patai (Editor), "The Chemistry of the Hydrazo, Azo, and Azoxy Groups", Willey, New York, 1975, Parts 1 and 2.
7. E,V.Brown and H.G.Padeken, in "Method.Chim.", (Edited by F.Zymalkowski), Acad.Press, New York, 1975, Vol.6, p.127; Chem.Abs., 85, 20168 (1976).
8. E.Buncel, Accounts Chem.Res., 8, 132 (1975).
9. M.Yamomoto, Senryo To Yakuhin, 21, 30, 58 (1976); Chem.Abs. 85, 178948 (1976).
10. V.N.Yandovskii, B.V.Gidaspov, and I.V.Tselinskii, Uspekhi Khim. (in the Press).
11. R.A.Moss and M.J.Landon, Tetrahedron Letters, 3897 (1969).
12. R.A.Moss, M.J.Landon, K.M.Luchter, and A.Mamantov, J.Amer.Chem.Soc., 94, 4392 (1972).
13. R.A.Moss and G.M.Love, J.Amer.Chem.Soc., 95, 3070 (1973).
14. R.A.Moss and G.M.Love, Tetrahedron Letters, 4701 (1973).
15. R.A.Moss and T.B.K.Lee, J.Chem.Soc., Perkin Trans.I, 2778 (1973).
16. R.A.Moss, Accounts Chem.Res., 7, 421 (1974).
17. W.J.McGahren, M.P.Kunstmann, J.Org.Chem., 37, 902 (1972).
18. E.H.White and D.J.Woodcock, in "The Chemistry of the Amino Group" (Edited by S.Patai), Intersci. Publ., London, 1968, p.440.
19. R.A.Moss, Chem.Eng.News, 49, No.48, 28 (1971).
20. E.Muller, H.Haiss, and W.Rundel, Chem.Ber., 93, 1541 (1960).
21. E.Muller, W.Hoppe, H.Hagenmaier, H.Haiss, R.Huber, W.Rundel, and H.Suhr, Chem.Ber., 96, 1712 (1963).
22. H.Suhr, Chem.Ber., 96, 1720 (1963).
23. T.K.Tandy Jr. and W.M.Jones, J.Org.Chem., 30, 4257 (1965).
24. R,A.Moss and F.C.Shulman, Tetrahedron, 24, 2881 (1968).
25. R.A.Moss and S.M.Lane, J.Amer.Chem.Soc., 89, 5655 (1967).
26. H.Hart and J.L.Brewbaker, J.Amer.Chem.Soc., 91, 706 (1969).
27. E.H.White, T.J.Ryan and K.W.Field, J.Amer.Chem. Soc., 94, 1360 (1972).
28. C.D.Gutsche and I.Y.C.Tao, J.Org.Chem., 32, 1778 (1967).
29. H.Hart and J.L.Brewbaker, J.Amer.Chem.Soc., 91, 716 (1969).
30. W.Kirmse, A.Engelmann, and J.Heese, Chem.Ber., 106, 3073 (1973).
31. R.A.Moss, J.Org.Chem., 31, 1082 (1966).
32. R.A.Moss and K.M.Luchter, J.Org.Chem., 37, 1155 (1972).
33. H.Zollinger, "Azo and Diazo Chemistry, Aliphatic and Aromatic Compounds", Intersci., New York, 1961, pp.47, 150.
34. B.A.Porai-Koshits, "Azokrasiteli" (Azo-Dyes), Izd. Khimiya, Leningrad, 1972, p.29.
35. R.Kübler and W.Lüttke, Ber.Bunsenges.Phys.Chem., 67, 2 (1963).
36. J.S.Littler, Trans.Faraday Soc., 59, 2296 (1963).
37. E.S.Lewis and M.P.Hanson, J.Amer.Chem.Soc., 89, 6268 (1967).
38. B.A.Porai-Koshits, Zhur.Org.Khim., 2, 1125 (1966).
39. A.P.Voropaeva, L.M.Gladysheva, V.A.Ketlinskii, I.L.Bagal, Ya.E.Bryuske, and A.V.El'tsov, Zhur. Org.Khim., 12, 401 (1976).
40. Ya.E.Bryuske and A.P.Voropaeva, Trudy Tambov. Inst.Khim.Mashinostr., No.4, 124 (1970); Chem.Abs. 78, 42449 (1973).
41. P.A.S.Smith, "Open-Chain Nitrogen Compounds", W.A.Benjamin, New York, 1966, Vol.2, p.44.
42. J.Hamer and A.Macaluso, Chem.Rev., 64, 473 (1964).
43. E.Buehler, J.Org.Chem., 32, 261 (1967).
44. E.L.Eliel and S.M.C.Knoeber, J.Amer.Chem.Soc., 88, 5347 (1966).
45. E.Buehler and G.B.Brown, J.Org.Chem., 32, 265 (1967).
46. R.J.MacConaill, F.L.Scott, and A.F.Hegarty, Tetrahedron Letters, 1217 (1972).
47. L.B.Volodarskii and A.Ya.Tikhonov, Izv.Akad. Nauk SSSR, Ser.Khim., 2341 (1969).

§The exchange reaction (4) was investigated for the first time by Wright and coworkers[70] in relation to 1-alkoxy-2-phenyldiazene 2-oxides, but, since they attributed an incorrect formula to the initial reactant, the experimental results were also incorrectly interpreted. Furthermore, they introduced benzylmagnesium halide into the substitution reaction and obtained a compound whose structure, incidentally, served as a touchstone throughout half a century, but was not [properly] elucidated until the study by Woodward[192]. In view of the enormous factual data contained in the publications by Wright and coworkers, Wright can be regarded as the pioneer in this field.

48. E.Bellasio, F.Parravicini, T.LaNoce, and E.Testa, Ann.Chim.(Italy), **58**, 407 (1968).
49. E.Bellasio, F.Parravicini, A.Vigevani, and E.Testa, Gazzetta, **98**, 1014 (1968); Chem.Abs., **71**, 21952 (1969).
50. L.B.Volodarskii and A.Ya.Tikhonov, Zhur.Org. Khim., **6**, 307 (1970).
51. G.Kh.Kamai, A.D.Nikolaeva, V.S.Perekhod'ko, and T.V.Zykova, Zhur.Org.Khim., 6, 394 (1970).
52. R.A.Moss and C.E.Powell, J.Amer.Chem.Soc., **98**, 283 (1976).
53. W.Kirmse, A.Engelmann, and J.Heese, J.Amer.Chem. Soc., **95**, 625 (1973).
54. W.Kirmse and A.Engelmann, Chem.Ber., **106**, 3086 (1973).
55. D.J.Northington and W.M.Jones, Tetrahedron Letters, 317 (1971).
56. A.Padwa, N.C.Das, and D.Eastman, J.Amer.Chem. Soc., **91**, 5178 (1969).
57. A.Padwa, P.Cimiluca and D.Eastman, J.Org.Chem., **37**, 805 (1972).
58. D.J.Northington and W.M.Jones, J.Org.Chem., **37**, 693 (1972).
59. P.A.S.Smith, "Open-Chain Nitrogen Compounds", W.A.Benjamin, New York, 1966, Vol.2, p.479.
60. R.Behrend and E.König, Annalen, **263**, 217 (1891).
61. R.Lindner, Annalen, **275**, 133 (1893).
62. E.Bamberger and T.Ekecrantz, Ber., 29, 2412 (1896).
63. E.Bamberger, Ber., **31**, 574 (1898).
64. O.Piloty and O.Ruff, Ber., **30**, 1656 (1897).
65. W.Traube, Annalen, **300**, 81 (1898).
66. W.Traube and H.Stelaff, Annalen, **300**, 129 (1898).
67. A.Hantzsch, Ber., **31**, 177 (1898).
68. H.Wieland and F.N.Kerr, Chem.Ber., **63B**, 570 (1930); Chem.Abs., **24**, 3211 (1930).
69. J.Cason and F.S.Prout, J.Amer.Chem.Soc., 71, 1218 (1949).
70. M.V.George, R.W.Kierstead, and G.F.Wright, Canad. J.Chem., **37**, 679 (1959).
71. M.J.Danzig and S.R.Riccitiella, J.Org.Chem., **27**, 686 (1962).
72. M.J.Danzig, R.F.Martel, and S.R.Riccitiello, J. Org.Chem., **26**, 3327 (1961).
73. J.P.Freeman, J.Org.Chem., **28**, 2508 (1963).
74. T.E.Stevens, J.Org.Chem., **29**, 311 (1964).
75. C.E.Wintner, Ph.D.Thesis; Diss.Abs., **24**, 1841 (1963).
76. R.B.Woodward and C.Wintner, Tetrahedron Letters, 2689 (1969).
77. A.H.Lamberton and H.M.Yusuf, J.Chem.Soc.C, 397 (1969).
78. H.Metzger and H.Meier, in "Houben-Weyl Methoden der Organischen Chemie", Georg Thieme Verlag, Stuttgart, 1971, Vol.10/1, p.891.
79. E.Bamberger and O.Baudisch, Ber., **42**, 3582 (1909).
80. A.Hantzsch and A.Sauer, Annalen, **229**, 67 (1897).
81. W.Traube, Ber., **27**, 3291 (1894).
82. W.Traube, Ber., **28**, 1785 (1895).
83. W.Traube, Ber., **28**, 2297 (1895).
84. M.Gomberg, Annalen, **300**, 59 (1898).
85. A.Angeli, Ber., **29**, 1884 (1896).
86. A.Angeli and F.Angelico, Atti accad.Lincei, **9**, II, 44 (1900).
87. A.Angeli, Atti accad.Lincei, **22**, I, 201, 282 (1913).
88. J.Thiele, Annalen, **376**, 239 (1910).
89. C.S.Marvel, "Organic Syntheses" (Translated into Russian), Inostr.Lit., Moscow, 1949, Collective Vol.1, p.238 (English edition, p.177).
90. E.G.Kovach, Chem.Ber., **91**, 844 (1958).
91. G.Charlot, "Les Méthodes de la Chimie Analytique. Analyse Quantitative Minérale" (Translated into Russian), Izd.Khimiya, Moscow, 1969, pp.95, 131.
92. T.Axenrod, M.J.Wieder, and G.W.A.Milne, Tetrahedron Letters, 401 (1969).
93. E.Bamberger and O.Baudisch, Ber., 42, 3568 (1909).
94. M.E.Jung, P.A.Blair, and J.A.Lowe, Tetrahedron Letters, 1439 (1976).
95. K.H.Shapiro, M.F.Lipton, K.Y.Kolonko, R.L.Buswell, and L.A.Capuano, Tetrahedron Letters, 1811 (1975).
96. N.D.Epiotis, J.Amer.Chem.Soc., **95**, 3087 (1973).
97. A.B.Boese, Jr., L.W.Jones, and R.T.Major, J.Amer.Chem.Soc., **53**, 3530 (1931).
98. G.Kortum, and B.Finckh, Z.phys.Chem., **48B**, 32 (1941).
99. M.Carmack and J.J.Leavitt, J.Amer.Chem.Soc., 71, 1221 (1949).
100. E.H.White, M.J.Todd, M.Ribi, T.J.Ryan, A.A.F. Sieber, R.E.Dickerson, and J.Bordner, Tetrahedron Letters, 4467 (1970).
101. E.H.White and D.W.Grishey, J.Amer.Chem.Soc., **83**, 1191 (1961).
102. E.H.White and C.A.Aufdermarsh, J.Amer.Chem.Soc., **83**, 1174 (1961).
103. E.H.White and C.A.Aufdermarsh, J.Amer.Chem.Soc., **83**, 1179 (1961).
104. E.H.White, R.H.McGirk, C.A.Aufdermarsh, H.P. Tiwari, and M.J.Todd, J.Amer.Chem.Soc., **95**, 8107 (1973).
105. J.P.Freeman and L.D.Lillwitz, J.Org.Chem., **35**, 3107 (1970).
106. L.B.Volodarskii and N.Yu.Tormysheva, Izd.Sibir. Otd.Akad.Nauk SSSR, Ser.Khim.Nauk, No.9, Issue 4, 136 (1976).
107. M.A.Ribi and E.H.White, Helv.Chem.Acta, **58**, 120 (1975).
108. J.P.Freeman, see footnote 21 in Ref.105.
109. K.V.Vatsuro and G.L.Mishchenko, "Imennye Reaktsii v Organicheskoi Khimii" (Name Reactions in Organic Chemistry), Izd.Khimiya, Moscow, 1976, p.324.
110. L.A.Neiman, V.S.Smolyakov, Y.S.Nekrasov, and M.M.Shemyakin, Tetrahedron, **26**, 4963 (1970).
111. M.Gotz and K.Grozinger, Tetrahedron, **27**, 4449 (1971).
112. T.N.Srivastava, J.Inorg.Nuclear Chem., 17, 1546 (1975).
113. M.N.Hughes, Quart.Rev., **22**, 1 (1968).
114. P.A.S.Smith and G.E.Hein, J.Amer.Chem.Soc., 82, 5731 (1960).
115. A.J.Hubert and G.Anthoine, Bull.Soc.chim.belges, **78**, 553 (1969).
116. R.E.Rondeau, R.N.Steppel, H.M.Rosenberg, and L.E.Knaak, J.Heterocyclic Chem., 10, 495 (1973).
117. M.P.Serve, W.A.Feld, P.G.Seybold, and R.N.Steppel, J.Heterocyclic Chem., **12**, 811 (1975).
118. H.P.Braun, K.-P.Zeller, and H.Meier, Chem.Z., **97**, 567 (1973).
119. H.P.Braun, K.-P.Zeller, and H.Meier, Annalen, 1257 (1975).
120. H.Meier, G.Trickes, and H.P.Braun, Tetrahedron Letters, 1257 (1976).
121. T.E.Stevens, J.Org.Chem., **32**, 1641 (1967).

122. T.E.Stevens and J.P.Freeman, J.Org.Chem., **29**, 2279 (1964).
123. W.V.Farrar and J.Masson Gulland, J.Chem.Soc., 368 (1944).
124. T.E.Stevens, quoted after Ref.74.
125. O.P.Shitov, S.L.Ioffe, V.A.Tartakovskii, and S.S.Novikov, Izv.Akad.Nauk SSSR, Ser.Khim., 490 (1972).
126. I.A.Leenson, G.B.Sergeev, O.P.Shitov, S.L.Ioffe, and V.A.Tartakovskii, Izv.Akad.Nauk SSSR, Ser. Khim., 1149 (1973).
127. Z.V.Todres and S.P.Avagyan, Zhur.Vses.Khim. Obshch.im Mendeleeva, **18**, 478 (1973).
128. Z.V.Todres, S.P.Avagyan, and D.N.Kursanov, Zhur.Org.Khim., **11**, 2457 (1975).
129. Z.V.Todres, S.P.Avagyan, and D.N.Kursanov, J. Organometal.Chem., **97**, 139 (1975).
130. R.J.Crawford and K.Takagi, J.Amer.Chem.Soc., **94**, 7406 (1972).
131. H.Lui and J.Warkentin, Canad.J.Chem., **51**, 1148 (1973).
132. V.Malatesta and K.U.Ingold, Tetrahedron Letters, 3311 (1973).
133. W.M.Cumming and G.S.Ferrier, J.Roy.Tech.Coll. (Glasgow), **2**, No.1, 49 (1929); Chem.Abs., 23, 3908 (1929).
134. D.N.Kursanov, A.S.Kursanova, and A.N.Blokhina, Zhur.Obshch.Khim., **8**, 1786 (1938).
135. K.G.Taylor, S.R.Isaac, and M.S.Clark, J.Org. Chem., **41**, 1135 (1976).
136. G.T.Knight and B.Saville, J.Chem.Soc., Perkin Trans., II, 1550 (1973).
137. W.J.Le Nobel and W.S.Chang, Synthesis, 106 (1973); Chem.Abs., **78**, 135785 (1973).
138. F.R.Sullivan, E.Luck, and P.Kovacic, J.Org. Chem., **39**, 2967 (1974).
139. C.G.Overberger, J.P.Anselme, and J.G.Lombardino, "Organic Compounds with Nitrogen–Nitrogen Bonds" (Translated into Russian), Izd.Khimiya, Moscow, 1970, p.107.
140. B.V.Ioffe and L.A.Kartsova, Zhur.Org.Khim., 9, 1209 (1973).
141. B.V.Ioffe and L.A.Kartsova, Zhur.Org.Khim., **10**, 989 (1974).
142. Weigand-Hilgetag, "Experimental Techniques in Organic Chemistry" (Translated into Russian), Izd. Khimiya, 1968, p.543.
143. Y.Tamura, J.Minamikawa, Y.Kita, J.H.Kim, and M.Ikeda, Tetrahedron, **29**, 1063 (1973).
144. A.H.Lamberton, Quart.Rev., **5**, 75 (1951).
145. H.Söll, in "Houben-Weyl Methoden der Organischen Chemie", Georg Thieme Verlag, Stuttgart, 1958, Vol.11/2, p.99.
146. A.L.Fridman, V.P.Ivshin, and S.S.Novikov, Uspekhi Khim., **38**, 1448 (1969) [Russ.Chem.Rev., No.8 (1969)].
147. G.F.Wright, "The Chemistry of Nitro- and Nitroso-groups", Vol.1 (Edited by H.Feuer), (Translated into Russian), Izd.Mir, Moscow, 1972, p.467.
148. S.S.Novikov, G.A.Shveikhgeimer, V.V.Sevost'-yanova, and V.A.Shlyapochnikov, "Khimiya Alifati-cheskikh i Alitsiklicheskikh Nitrosoedinenii" (The Chemistry of Aliphatic and Alicyclic Nitro-com-pounds), Izd.Khimiya, Moscow, 1974, p.282.
149. P.A.S.Smith, see Ref.41, Chapter 15.
150. J.T.Millar and H.D.Springall, "Sidgwick's Organic Chemistry of Nitrogen", Clarendon Press, Oxford, 1966, p.592.
151. W.Traube, Ber., **27**, 1507 (1894).
152. S.S.Novikov, G.A.Shveikhgeimer, V.V.Sevost'-yanova, and V.A.Shlyapochnikov, "Khimiya Alifati-cheskikh i Alitsiklicheskikh Nitrosodinenii" (The Chemistry of Aliphatic and Alicyclic Nitro-compounds), Izd.Khimiya, Moscow, 1974, pp.350, 360.
153. J.C.A.S.Thomas, Rec.Trav.chim., **9**, 69 (1890).
154. H.Van Erp, Rec.Trav.chim., **14**, 1 (1895).
155. A.P.N.Franchimont, Rec.Trav.chim., **14**, 235 (1895).
156. H.Umbgrove and A.P.N.Franchimont, Rec.Trav. chim., **15**, 195 (1896).
157. H.Umbgrove and A.P.N.Franchimont, Rec.Trav. chim., **16**, 385 (1897).
158. H.Umbgrove and A.P.N.Franchimont, Rec.Trav. chim., 16, 401 (1897).
159. H.Umbgrove and A.P.N.Franchimont, Rec.Trav. chim., 17, 270 (1898).
160. W.J.Chite, G.E.Dunn, J.C.MacKenzie, G.S.Myers, G.N.R.Smart, J.W.Suggitt, and G.F.Wright, Canad. J.Res., **B26**, 114 (1948).
161. G.N.R.Smart and G.F.Wright, Canad.J.Res., B26, 284 (1948).
162. P.Bruck and A.H.Lamberton, J.Chem.Soc., 3997 (1955).
163. B.Unterhald and D.Thamer, Synthesis, 302, 676 (1973).
164. P.Bruck and A.H.Lamberton, Synthesis, 4198 (1957).
165. A.H.Lamberton and G.Newton, Synthesis, 1797 (1961).
166. A.H.Lamberton, R.D.Porter, and H.M.Yusuf, J. Chem.Soc., Perkin Trans.I, 956 (1974).
167. B.Unterhalt and D.Thamer, Tetrahedron Letters 4905 (1971).
168. B.Unterhald and D.Thamer, Arch.Pharm., **307**, 466 (1974).
169. V.G.Avagyan, V.A.Shlyapochnikov, O.A.Luk'yanov, and V.A.Tartakovskii, Izv.Akad.Nauk SSSR, Ser. Khim., 590, 1972.
170. V.P.Tverdokhlobov, I.V.Tselinskii, and B.V.Gida-spov, Zhur.Org.Khim., **12**, 359 (1976).
171. V.P.Tverdokhlebov, I.V.Tselinskii, B.V.Gidaspov, and L.A.Fedorova, Zhur.Org.Khim., 12, 362 (1976).
172. V.P.Tverdokhlebov, I.V.Tselinskii, B.V.Gidaspov, and G.Yu.Chikisheva, Zhur.Org.Khim., 12, 2335 (1976).
173. R.Gompper, Angew.Chem., **76**, 412 (1964).
174. H.Becker, "Einfuehrung in die Elektronentheorie Organisch-Chemischer Reaktionen" (Translated into Russian), Izd.Mir, Moscow, 1965, p.81.
175. J.R.Johnson and A.T.Blomquist, US P., 2683165 (1954); Chem.Abs., 49, 7590 (1955).
176. B.Unterhalt and D.Thamer, Arch.Pharm., **308**, 954 (1975); Chem.Abs., **84**, 121061 (1976).
177. S.N.Shvedova, V.G.Avagyan, N.O.Cherskaya, T.A.Arestova, V.A.Shlyapochnikova, and S.S. Novikov, Izv.Akad.Nauk SSSR, Ser.Khim., 1298 (1973).
178. Yu.A.Zhdanov and V.I.Minkin, "Korrelyatsionnyi Analiz v Organicheskoi Khimii" (Correlation Analysis in Organic Chemistry), Izd.Rostov.Univ., 1966, p.328.
179. B.Unterhalt and D.Thamer, Arch.Pharm., **307**, 731 (1974).
180. O.A.Luk'yanov, A.A.Onishchenko, V.P.Gorelik, and V.A.Tartakovskii, Izv.Akad.Nauk SSSR, Ser.Khim., 1294 (1973).

181. M.Ya.Myagi, T.T.Lipmaa, S.L.Ioffe, V.A.Tartakovskii, A.S.Shashkov, B.N.Khasapov, and L.M. Nakarenkova, Izv.Akad.Nauk SSSR, Ser.Khim., 1431 (1973).
182. S.L.Ioffe, L.M.Makarenkova, and V.A.Tartakovskii, Izv.Akad.Nauk SSSR, Ser.Khim., 463 (1974).
183. L.J.Winters and D.T.Hill, Inorg.Chem., **4**, 1433 (1965).
184. O.Degner and H.V.Pechmann, Ber., **30**, 647 (1897).
185. G.N.Smart and G.F.Wright, J.Amer.Chem.Soc., **70**, 3142 (1948).
186. P.A.S.Smith, see Ref.41, p.231.
187. M.I.Gillibrand and A.H.Lamberton, J.Chem.Soc., 1883 (1949).
188. O.A.Luk'yanov, N.I.Shlykova, and V.A.Tartakovskii, Izv.Akad.Nauk SSSR, Ser.Khim., 659 (1976).
189. S.L.Ioffe, L.M.Leont'eva, L.M.Makarenkova, A.L.Blyumenfel'd, V.F.Pyaterikov, and V.A.Tartakovskii, Izv.Akad.Nauk SSSR, Ser.Khim., 1146 (1975).
190. A.A.Onishchenko, O.S.Reshetova, V.P.Gorelik O.A.Luk'yanov, and V.A.Tartakovskii, Izv.Akad. Nauk SSSR, Ser.Khim., 1166 (1976).
191. O.A.Luk'yanov, I.K.Kozlova, and V.A.Tartakovskii, Izv.Akad.Nauk SSSR, Ser.Khim., 421 (1976).
192. R.B.Woodward and C.Wintner, Tetrahedron Letters, 2693 (1969).
193. V.I.Erashko, S.A.Shevelev, and A.A.Fainzil'berg Uspekhi Khim., **35**, 1740 (1966) [Russ.Chem.Rev., No.10 (1966)].
194. A.T.Nielsen, in "The Chemistry of Nitro- and Nitroso-Groups" (Edited by H.Feuer), (Translated into Russian), Izd.Mir, Moscow, 1972, p.314.

Zhdanov Leningrad State University

Lensovet Leningrad Technological Institute

Translated from *Uspekhi Khimii*, **49**, 470 - 493 (1980) U.D.C. 547.219

Cathodic Coupling Reactions

A.V.Bukhtiarov and A.P.Tomilov

Cathodic coupling reactions, occurring in the electrolysis of mixtures of two activated olefins and of a carbonyl compound with olefins and alkyl halides, as well as reactions occurring in the electrolysis of onium salts in the presence of olefins and chemical reactions catalysed by electrochemically generated anions are examined.
The bibliography includes 55 references.

CONTENTS

I. Introduction 249
II. Coupling of activated olefins 249
III. Reactions of carbonyl compounds 251
IV. Cathodic reduction of onium salts 255
V. Other reactions involving electrochemically generated anions 256

I. INTRODUCTION

Numerous studies dealing with the cathodic reduction of an organic compound to a carbanion or a radical in the presence of compounds capable of interacting with them have been published in recent years. It has been established that there is a possibility of the formation of "mixed hydrodimers", which can be the main reaction products under certain conditions. The number of examples of cathodic coupling reactions has become so great that they can be regarded as constituting a kind of electrochemical method of synthesis. It is quite timely to survey the accumulated data.

The study of the mechanism of the cathodic reduction of organic substances has shown that in many instances electron transfer to a molecule gives rise to highly reactive anions or radicals, which react exceptionally readily with certain organic compounds. The use of this phenomenon made it possible to achieve recently an enormous number of syntheses, some of which have no chemical analogs and are therefore of special interest for organic chemists.

The cathodic coupling reaction was achieved for the first time in 1955 by Wawzonek et al.[1], who obtained diphenylsuccinic acid by the electrochemical reduction of styrene dissolved in dimethylformamide in the presence of carbon dioxide. The authors explained the formation of diphenylsuccinic acid by the fact that the addition of two electrons to stilbene results in the formation of a dianion:

$$C_6H_5CH{=}CHC_6H_5 \xrightarrow{2e} C_6H_5\bar{C}H{-}\bar{C}HC_6H_5$$

The latter is stabilised by the addition of two molecules of carbon dioxide and two protons derived from the solvent:

$$C_6H_5\bar{C}H{-}\bar{C}HC_6H_5 \xrightarrow{2CO_2;\ 2H^+} C_6H_5CH(COOH)CHC_6H_5(COOH)$$

However, this study[1] did not arouse much response. At the beginning of the 1960s vigorous investigation of the electrochemical reduction of activated olefins, particularly acrylonitrile, began. This research demonstrated fairly convincingly that the addition of two electrons and one proton results in the formation under these conditions† of a relatively stable anion, which combines in a readily protonating medium with a second proton to form a product without a double bond. In a medium with a limited proton-donating activity, this anion behaves as a powerful nucleophile and can enter into various reactions. In the simplest case the nucleophile adds to the molecule of the initial substance and the addition product is stabilised as a result of protonation with formation of a hydrodimer. A number of reviews have been devoted to the cathodic hydrodimerisation reaction[2,3]; examination of this reaction is outside the scope of the present article, which deals only with the reactions of organic anions with other substances capable of nucleophilic addition.

† Although this view is not in fact generally accepted, it has been confirmed in many investigations.

II. COUPLING OF ACTIVATED OLEFINS

The cathodic hydrodimerisation of activated olefins achieved at the beginning of the 1960s made it possible to undertake the study of the coupling reaction of two different olefins in accordance with the equation

$$X{-}C{=}C{+}C{=}C{-}Y \xrightarrow{2e,\ 2H^+} X{-}\underset{H}{C}{-}\underset{}{C}{-}\underset{}{C}{-}\underset{H}{C}{-}Y \quad ;$$

X,Y=CN, COOR, $CONH_2$ etc.

The possibility, in principle, of achieving this reaction was first demonstrated in a study[4] where cathodic coupling reactions of acrylonitrile with benzylideneacetone and mesityl oxide, of diethyl fumarate with methyl vinyl ketone, and of methyl vinyl sulphone with cinnamic acid diethylamide were carried out; a high yield of products was noted. In the above study it was already suggested that only one reactant is reduced at the cathode with formation of organic anions, which interact with the second component.

The real possibility that the cathodic coupling reaction proceeds via this mechanism was demonstrated in relation to the cathodic coupling of acrylonitrile and methyl acrylate[5]. Methyl acrylate is the more readily reducible olefin. When present jointly, the two substances give rise to separate well defined polarographic waves. If methyl acrylate is added to a solution with a constant acrylonitrile concentration, then the acrylonitrile wave begins to decrease with increase of the methyl acrylate concentration. This phenomenon can be explained by the fact that the methyl acrylate anions generated in the first electrochemical stage interact with acrylonitrile, which reduces the concentration of the latter in the layer near the electrode. Thus the cathodic coupling of acrylonitrile with methyl acrylate can be represented by the

following scheme:

$$H_2C{=}CHCOOCH_3 \xrightarrow{2e,\ H^+} \bar{C}H_2CH_2COOCH_3 \ ,$$

$$\bar{C}H_2CH_2COOCH_3 \xrightarrow{H_2C=CHCN} CH_3OOCCH_2CH_2CH_2\bar{C}HCN \ ,$$

$$CH_3OOCCH_2CH_2CH_2\bar{C}HCN \xrightarrow{H^+} CH_3OOCCH_2CH_2CH_2CH_2CN \ .$$

Evidently it follows from this mechanism that the yield of the cathodic coupling reaction product depends to a large extent on the ratio of the reduction potentials of the coupled components and on the potential of the cathode at which the electrolysis is carried out.

A study of the effect of the cathodic potential ϕ on the yield of the cross-coupling product W was undertaken[6]. The following relation was obtained for the diethyl maleate–ethyl acrylate system [here (I) = diethyl maleate dimer and (II) = ethyl acrylate]:

φ, V(sat. cal. e-de)	1.314	1.425	1.500
W, mmole	1.18	5.95	12.10
Yield of (I), mmole	3.64	8.50	6.00
Yield of (II), mmole	-	-	8.66

Evidently at cathodic potentials of 1.314 and 1.425 V only diethyl maleate is reduced and the cross-coupling product is formed exclusively as a result of the interaction of the diethyl maleate anions with ethyl acrylate molecules. A further increase of the cathodic potential favours the formation of the cross-coupling product, but, apart from the ethyl maleate dimer, the electrolysis products indicate the formation of the dimer of the component which is harder to reduce, namely ethyl acrylate. Analogous results were obtained in the electrochemical reduction of the diethyl maleate–acrylonitrile system. On the basis of these results, it was concluded[6] that, if the reduction potentials of two substances A and B differ by ~0.2 V (under effective potentiostatic conditions, the difference can be even smaller) and there is an excess of the harder substance to reduce (suppose that this is substance B), a high yield of the cross-coupling product is observed. The influence of the difference between the reduction potentials ($\Delta E_{1/2}$) of the coupled components on the yield of the cross-coupling product with respect to the current W can be demonstrated in relation to the reaction of acrylonitrile with α,β-unsaturated nitriles B:

B	Methyleneglutaronitrile	1,4-Dicyanobut-1-ene	1-Cyanobuta-1,3-diene
$\Delta E_{1/2}$, V	0.02	0.10	0.17
W, %	35.4	54.3	81.0
References	7	8	9

However, the yield of the coupling reaction product is not influenced solely by the cathodic potential and the reduction potentials of the coupled compounds. For example, in the electrolysis of a mixture of acrylonitrile and methyl acrylate the yield of the cross-coupling product depends significantly on the material of the cathode other conditions being equal[5]:

Material of cathode	Graphite	Sn	Pb	Cd	Hg	Al
Yield of ω-cyanovaleric acid ester	50.4	31.0	25.5	22.5	17.3	1.0

The highest yield of cathodic coupling products was obtained at a graphite cathode, which probably indicates a considerable influence of the surface concentration of the reactants. The component ratio also plays a significant role. As a rule, the component which is more difficult to reduce should be present in a greater excess. Thus, when methyl acrylate was coupled with acrylonitrile, the maximum yield of ω-cyanovaleric acid was obtained for a molar reactant ratio of 1 : 12.[5]

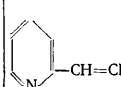
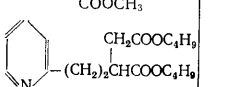
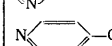
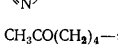
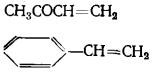
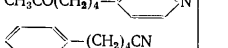
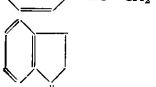
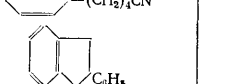
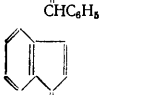
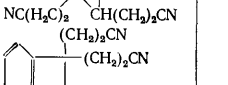
The cross-coupling reactions of the olefins investigated are presented in Table 1, which illustrates effectively the preparative scope of this method. Certain additional information about the olefin coupling reaction can be found in other reviews[2,13].

Subsequent studies showed that alkylidenemalononitriles having the general formula[14]



readily enter into the cathodic coupling reaction with acrylonitrile and methyl acrylate. The nature of the alkyl substituents R′ and R″ has a significant influence on the yield of the coupling products. Certain quantitative characteristics of this reaction are presented in Table 2. It is seen that an increase in the number of carbon atoms in the alkyl group and particularly the branching of the carbon chain lower the yield of the coupling product, evidently in consequence of steric hindrance.

Table 1. The coupling reactions of activated olefins.

Substance A	Substance B	Coupling product	Refs.
$CHCOOC_2H_5$ ‖ $CHCOOC_2H_5$	$H_2C{=}CHCOCH_3$	$CH_2COOC_2H_5$ | $CHCOOC_2H_5$ | $CH_2CH_2COCH_3$	4
$C_6H_5CH{=}CHCOCH_3$	$H_2C{=}CHCN$	$C_6H_5CHCH_2COCH_3$ | CH_2CH_2CN	4
H_3C \ $C{=}CHCOCH_3$ / H_3C	$H_2C{=}CHCN$	$(CH_3)_2CCH_2COCH_3$ | CH_2CH_2CN	4
$CH_3SO_2CH{=}CH_2$	$C_6H_5CH{=}CHCON(C_2H_5)_2$	$C_6H_5CHCH_2CON(C_2H_5)_2$ | $CH_2CH_2SO_2CH_3$	4
$H_2C{=}CHCOOC_2H_5$	$H_2C{=}CHCN$	$CH_2CH_2COOC_2H_5$ | CH_2CH_2CN	9
$CHCOOC_2H_5$ ‖ $CHCOOC_2H_5$	$H_2C{=}CHCN$	$CH_2COOC_2H_5$ | $CHCOOC_2H_5$ | CH_2CH_2CN	9
$H_2C{=}C$ (NHCOCH$_3$, COOCH$_3$)	$H_2C{=}CHCN$	$NC(CH_2)_3CH$ (NHCOCH$_3$, COOCH$_3$)	9
$CHCOOC_4H_9$ ‖ $CHCOOC_4H_9$			10
$CH_3COCH{=}CH_2$		$CH_3CO(CH_2)_4$— 	10
	$H_2C{=}CHCN$		11
	$H_2C{=}CHCN$		12
	$H_2C{=}CHCN$		12

One should note that activated olefins are capable of undergoing the cathodic coupling reaction also with alkyl halides[15]. Unfortunately this interesting reaction has been studied only in relation to a few examples.

The electrochemical reduction of a mixture of acrylonitrile and carbon tetrachloride (in methylene chloride plus water as the solvent) in the presence of the Mackie salt (tetraethylammonium toluene-*p*-sulphonate) as the supporting electrolyte led to the formation of trichlorobutyronitrile (with a current yield up to 28%)[15]:

$$H_2C{=}CHCN + CCl_4 \xrightarrow[-Cl^-]{2e,H^+} CCl_3CH_2CH_2CN$$

Carbon tetrachloride is more readily reducible in this system. Evidently, the first stage of the reaction is transfer of the electrons to the carbon tetrachloride molecule and the formation of the ion $\bar{C}Cl_3$, which interacts with acrylonitrile and is then protonated.

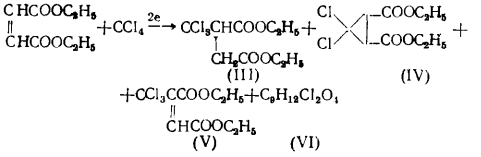
Table 2. The current yields of the products of the cathodic coupling of alkylidenemalononitriles.

R′	R″	Acrylonitrile	Methyl acrylate	R′	R″	Acrylonitrile	Methyl acrylate
CH_3	CH_3	24.0	19.0	CH_3	t-C_4H_9	5.9	7.6
CH_3	C_2H_5	7.6	8.1	C_2H_5	C_2H_5	14.4	14.3
CH_3	iso-C_3H_7	12.5	7.9	$(CH_2)_4$	—	21.0	12.3

The analogous reaction with ethyl acrylate takes place less selectively[15]; a mixture of at least two products is formed:

$$H_2C{=}CHCOOC_2H_5 + CCl_4 \begin{cases} \xrightarrow{2e,H^+} CCl_3CH_2CH_2COOC_2H_5 \ (9\%) \\ \xrightarrow{2e} CCl_3CH_2CHClCOOC_2H_5 \ (24\%) \end{cases}$$

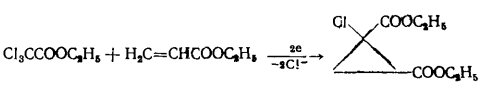
The reaction of carbon tetrachloride with diethyl fumarate is characterised by an even lower selectivity. An interesting feature of this reaction is that, together with products having a linear structure, cyclopropane derivatives are formed:



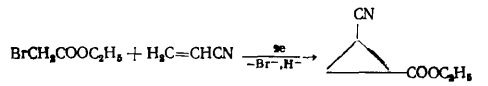
The yields of the individual coupling products (%) depend significantly on the cathodic potential ϕ:

Product	(III)	(IV)	(V)	(VI)
φ = -1.00 V	11.8	1.7	9.6	1.7
φ = -1.20 V	38	28	49.5	—

In the electrolysis of a mixture of ethyl acrylate and ethyl trichloroacetate [in an *N*,*N*′-dimethylformamide (DMF) + dichloroacetic acid mixture as the solvent] in the presence of tetraethylammonium chloride as the supporting electrolyte, the only reaction product is a cyclopropane derivative:



An analogous product is formed on coupling the bromoacetic ester with acrylonitrile (2.8%)[15]:



Allyl bromide reacts with acrylonitrile to form 1-cyanooct-4-ene in 12.6% yield[15]:

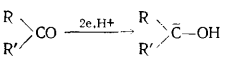
$$H_2C{=}CHCH_2Br + H_2C{=}CHCN \xrightarrow[-Br^-]{2e,H^+} H_2C{=}CH(CH_2)_3CN$$

In conclusion of the discussion of the reactions of activated olefins, mention should be made of their interaction with carbon dioxide. For example, electrolysis of a solution of allyl chloride in DMF with a continuous supply of CO_2 leads to the formation of allyl crotonate in a low yield[15]:

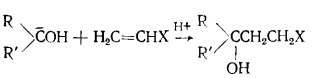
$$H_2C{=}CHCH_2Cl + CO_2 \xrightarrow[-Cl^-]{2e,H^+} CH_3CH{=}CHCOOCH_2CH{=}CH_2 \ .$$

III. REACTIONS OF CARBONYL COMPOUNDS

In the presence of quaternary ammonium salts as supporting electrolytes, aliphatic ketones undergo two-electron reduction. In acid solutions the reduction process is significantly facilitated apparently in consequence of protonation. It has been suggested[2] that in acid media the primary electrode process proceeds in accordance with the equation

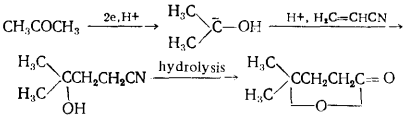


The carbanion formed is capable of adding to Michael acceptors, forming a cross-coupling product:



The reaction has been studied in greatest detail in relation to the cathodic coupling of acetone and acrylonitrile.

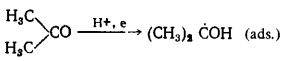
A brief communication[16], showing that the electrochemical reduction of a mixture of acetone and acrylonitrile in 20% sulphuric acid at a controlled potential of the mercury cathode of -1.2 V (sat.cal.e-de) leads to a mixture of γ-hydroxy-γ-methylvaleronitrile and its hydrolysis product γ,γ-dimethylbutyrolactone, was published in 1965; the overall yield of the cross-coupling product was ~70%. Since only acetone undergoes electrochemical reduction under the conditions described (the reduction potential of acrylonitrile in acid solutions is -1.5 V), the authors[16] proposed the following mechanism for the formation of the cross-coupling products:



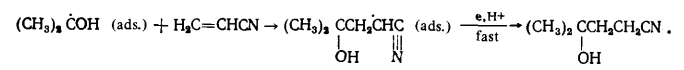
Subsequently this reaction was studied in greater detail[17]. Cyclic voltamperometric data showed that, in an acid solution at a mercury cathode, acetone forms unstable species at a potential of approximately -1.2 V, which undergo reversible oxidation. These species could be detected only at rate of application of potential of 960 V s^{-1}. It has been suggested[17] that these species are of a radical type, since the reduction of acetone is accompanied by the formation of organomercury compounds. The addition of acrylonitrile to the system decreases sharply the surface concentration of these reversibly oxidised species, which indicates their involvement in the interaction with the nitrile. The absence of polyacrylonitrile from the electrolyte solutions shows that the radical species are present on the surface of the electrode and do not diffuse into the bulk of the solution.

The presence of reactive species on the surface of the mercry cathode in the presence of acetone has also been confirmed by the method involving the application of a brief current

pulse against the background of triangular scanning. On the basis of the results, it was suggested[17] that the primary electrode step is the formation of adsorbed radical species:



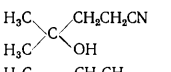
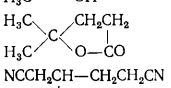
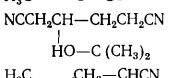
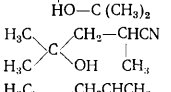
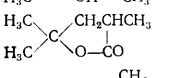
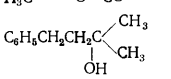
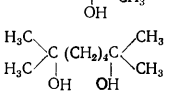
In this case the reaction is first order with respect to acetone; with increase in the acetone concentration to 1 M, the reaction order falls to zero, which shows that molecules of acetone (or of its protonated form) are adsorbed on the electrode before electron transfer. In the second stage of the reaction the adsorbed radicals react with acrylonitrile:



However, although this mechanism agrees with the observed change in the current on pulsation of the potential, it cannot be regarded as rigorously proved, since no direct measurements, indicating the transfer of a single electron to the acetone molecule in the primary electrochemical step, have been made.

Later it was shown[18] that the cathodic coupling of acetone with acrylonitrile can be achieved in a neutral medium at pH 7. The advantage of the neutral medium is that the cross-coupling product is stable under these conditions and the process can be used for the preparative synthesis of γ-hydroxyl-γ-methylvaleronitrile.

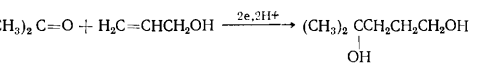
Table 3. The influence of the nature of the olefin on the yield of the product of the cathodic cross-coupling with acetone[18,19] (with respect to the given substance).

Olefin	Coupling product	Yield
Acrylonitrile		73
Methyl acrylate		70
Dicyanobut-1-ene		30
Methacrylonitrile		20
Methyl methacrylate		19
Styrene		8
Butadiene		6

When the reaction is carried out at a graphite cathode in 1 M aqueous solution of dipotassium hydrogen phosphate acidified with phosphoric acid to pH 7 at a temperature of 7–8 °C, a current density of 0.02–0.03 A cm^{-2}, and for a molar acetone : acrylonitrile ratio of 12 : 1, the yield of γ-hydroxy-γ-methylvaleronitrile is 52% with respect to the current and 85% with respect to the reacted acrylonitrile. By measuring the differential capacitance, it was shown that the maximum yield of the cross-coupling product at a mercury cathode is attained under the conditions of the preliminary adsorption of acrylonitrile on the surface of the electrode[18].

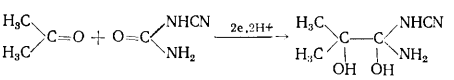
The development of the cathodic coupling of acetone with acrylonitrile on a preparative scale was followed by numerous studies of the applications of this reaction and of its extension to other carbonyl compounds and activated olefins. It was established that acetone enters into the cathodic coupling reaction with numerous activated olefins, forming tertiary alcohols[18,19]. Since the experiments were performed under comparable conditions (graphite cathode, 1 *N* solution of dipotassium hydrogen phosphate, molar ratio acetone : olefin = 10 : 1), it is possible to follow the influence of the nature of the olefin on the yield of the cross-coupling product (Table 3).

It follows from Table 3 that the highest yields of the cross-coupling products have been obtained from acrylonitrile and methyl acrylate, i.e. compounds with a strongly polarised bond. Unexpectedly, acetone undergoes the coupling reaction (albeit with a low yield) with olefins of low polarity such as styrene and butadiene. The yields of the coupling products can apparently be increased, since it has been reported that acetone has been coupled with styrene to give a yield of 42%, with butadiene to give a yield of 32%, and with stilbene to give a yield of 45%. The experimental conditions were not described in detail[20]. It has also been reported[21] that the coupling of acetone with allyl alcohol was achieved to give a high yield of product; electrolysis of a mixture of these substances in an aqueous solution of potassium phosphate at a graphite cathode yielded 2-methylpentane-2,5-diol:

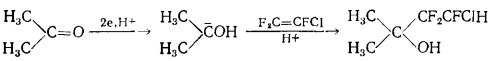


The yield of product was ~70% with respect to the current and 95–98% with respect to the reacted allyl alcohol.

The cross-coupling of acetone with cyanourea was described comparatively recently[22]:



At a mercury cathode in 40% sulphuric acid solution acetone couples with chlorotrifluoroethylene to give a current yield of ~43%.[23] The following reaction mechanism has been proposed:

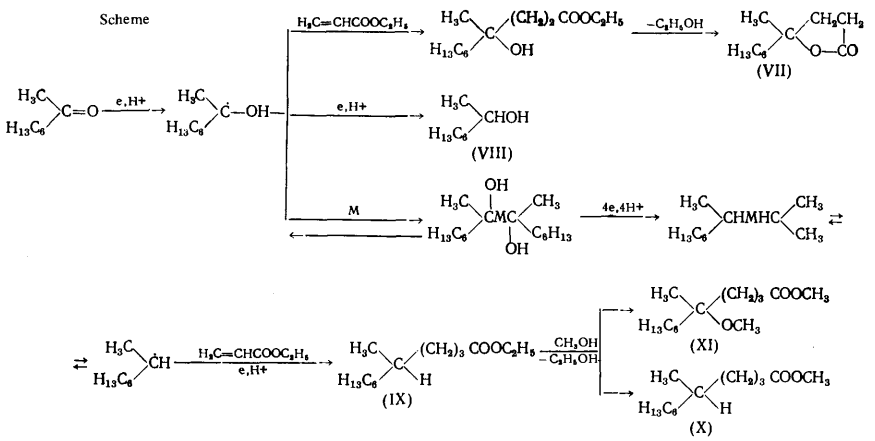


This reaction resembles the radical addition of 2-propanol to chlorotrifluoroethylene.

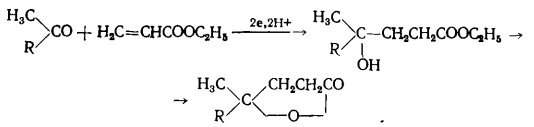
Apart from acetone, many other aliphatic ketones undergo the coupling reaction. It was already mentioned in an early study[16] that ethyl methyl ketone and diethyl ketone undergo the coupling reaction with acrylonitrile, giving current yields of 60 and 30% respectively. Under the same conditions, i.e. in an acid medium, the coupling of acetone with methyl pentyl and hexyl methyl ketones was achieved[24], giving overall yields of coupling products of 70 and 72% respectively. Thus the coupling reaction in an acid medium is also entirely suitable for preparative purposes with high aliphatic ketones.

However, we may note that in an acid medium a considerable proportion of the hydroxynitrile formed (~30%) hydrolyses[24]. It is therefore more convenient to couple the ketone with an

Scheme



acrylate ester, for example ethyl acrylate:



In this case the reaction is no longer complicated by the hydrolysis and fairly high yields of lactones were obtained under the same conditions:

Ketone	$CH_3COC_2H_5$	$CH_3COC_3H_7$	$CH_3COC_5H_{11}$	$CH_3COC_6H_{13}$
Yield, %	80	70	74	42

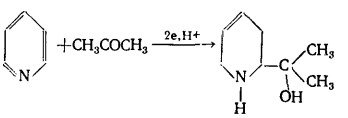
When ketones are coupled with acid ester, side products are always formed[24]. The processes occurring in the electrolyis of a mixture of a ketone and an ester are presented in the Scheme below (M is the material of the cathode).

During the coupling of ethyl acrylate with hexyl methyl ketone in aqueous methanol, the formation of the main product, which is the γ-lactone (VII), is accompanied by that of 2-octanol (VIII), the amount of which increases as the potential is displaced to the cathodic region, ethyl 4-methyldecanoate (IX), considerable amounts of which have been noted only at a more cathodic potential, as well as small amounts of its methyl ester (X) together with traces of methyl 4-methoxy-4-methyldecanoate (XI).[24] Apart from the products indicated, also detected were insignificant amounts of hydrocarbons with molecular weights of 224 and 226, which were identified as 7,8-dimethyltetradecane and 7,8-dimethyltetradodecane respectively, and diisopropylmercury; pinacone was not detected as a side product.

In electrolysis in a neutral medium a smaller amount of side products is found[19]. Table 4 presents data for the cathodic coupling of various aliphatic ketones with acrylonitrile and methyl acrylate. A distinct decrease in the reactivity of the ketone with increasing complexity of its carbon skeleton is obseerved in both acid and neutral media.

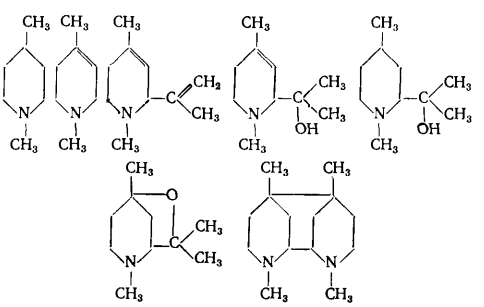
The coupling reaction of higher aliphatic ketones with unsaturated hydrocarbons has been studied in detail[25]. The electrolyte used in the experiments was tetraethylammonium toluene-*p*-sulphonate. The correct choice of solvent is very important in this instance. Preliminary experiments showed that cathodic coupling does not occur in *t*-butyl alcohol, *N*,*N*-dimethylformamide, the monomethyl ether of diethylene glycol, and s-butyl alcohol; in methanol reaction proceeds with an insignificant yield. Mixed solvents proved to be most effective: isopropyl alcohol (20%)–dioxan (80%) and isopropyl alcohol (25%)–dimethyl ether of triethylene glycol (75%). At a graphite electrode coupling proceeds with a higher yield than at a mercury electrode (Table 5).

Interesting information concerning the cathodic coupling of acetone with pyridine has been published in a communication[26], whose authors showed that in an acid medium the reaction is directed preferentially to the α-position and proceeds with partial hydrogenation of the pyridine ring:

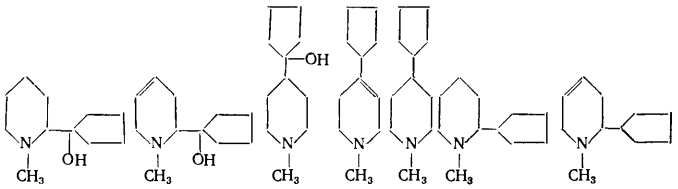


A more detailed investigation of this process showed[27] that the best electrode material in this instance is mercury. Under comparable conditions, the yields of the cross-coupling product at mercury, lead, and cadmium cathodes are 85, 59, and 39% respectively. Cathodic coupling requires the use of acid solutions, since cross-coupling products have not been detected in an alkaline solution. Both an increase in the length of the carbon chain of the aliphatic ketone and the introduction of substituents into the pyridine ring reduce the yield of the coupling product.

The coupling of 4-methylpyridine with acetone and of *N*-methylpyridinium with cyclopentanone has been studied in detail[28]. It was found that in both cases the coupling involves the 2-position of the pyridine ring. However, according to the authors[28], these reactions are of no preparative interest in view of their low selectivity. Thus the formation of the following products was observed in the electrolysis of a mixture of acetone and *N*,4-dimethylpyridinium:

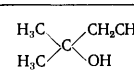
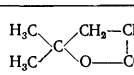
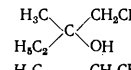
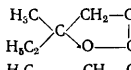
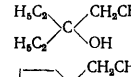
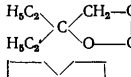
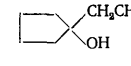
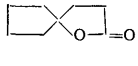


while the products



were isolated in the reduction of *N*-methylpyridinium with cyclopentanone. Further investigation of this reaction showed that the hydrocarbons are formed as a result of the reduction of the tertiary alcohols formed in the first stage of the cross-coupling reaction[29].

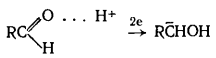
Table 4. The influence of the structure of the ketone on the yields of the products of the cathodic coupling of aliphatic ketones with acrylonitrile and methyl acrylate[19].

Ketone	Product of coupling with acrylonitrile*	Yield, %	Product of coupling with methyl acrylate**	Yield, %
Acetone		50		70
Ethyl methyl ketone		35		30
Diethyl ketone		28		21
Cyclopentanone		13		19

*Graphite cathode, 1 *N* solution of dipotassium hydrogen phosphate.

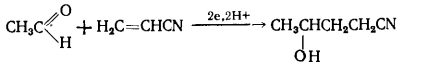
**Mercury cathode, 20% sulphuric acid.

The cross-coupling processes involving aliphatic aldehydes have been studied in less detail. As in the reduction of aliphatic ketones, the reduction of aliphatic aldehydes gives rise to a single two-electron wave[30] and it has been established that the protonated form of the aldehyde is electrochemically active[31]. The first stage of the electrochemical reduction of aliphatic aldehydes involves the formation of an anion:



This anion readily reacts with Michael acceptors.

The first report of the possibility, in principle, of the cathodic coupling reaction with activated olefins appeared in a Japanese patent[32]. Later this reaction was investigated in greater detail. For example, it has been shown[33] that the electrochemical reduction of a mixture of acetaldehyde and acrylonitrile leads to the formation of a hydroxynitrile (1-cyano-3-hydroxybutane) in a high yield:



If acrylic acid or its esters are used instead of acrylonitrile, then in both instances the reduction leads to the formation of γ-lactones, since the γ-hydroxyacids and their esters, formed initially, are unstable under the electrolysis conditions and hydrolyse with formation of the corresponding lactones[34], for example:

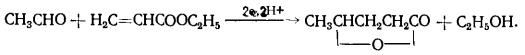
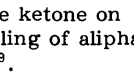
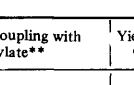
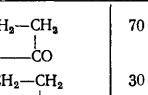
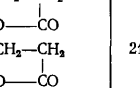
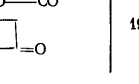
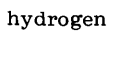
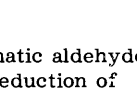
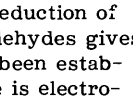
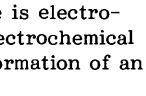


Table 5. Products of the coupling of aliphatic ketones RCOR′ with olefins (cathodic current density 0.014 A cm^{-2}).

R	*R′*	Coupling product	Yield, % w.r.t. ketone	Yield, % w.r.t current
CH_3	CH_3		18	15
CH_3	C_2H_5		22	18
CH_3	C_3H_7		18	15
CH_3	C_6H_{13}		20	17
CH_3	C_7H_{15}		18	15
CH_3	C_8H_{19}		17	14
CH_3			12	10
CH_3			5	4
C_3H_7	C_3H_7		8	6.5
CH_3*	C_2H_5		10	8
CH_3**	C_2H_5		14	12
CH_3***	CH_3		10	10

*Hex-1-ene. ** Dec-1-ene. ***Penta-1,3-diene. In the remaining cases the olefin was oct-1-ene.

The available information about the cathodic coupling of aldehydes with activated olefins is presented in Table 6. [These data refer to the electrolysis of weakly acid solutions (pH4–6) using a graphite cathode[35]]. It has been shown that, under the conditions described by Tomilov and coworkers[34,35], there is a possibility of the cross-coupling of aldehydes also with alkyl halides. Thus the electrochemical reduction of acetaldehyde in the presence of carbon tetrachloride involves the following process:



An analogous reaction has been observed when other halogeno-compounds were used, such as methylene chloride, allyl chloride, chloroform, etc. The cross-coupling of aldehydes is carried out at the graphite cathode in potassium phosphate solutions in a weakly acid medium (pH 2.0–2.5). The required pH is maintained by the gradual addition of phosphoric acid to the cathodic compartment during electrolysis. Table 7 shows the products obtained in the interaction of aliphatic aldehydes with alkyl halides.

Table 6. Products of the cathodic coupling of aliphatic aldehydes with activated olefins[34,35].

Aldehyde	Olefin	Coupling product	Yield, %	
			w.r.t. current	w.r.t substance
CH_3CHO	$H_2C=CHCOOCH_3$	$CH_3CHCH_2CH_2C(=O)-O$	99	92
CH_3CHO	$H_2C=CHCOOH$	ditto	14	52
CH_3CHO	$H_2C=CHCH_2Cl$	$CH_3CHCH_2CH=CH_2$ (OH)	34	82
CH_3CHO	$H_2C=CHCH_2OH$	$CH_3CHCH_2CH_2CH_2OH$ (OH)	—	19
CH_3CH_2CHO	$H_2C=CHCOOCH_3$	$CH_3CH_2CHCH_2CH_2CO$ (O)	86.0	91
CH_3CH_2CHO	$H_2C=CHCOOH$	ditto	20	59
CH_3CH_2CHO	$H_2C=CHCN$	$CH_3CH_2CHCH_2CH_2CN$ (OH)	68	91
CH_3CH_2CHO	$H_2C=CHCH_2OH$	$CH_3CH_2CHCH_2CH_2CH_2OH$ (OH)	6	25
$CH_3CH_2CH_2CHO$	$H_2C=CHCH_2Cl$	$CH_3CH_2CH_2CHCH_2CH_2CH_2Cl$ (OH)	42	86
CH_3CHO	$H_2C=CHCN$	$CH_3CHCH_2CH_2CN$ (OH)	80	93

Table 7. Products of the cross-coupling of aldehydes with alkyl halides[34,35].

Aldehyde	Alkyl halide	Coupling product	Yield, %	
			w.r.t current	w.r.t substance
CH_3CHO	CCl_4	CH_3CHCCl_3 (OH)	72	83
CH_3CHO	$CHCl_3$	$CH_3CHCHCl_2$ (OH)	54	79
CH_3CHO	CH_2Cl_2	CH_3CHCH_2Cl (OH)	4.8	89
CH_3CHO	$H_2C=CHCH_2Cl$	$CH_3CHCH_2CH=CH_2$ (OH)	34.0	82
CH_3CH_2CHO	CCl_4	$CH_3CH_2CHCCl_3$ (OH)	77.0	86
CH_3CH_2CHO	$CHCl_3$	$CH_3CH_2CHCHCl_2$ (OH)	54.6	87
$CH_3CH_2CH_2CHO$	$H_2C=CHCH_2Cl$	$CH_3CH_2CH_2CHCH_2CH=CH_2$ (OH)	42.0	86

All the examples examined above refer to reactions of aliphatic carbonyl compounds. This type of reaction is not characteristic of aromatic carbonyl compounds. However, in a concentrated aqueous solution of the Mackie salt, it was possible to achieve the cathodic coupling of benzophenone with ethyl acrylate[20]. The yield of the cross-coupling product, γγ-diphenyl-γ-butyrolactone, is ~25%:

$$(H_5C_6)_2CO + H_2C=CHCOOCH_3 \xrightarrow{2e,2H^+} (H_5C_6)_2C(CH_2-CH_2)O-C=O$$

Acrylonitrile has been coupled with benzophenone and benzaldehyde under similar conditions[11]. In the latter case the reaction proceeds in accordance with the equation

$$C_6H_5C(=O)H + 2H_2C=CHCN \xrightarrow{3e,3H^+} C_6H_5CH(OCH_2CH_2CN)CH_2CH_2CN$$

An unusual type of cathodic coupling reaction has been observed[36] in the electrochemical reduction of an anhydrous mixture of benzaldehyde and ethyl iodide, which was saturated with tetraethylammonium iodide to make it electrically conducting. The following reaction takes place at a copper cathode with a low yield:

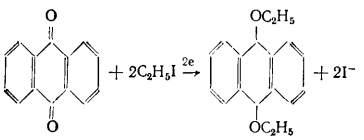
$$C_6H_5CH(=O) + 2C_2H_5I \xrightarrow{2e} C_6H_5CH(OC_2H_5)C_2H_5 + 2I^-$$

It leads to the formation of the ethyl ether of ethylphenylmethanol[36]; its mechanism has not been studied.

When a mixture of benzophenone and ethyl iodide was electrolysed in *N*,*N*-dimethylformamide, ethyldiphenylmethanol was obtained[37]:

$$C_6H_5C(=O)C_6H_5 + C_2H_5I \xrightarrow{2e,H^+} C_6H_5C(C_2H_5)(OH)C_6H_5 + I^-$$

The ethyl ether of 9,10-hydroanthroquinone is obtained from anthraquinone and ethyl iodide[38]:



IV. CATHODIC REDUCTION OF 'ONIUM SALTS

Conditions favourable for the reduction of 'onium cations are created in the electrolysis of solutions of 'onium salts in a medium with low conductivity or in aprotic solvents. The reduction of the cation is followed by its decomposition, leading to the generation of unstable reactive species. When the solution contains substances reacting with these species, a kind of cathodic coupling reaction takes place.

This type of reaction was achieved for the first time in relation to the generation of cyanomethylene anions[39]:

$$[(H_3C)_2SCH_2CN]^+ \xrightarrow{2e} (CH_3)_2S + \bar{C}H_2CN$$

The electrolysis of a solution of this salt in the presence of acrylonitrile yielded glutarodinitrile with a current yield of 83%. The reaction apparently proceeds as follows:

$$\bar{C}H_2CN + H_2C=CHCN \xrightarrow{H^+} CNCH_2CH_2CH_2CN$$

The electrolysis of a dimethylbenzylsulphonium salt in the presence of acrylonitrile under the same conditions gave a 68%

yield of 3-phenylbutyronitrile[39]:

$$(CH_3)_2\overset{+}{S}CH_2C_6H_5 + H_2C{=}CHCN \xrightarrow{2e,H^+} C_6H_5CH_2CH_2CH_2CN + S(CH_3)_2$$

An analogous reaction takes place with phosphonium salts[40], but the yields of coupling products are appreciably lower (on average, they do not exceed 10–13%). It has been suggested[40] that the reaction proceeds via an intermediate stage involving the formation of an organomercury compound:

$$(C_6H_5)_3\overset{+}{P}(CH_2)_n CN \xrightarrow[Hg]{e} (C_6H_5)_3\dot{P}(CH_2)_n CN \,\|\, Hg \rightarrow$$
$$\rightarrow \begin{cases} \rightarrow (C_6H_5)_3P + [Hg(CH_2)_n CN]^{\cdot} \\ \rightarrow (C_6H_5)_3\dot{P}(CH_2)_n CN + Hg \rightarrow (C_6H_5)_3P + {}^{\cdot}(CH_2)_n CN \rightarrow \end{cases}$$
$$\xrightarrow{C_6H_5HC=CH_2} C_6H_5\dot{C}H(CH_2)_{n+1}CN \xrightarrow{e,H^+} C_6H_5(CH_2)_{n+2}CN$$

The nitriles of phenylvaleric ($n = 2$), phenylcaproic ($n = 3$), and phenyloenanthic ($n = 4$) acids have been synthesised in this way. Unfortunately, owing to the low yields, this reaction is hardly likely to find preparative applications. In the electrolysis of phosphonium salts with $n = 1$ neither dimerisation products nor organomercury compounds were detected.

V. OTHER REACTIONS INVOLVING ELECTROCHEMICALLY GENERATED ANIONS

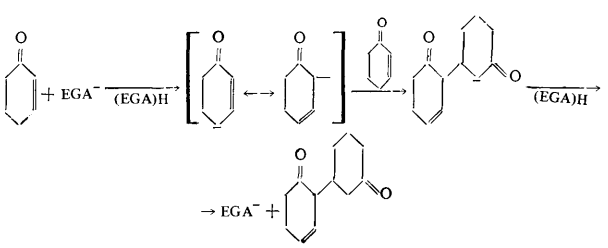
Attempts have been made recently to carry out electrochemically certain classical reactions of organic synthesis, which proceed via a stage involving an organic anion, using the electric current to generate the latter. One of the most promising features of this field of research involves the Michael reaction.

The initiation of the Michael reaction by electrochemically generated anions (EGA^-), which behave as a strong base (for example, in the condensation of malonic ester with acrylonitrile), can be represented by the following equations:

$$EGA^- + CH_2(COOC_2H_5)_2 \rightleftarrows (EGA)H + \bar{C}H(COOC_2H_5)_2 \quad ,$$
$$\bar{C}H(COOC_2H_5)_2 + H_2C{=}CHCN \rightarrow (C_2H_5OOC)_2CHCH_2\bar{C}HCN \quad ,$$
$$(C_2H_5OOC)_2CHCH_2\bar{C}HCN + CH_2(COOC_2H_5)_2 \rightarrow$$
$$\rightarrow (C_2H_5OOC)_2CHCH_2CH_2CN + \bar{C}H(COOC_2H_5)_2 \quad .$$

For the reaction to go virtually to completion, catalytic amounts of EGA^- are sufficient. The process described has been carreid out[41] using azobenzene, which on reduction in an aprotic medium gives rise to the fairly active dianions $C_6H_5\bar{N}-\bar{N}C_6H_5$, as the source of EGA^-.[42] The experiments carried out in the above study[41] showed that it is sufficient to add to the solution 0.0025 mole of azobenzene per mole of malonic ester for the above reaction to take place with a yield of 75%.

Furthermore, EGA^- can also be used to obtain dimerisation products when the same substance can behave as the donor and acceptor in the Michael reaction[41]. The reaction involving cyclohex-2-en-1-one can be formulated thus:



The dimer was obtained in 65 mole % yield with reduction of only 0.13 mole % of the monomer[41]. The reactions given in Table 8 were carried out similarly. However, in most cases there is no need to introduce a special substance generating anions. The acceptor itself can function as a substance of this kind. Thus in the above reaction of malonic ester with acrylonitrile, acrylonitrile can function as the source of EGA^- [41]:

$$H_2C{=}CHCN \xrightarrow{2e,H^+} \bar{C}H_2CH_2CN$$

Table 8. Examples of dimerisation reactions initiated by EGA^-.[41]

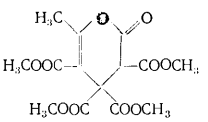
Monomer	Dimer	Amount of reduced monomer, %	Yield of dimer, %
$H_2C{=}CHCH_2CN$	$CNCH_2CH_2CH_2CHCH{=}CH_2$ (CN)	1.0	35
$CH_3OOCCH_2C{=}CHCOOCH_3$ (COOCH₃)	$CH_3OOCCH_2CHCH_2COOCH_3$ (COOCH₃)	1.5	88
	$CH_3OOCCH{=}CCHCOOCH_3$ (COOCH₃)		
$C_2H_5OOCCH_2CH{=}CHCOOC_2H_5$	$C_2H_5OOCCH_2CHCH_2COOC_2H_5$ (CHCOOC₂H₅)	2.0	50
	$C_2H_5OOCCH{=}CHCHCOOC_2H_5$ (CH₂COOC₂H₅)		

At a mercury cathode in solution in *N*,*N*-dimethylformamide in the presence of tetrabutylammonium fluoroborate as the supporting electrolyte the coupling reaction proceeds with a yield of 18.5% when 0.024 of a faraday of electricity per mole of acrylonitrile is passed through the system. Under these conditions, the coupling of ethyl acrylate with malonic ester was carried out to give a yield of 77% after passing 0.055 of a faraday of current[41].

$$CH_2(COOC_2H_5)_2 + H_2C{=}CHCOOC_2H_5 \xrightarrow{2e,H^+} (C_2H_5OOC)_2CH{-}CH_2CH_2COOC_2H_5$$

The coupling of methyl ethylenetetracarboxylate with methyl pyruvate proceeds to give a yield of 60% [41]:

$$(CH_3OOC)_2C{=}C(COOCH_3)_2 + CH_3COCH_2COOCH_3 \xrightarrow{2e}$$



The yield of the product of the coupling reaction between ethyl ethylenetetracarboxylate and malonic ester is 93%. All the reactions examined are undoubtedly of preparative value. Their characteristic feature is that the electric current is used solely to regenerate the catalyst of the chemical reaction.

The familiar Wittig reaction involves the conversion of carbonyl compounds under the influence of ylids, which are usually obtained by treating a quaternary phosphonium salt with phenyl-lithium:

$$((C_6H_5)_3\overset{+}{P}CH_3)Br + C_6H_5Li \rightarrow (C_6H_5)_3\overset{+}{P}\cdot\bar{C}H_2 + LiBr + C_6H_6$$

Ylids are also formed electrochemically in the electrolysis of phosphonium and sulphonium salts[43,44]. The electrochemical generation of ylids includes oxidation-reduction and acid–base reactions. This process can be achieved by electrolysing a mixture of a phosphonium salt and a substance which readily gives rise to organic anions, for example, azobenzene[45]. The electrolysis of such a mixture at the azobenzene reduction potential (-0.90 V) leads to the formation of the

anions of the latter, which split off protons from the phosphonium salt with formation of an ylid; next the yild interacts with a carbonyl compound, for example, benzaldehyde. The overall mechanism of the reactions can be expressed by the following equations:

$$C_6H_5N{=}NC_6H_5 \xrightarrow{2e} C_6H_5\bar{N}{-}\bar{N}C_6H_5 \text{ (reduction)},$$

$$(C_6H_5)_3\overset{+}{P}CH_2C_6H_5 \xrightarrow{1/2C_6H_5\bar{N}-\bar{N}C_6H_5} (C_6H_5)_3\overset{+}{P}{-}\bar{C}HC_6H_5 + 1/2C_6H_5NHNHC_6H_5 \text{ (abstraction of a proton)},$$

$$(C_6H_5)_3\overset{+}{P}{-}\bar{C}HC_6H_5 \xrightarrow{C_6H_5CHO} (C_6H_5)_3PO + C_6H_5CH{=}CHC_6H_5 \text{ (Wittig reaction)}.$$

It has been shown[45] that the Wittig reaction takes place with a high yield in the electrolysis of a mixture of azobenzene, benzyltriphenylphosphonium bromide, and benzaldehyde in anhydrous *N,N*-dimethylformamide containing lithium bromide. According to the authors[45], the electrochemical version of the Wittig reaction has definite advantages, since it becomes possible to establish readily the required concentration of the base by regulating the current and hence side reactions can be virtually eliminated.

Another example of this reaction is provided by the electrochemical version of the Stevens rearrangement, which involves the conversion of an ammonium salt into a tertiary amine under the influence of, for example, sodium amalgam {Na[Hg]}:

$$C_6H_5COCH_2\overset{+}{N}(CH_3)_2CH_2C_6H_5\ Br^- \xrightarrow{Na[Hg]} \left[C_6H_5CO\bar{C}H\overset{+}{N}(CH_3)_2CH_2C_6H_5\right] \rightarrow C_6H_5COCHN(CH_3)_2CH_2C_6H_5 .$$

In this case azobenzene cannot be used as a depolariser, because it is reduced at a more negative potential than benzyldimethylphenacylammonium bromide. However, the initial substance itself can be employed as the depolariser[46]. The overall chain of processes occurring can be represented by the equation

$$2C_6H_5COCH_2\overset{+}{N}(CH_3)_2CH_2C_6H_5 \xrightarrow[DMF/LiCl]{2e} C_6H_5COCH_3 + C_6H_5CH_2N(CH_3)_2 + C_6H_5CO\bar{C}H\overset{+}{N}(CH_3)_2CH_2C_6H_5 \rightarrow C_6H_5COCHN(CH_3)_2CH_2C_6H_5$$

The reductive acetylation reaction is an example of the use of electrochemically generated bases for organic synthesis. This process was initially investigated in relation to the acetylation of *N*-heterocyclic compounds[47]. The cathodic acetylation reaction consists of the electrolysis of a mixture of nitro- or nitroso-compounds with acetic anhydride in solution in anhydrous acetonitrile. A 0.8 M solution of sodium perchlorate is used as the supporting electrolyte:

$$RNO_2 \xrightarrow{e} [RNO_2]^{\cdot-} \xrightarrow[-AcO^-]{Ac_2O} \left[RN\begin{matrix}O\\OAc\end{matrix}\right]^{\cdot} \xrightarrow[-AcO^-]{e,Ac_2O} RN\begin{matrix}OAc\\OAc\end{matrix}$$

For a nitroso-compound, the process can be formulated as follows:

$$RNO \xrightarrow{e} [RNO]^{\cdot-} \xrightarrow[-AcO^-]{Ac_2O} [RNOAc]^{\cdot} \xrightarrow[-AcO^-]{e,Ac_2O} RN\begin{matrix}OAc\\Ac\end{matrix}$$

N-Substituted *N,O*-diacetylhydroxylamines have been obtained from various nitroso-compounds with the following yields[48]: CH_3NO_2—54%; $t\text{-}C_4H_9NO_2$—47%; $t\text{-}C_4H_9NO$—57%; $C_6H_5NO_2$—55%; C_6H_5NO—71%; $p\text{-}CH_3C_6H_4NO_2$—77%; $C_6H_4(NO_2)_2$—87%. This reaction is undoubtedly of preparative value.

Data on the electrochemical acetylation and alkylation in the cathodic cleavage of disulphides are of interest[49,50]. The reaction is carried out in dimethyl sulphate or in *N,N*-dimethylformamide. A mixture of a disulphide with an alkyl halide or acetic anhydride is electrolysed. Alkylation and acetylation are observed in the former and latter case respectively:

$$RSSR \xrightarrow{2e} 2RS^- \begin{cases} \xrightarrow{2R'X} 2RSR' + 2X^- \\ \xrightarrow[2Ac_2O]{} 2RSAc + 2AcO^- \end{cases}$$

The experiments showed that methylene chloride can be most conveniently used as the methylating agent[49]. The yields of methylation products obtained under these conditions in solution in *N,N*-dimethylformamide in the presence of lithium chloride as the supporting electrolyte are listed in Table 9.

Table 9. The yields of the products of the electrochemical methylation of disulphides[49].

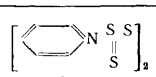
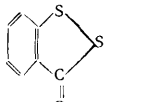
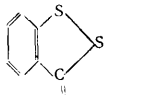
Starting material	Yield, %	Starting material	Yield, %
$[C_6H_5CH_2S]_2$	82		78
$[C_6H_5S]_2$	83		
$[p\text{-}CH_3C_6H_4S]_2$	85		85
$[C_6H_5COS]_2$	70		
$[o\text{-}NO_2C_6H_4S]_2$	91		78
$[o\text{-}C_2H_5OC_6H_4S]_2$	89		
		$[(CH_3)_2NCS]_2$	81
			88

Table 10. Electrochemical alkylation and acylation of disulphides[49].

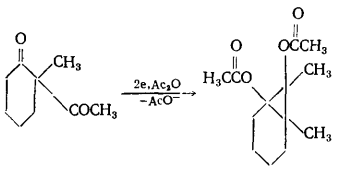
Initial disulphide	Electrode reagent	Yield of cathodic coupling product, %
CH_3SSCH_3	$C_6H_5CH_2Cl$	63
$CH_3COSSCOCH_3$	$C_6H_5CH_2Cl$	76
$C_6H_5SSC_6H_5$	$C_6H_5CH_2Cl$	92
$C_6H_5CH_2SSCH_2C_6H_5$	$CH_3CHClCH_3$	75
$C_6H_5CH_2SSCH_2C_6H_5$	$(CH_3CO)_2O$	83
$o\text{-}O_2NC_6H_4SSC_6H_4NO_2\text{-}o$	$(CH_3CO)_2O$	68
ditto	CH_3COCl	39
»	CH_3I	84
»	$(CH_3O)_2SO_2$	91
»	$(CH_3CH_2O)_2SO_2$	76
$(CH_3)_2NC(S)SSC(S)N(CH_3)_2$	$(CH_3)_2NCOCl$	37
$C_6H_5COSSCOC_6H_5$	CH_2Br_2	66

Somewhat lower yields have been obtained using other alkylating agents, but they nevertheless remain within limits adequate for a preparative process (Table 10).[49] The advantage of the electrochemical alkylation of disulphides over known chemical methods is that the electrochemical procedure makes it possible to obtain thioethers even when the corresponding thiols are unstable or do not exist at all[49].

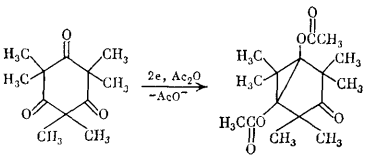
The study of the polarographic behaviour of benzophenone in solution in acetonitrile showed that the addition of acetic anhydride to the solution suppresses the second benzophenone reduction wave. Preparative electrolytic processes carried out at the potential of the first wave showed that benzophenone is acetylated under the conditions indicated[51]:

$$(C_6H_5)_2C{=}O \xrightarrow{+e} [(C_6H_5)_2C{-}O]^{\cdot-} \xrightarrow[-AcO^-]{Ac_2O} [(C_6H_5)_2COAc]^{\cdot} \xrightarrow{+e}$$
$$\rightarrow [(C_6H_5)_2COAc]^- \xrightarrow[-AcO^-]{Ac_2O} (C_6H_5)_2C(COCH_3)OAc \quad .$$

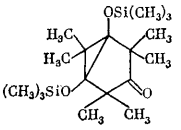
The electrochemical acetylation of diketones was achieved analogously[52]. An acetylated internal cyclisation product has been obtained by the reduction of 2-acetyl-2-methylcyclohexanone in solution in acetonitrile in the presence of tetraethylammonium bromide as the supporting electrolyte at a potential of -2.8 V (sat.cal.e-de) and with continuous supply of acetic anhydride:



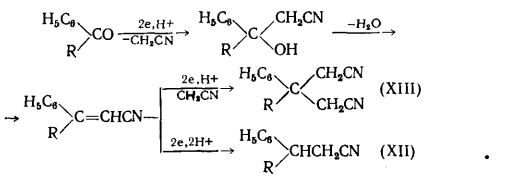
The reduction of 2,2,4,4,6,6-hexamethylcyclohexane-1,3,5-trione takes place similarly, the yield of the acetylation product reaching 71%:



If chlorotrimethylsilane is added to the solution instead of acetic anhydride, an unstable trimethylsilyl derivative is formed[53]:



An unusual reaction has been observed in the reduction of aromatic ketones in anhydrous acetonitrile; 3-substituted propionitriles and glutaronitriles are formed under these conditions[54]. In order to explain this reaction, it has been assumed that the anion formed as a result of electron transfer to a molecule of the carbonyl compound exhibits such a high proton affinity that a proton is abstracted from a solvent molecule, generating the anion $\bar{C}H_2CN$:



For acetophenone, the yields of products (XII) and (XIII) are 35–50% and 35–45% respectively. Related carbonyl compounds—benzaldehyde and benzophenone—give rise to similar products. A more detailed study of the reaction mechanism[55] confirmed the involvement of the $\bar{C}H_2CN$ anions.

---oOo---

Thus cathodic coupling reactions are not only of theoretical but also of practical interest, since they extend significantly the applications of electrochemical methods in the synthesis of organic compounds. It is therefore of interest to carry out further studies in this field.

REFERENCES

1. S.Wawzonek, E.Blaha, R.Berkey, and H.Runner, J.Electrochem.Soc., **102**, 3, 235 (1955).
2. A.P.Tomilov, in "Elektrokhimiya 1968. Itogi Nauki, Seriya 'Khimiya'" (Electrochemistry 1968. Advances in Science. "Chemistry" Series), Izd.VINITI, Moscow, 1970, p.166.
3. M.Baizer and J.Petrovich, "Progress in Physical Organic Chemistry", M.Dekker, New York, 1957, Vol.7, p.189.
   Chemistry", M.Dekker, New York, 1957, Vol.7, p.189.
4. M.Baizer and J.Anderson, J.Org.Chem., **30**, 3138 (1965).
5. S.M.Makarochkina and A.P.Tomilov, Zhur.Obshch. Khim., **40**, 676 (1970).
6. M.Baizer, J.Petrovich, and D.Tysse, J.Electrochem. Soc., 117, 173 (1970).
7. M.Baizer and J.Anderson, J.Org.Chem., **30**, 1357 (1965).
8. A.P.Tomilov, Yu.D.Smirnov, S.K.Smirnov, and S.L.Varshavskii, Zhur.Org.Khim., **3**, 954 (1967).
9. M.Baizer, J.Org.Chem., **29**, 1670 (1964).
10. J.Anderson, M.Baizer, and E.Pull. J.Org.Chem., **30**, 1645 (1965).
11. M.Baizer and J.Chruma, J.Electrochem.Soc., **118**, 450 (1971).
12. M.Baizer and J.Anderson, J.Org.Chem., **30**, 1348 (1965).
13. A.P.Tomilov, Yu.D.Smirnov, and S.K.Smirnov, in "Elektrosintez i Elektrokhimiya" (Electrosynthesis and Electrochemistry), Izd.Nauka, Moscow, 1975, p.66.
14. Yu.D.Smirnov, S.K.Smirnov, and A.P.Tomilov, Zhur.Org.Khim., **10**, 1597 (1974).
15. M.Baizer and J.Chruma, J.Org.Chem., **37**, 1951 (1972).
16. K.Sugino and T.Nonaka, J.Electrochem.Soc., **112**, 1241 (1965).
17. O.Brown and K.Lister, Discuss. Faraday Soc., **45**, 106 (1968).
18. A.P.Tomilov, S.M.Makarochkina, L.A.Fedorova, and G.A.Tedoradze, Elektrokhimiya, **9**, 525 (1973).
19. S.M.Makarochkina and A.P.Tomilov, Zhur.Obshch. Khim., **41**, 2566 (1974).
20. M.Nicolas and R.Pallaud, Compt.rend., **267c**, 1834 (1968).
21. A.P.Tomilov and B.L.Klyuev, Zhur.Obshch.Khim., **39**, 470 (1969).
22. T.Nonaka, N.Yui,,and K.Odo, Denki Kagaku, **42**, 160 (1974).
23. F. Liska, V.Dedek, and M.Nemec, Coll.Czech.Chem. Comm, **39**, 689 (1974).
24. A.Fröling, Rec.Trav.chim., **93**, 47 (1974).
25. T.Shono and M.Mitani, J.Chem.Soc.Japan.Ind.Chem. Sect., 975 (1973).
26. T.Nonaka and K.Sugino, J.Electrochem.Soc., **116**, 615 (1969).
27. T.Nonaka and K.Sugino, Denki Kagaku, **38**, 105 (1970).

28. M.Ferleg, M.Lebe, P.Stern, and P.Trska, Coll.Czech. Chem.Comm, **40**, 2183 (1975).
29. M.Ferleg, O.Kocian, M.Lebl, J.Lövy, S.Radl, A.Silhankova, and P.Stern, Coll.Czech.Chem.Comm, **41**, 598 (1976).
30. B.G.Soldatov, V.F.Khomyakov, and A.P.Tomilov, Trudy Moskov.Khim.-Tekhnol.Inst.im Mendeleeva No.58, 131 (1968).
31. A.P.Tomilov, V.G.Khomyakov, and B.G.Soldatov, Zhur.Vses.Khim.Obshch.im Mendeleeva, **14**, 230 (1969).
32. Japanese P.4 920 298 (1974); Ref.Zhur.Khim., 5N71 (1975).
33. A.P.Tomilov, B.L.Klyuev, and V.D.Nechepurnoi, Zhur.Org.Khim., **11**, 1356 (1975).
34. A.P.Tomilov, B.L.Klyuev, and V.D.Nechepurnoi, Zhur.Org.Khim., **11**, 1984 (1975).
35. N.L.Askerov, S.I.Mekhtiev, V.M.Mamedova, A.P.Tomilov, and A.E.Portyanskii, in "Novosti Elektrokhimii Organicheskikh Soedinenii. Tezisy Dokladov IX Vsesoyuznogo Soveshchaniya po Elektrohimii Organicheskikh Soedinenii" (Advances in the Electrochemistry of Organic Compounds. Abstracts of Reports at the IXth All-Union Conference on the Electrochemistry of Organic Compounds), Moscow, 1976, p.44.
36. J.Nelson and A.Collins, J.Amer.Chem.Soc., **46**, 2256 (1924).
37. S.Wawzonek and A.Gundersen, J.Electrochem.Soc., **107**, 537 (1966).
38. S.Wawzonek, J.Electrochem.Soc., **103**, 456 (1902).
39. M.Baizer, J.Org.Chem., **31**, 3847 (1966).
40. J.Wagenknecht and M.Baizer, J.Org.Chem., **31**, 3885 (1966).
41. M.Baizer, J.Chruma, and D.White, Tetrahedron Letters, 5209 (1973).
42. P.Iversen and H.Lund, Tetrahedron Letters, 3523 (1969).
43. T.Shono and M.Mitani, J.Amer.Chem.Soc., **90**, 2728 (1968).
44. T.Shono and M.Mitani, Tetrahedron Letters, 687 (1969).
45. P.Iversen and H.Lund, Tetrahedron Letters, 3523 (1969).
46. P.Iversen, Tetrahedron Letters, 55 (1974).
47. H.Lund and J.Simonet, Compt.rend., **C227**, 1387, 1379 (1973).
48. L.Klemm, P.Iversen, and H.Lund, Acta Chem.Scand., **B28**, 593 (1974).
49. P.Iversen and H.Lund, Acta Chem.Scand., **B28**, 827 (1974).
50. D.Kunz, H.Hartmann, and R.Mayer, Z.Chem., **9**, 60 (1969).
51. T.Gurphey, L.Trivedi, and T.Layloff, J.Org.Chem., **39**, 3831 (1974).
52. T.Gurphey, C.Amelotti, T.Layloff, R.McCerteny, and J.Williams, J.Amer.Chem.Soc., **91**, 2817 (1969).
53. T.Curphey and R.McCartney, Tetrahedron Letters, 5295 (1969).
54. E.Abbot, A.Bellamy, and J.Kerr, Chem.Ind.(London) 826 (1974).
55. A.Bellamy, Chem.Comm, 944 (1975).

Translated from *Uspekhi Khimii*, **49**, 494 - 517 (1980) U.D.C. 678.644'142

Biochemical Applications of Poly(Ethylene Glycol)

I.N.Topchieva

The literature data on the use of poly(ethylene glycol) (PEG) in biochemistry and molecular biology are analysed from the standpoint of the physical chemistry of polymers. The exclusion properties of PEG, used as a factor influencing the rate of enzymatic reactions, the intra- and intermolecular transitions in polymers, and biopolymer precipitation and crystallisation processes are examined. The suitability of three-component PEG-dextran-water mixtures for the purification and separation of mixtures of biopolymers and for analytical purposes as well as the possibility of using functional derivatives of PEG in immunological research and for the immobilisation of enzymes are discussed. A special section is devoted to the synthesis of PEG derivatives containing different functional groups at the ends of the polymer chain. The surface-active properties of PEG are examined.
The bibliography includes 78 references.

CONTENTS

I. Introduction 260
II. Exclusion properties of poly(ethylene glycol) 260
III. The use of three-component poly(ethylene glycol)-dextran-water systems for preparative and analytical purposes 263
IV. Biochemical aspects of the use of mono- and bi-functional derivatives of poly(ethylene glycol) 265
V. The surface-active properties of poly(ethylene glycol) 266
VI. The synthesis of disubstituted derivatives of poly(ethylene glycol) 267

I. INTRODUCTION

The interest in poly(ethylene glycol) (PEG) has been recently stimulated by its successful application in biochemistry and molecular biology, where this polymer is widely used in different kinds of research. Analysis of literature data shows that the experience accumulated by biochemists in the use of PEG (mainly of its aqueous solutions) for the purification and separation of natural products and for analytical purposes can be extended and applied successfully in the solution of certain problems of the physical chemistry of high-molecular-weight compounds. On the other hand, these studies necessitate a more detailed investigation of the chemical and physicochemical properties of PEG and especially of reactions involving its end groups.

Furthermore, there have been a number of studies of the effect of PEG on certain processes in living systems. In its turn, this faces chemists with the problem of the study of the molecular mechanisms of such effects and leads to new prospects for the investigation of the physicochemical properties of PEG and its possible applications.

The aim of this review is to acquaint chemists, mainly specialists in the field of high-molecular-compounds, with experimental data on the applications of PEG in biochemical research and an attempt is made to interpret these results from the standpoint of the physical chemistry of polymers.

II. EXCLUSION PROPERTIES OF POLY(ETHYLENE GLYCOL)

The widest applications of PEG in biochemistry are associated with its use as an exclusion agent. The term "exclusion" was first introduced in biochemical literature and is in essence a synonym of the concept of the "incompatibility of polymers" familiar in the physical chemistry of polymer solutions.

The exclusion principle can be explained by considering the question of the influence of the presence of polymers on the properties of low- and high-molecular-weight substances in solution. In polymer solutions the mobility of small ions and molecules is determined by the "microscopic" viscosity of the system, which becomes appreciable in the range of polymer concentrations where the macromolecular coils appreciably interpenetrate one another (critical concentration). At lower concentrations the microscopic viscosity of the system is small and the diffusion coefficients of small molecules therefore change very little. On the other hand, if another high-molecular-weight compound is introduced into a solution containing a linear polymer, then an apparent increase of the true concentration of the components in relation to the case where the substances are present in solution in a pure state is observed. This effect is usually interpreted as the mutual exclusion of the macromolecules from part of the solution. The hypothesis of exclusion is based on the observation that the change in chemical potentials is a function of the size of the excluded molecules[1].

Studies on the influence of polymers on biochemical processes can be divided into three groups.

1. The study of enzymatic reactions in polymer solutions, i.e. in systems simulating the environment of intracellular enzymes.
2. The study of intra- and inter-molecular transitions in polymers in the presence of exclusion agents.
3. The use of polymers for the precipitation and crystallisation of biopolymers.

The point is that in vitro biochemical processes are in most cases investigated in aqueous buffer solutions. However, the same reactions in vivo take place in the presence of high concentrations of high-molecular-weight substances—proteins, nucleic acids, and carbohydrates, which influence various chemical equilibria.

The first step in the study of enzymatic reactions under conditions approaching those in nature involves enzymatic reactions in the presence of neutral linear polymers which do not interact specifically with the components of the enzymatic reaction. When a polymer is introduced into the system, the chemical activity of enzymes, substrates, and inhibitors increases. Consider a one-substrate reaction described by the equation

$$E+S \rightleftharpoons ES \rightarrow E+P \quad ,$$

where E is the enzyme, S the substrate, ES the enzyme–substrate complex, and P the reaction product. The dissociation constant of the enzyme–substrate complex can be formulated as follows:

$$K = \frac{\gamma_E \gamma_S}{\gamma_{ES}} \cdot \frac{c_E c_S}{c_{ES}}.$$

We shall consider how the size of the reaction components affects the ratio of the activity coefficients†. If the substrate has a low molecular weight, one can assume that the size of the enzyme molecule and of the enzyme–substrate complex and hence also their activity coefficients are similar. The activity coefficient ratio will therefore depend on γS; since the latter quantity apparently differs little from unity, the entire activity coefficient ratio will be close to unity. Thus, in the conversion of lactate into pyruvate catalysed by lactate dehydrogenase,

$$\text{lactate} + NAD^+ \rightleftharpoons \text{pyruvate} + NADH + H^+,$$

$\gamma_S = 0.76$ for pyruvate and lactate in 23% dextran gel, while its value for NAD^+ is 0.62.[1]

On the other hand, if the substrate is a high-molecular-weight compound, whose molecular size significantly exceeds the molecular size of the enzyme, the activity coefficient ratio will be determined by the activity coefficient of the enzyme γ_E, which is as a rule appreciably greater than unity; for example, $\gamma_E = 4$ for the hyaluronic acid–hyaluronate lyase–dextran system and the Michaelis constant K_M should increase approximately by a factor of four. The same order of magnitude of the changes in K_M is in fact observed for enzymatic systems under experimental conditions.

In addition to increasing the chemical potentials, the presence of polymers in solutions can cause a decrease of the diffusion coefficients of other system components, manifesting the so-called sieve effect[1]. This leads to a decrease of the frequency of collisions between the reactants and to a decrease of the maximum rate of reaction v_{max}. However, this effect should not influence the equilibrium constants for the reactions.

We may note that the view that the action of polymers on enzymatic reactions involves energy exchange between the polymeric medium and the enzyme–substrate complex has been expressed in a number of studies#.

The second group of studies is associated with the investigation of intra and inter-macromolecular processes in biopolymers. If the macromolecules can exist in solution in different conformational states characterised by different molecular volumes, then the presence of another polymer in the system should lead to different exclusions of different forms and in the presence of the added polymer the conformation having the smallest volume should be stabilised. The study of the conformational transitions of three polynucleotides from an ordered to a disordered conformation in the presence of dextran and PEG showed[2] that the increase of the stability of the ordered conformation depends on the concentration of the added polymers, PEG showing a higher efficiency in exclusion than dextran. The increase of the stability of the ordered conformation was inferred in the above study[2] from the change in the hypochromic effect as a function of temperature. Two families of melting curves for the poly(deoxyadenylic–thymidylic acid) helix, measured in the presence of PEG of different molecular weight and different dextran fractions, were obtained (Fig.1). The curves in Fig.1*a* show that the change in the melting temperature of the helix depends significantly on the molecular weight of the PEG for the low-molecular-weight fractions, while the dependence is slight for high-molecular-weight specimens (molecular weights of 4000 and 6000). In the case of dextran all the specimens had a high molecular weight, so that the melting temperature of the polynucleotide helix were the same in all cases.

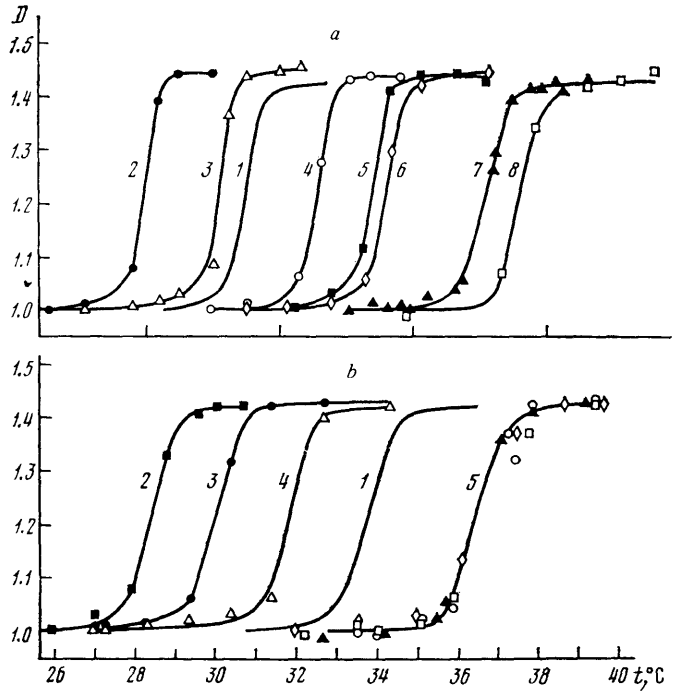


Figure 1. The influence of the molecular weights of PEG (*a*) and dextran (*b*) on the melting of the poly[d(A – T)·d(A – T)] helix in a saline tris buffer[2]; D = optical density at 260 nm: *a*) PEG concentration 20.6 g/100 ml of buffer [1) without addition of polymer; 2) monomer; 3) PEG-200; 4) PEG-400; 5) PEG-600; 6) PEG-1500; 7) PEG-4000; 8) PEG-6000]; *b*) dextran concentration 19.3–19.9 g/100 ml of buffer [1) without addition of polymers; 2) sucrose; 3) glucose; 4) raffinose; 5) dextran-10, dextran-40, dextran-80, dextran-500].

†The activity coefficients γ are found from the relation $K_{av} = 1/\gamma_E$, where K_{av} is the partition coefficient of the given substance between the polymer gel at a known concentration and a buffer.

#S.Damjanovich and B.Somogyi, "Symposia Biologica Hungarica. New Trends in the Description of the General Mechanism and Regulation of Enzymes", Academiai Kiado, Budapest, 1978, pp.159–184.

A good illustration of the exclusion effect is provided by the conversion of a two-stranded DNA molecule into a compact form in an aqueous salt solution after the addition of PEG.[3] This process can be regarded as a model of the structural transitions of DNA in the cell occurring under the influence of of polymers of biological origin.

The idea of using linear water-soluble polymers to act upon other important equilibrium processes in a living organism, such as, for example, the enzyme association–dissociation processes, proved to be very attractive in this connection. This possibility was first pointed out by Laurent[1]. It was realised experimentally in a study[4] where a system containing the enzyme phosphorylase B, which is capable of association, was treated with PEG having a molecular weight of 40000 at a concentration of 4 g/100 ml. The enzyme association process was followed by the sedimentation method in an ultracentrifuge. The enzyme concentration in the system without PEG is selected in such a way that the contents of the dimer and tetramer are 55 and 45%. In the presence of PEG the dimer ⇌ tetramer equilibrium is displaced towards the formation of the tetramer, whose fraction increases to 75%. One should note that in the above study[2] on the compaction of polynucleotides use was made of PEG solutions at concentrations higher by an order of magnitude than in the investigation of Kurganov et al.[4] In the latter case the method of observation precludes the use of such high polymer concentrations in view of the marked increase of the viscosity of the system; this can probably explain the relatively small influence of PEG on the association of the dimeric form of phosphorylase B. Furthermore, the use of higher PEG concentration becomes impossible because the enzyme precipitates at a PEG concentration exceeding 5 g/100 ml.

Yet another striking example of the important role of the polymeric medium in biochemical processes is provided by the observation of the interaction between unlike proteins in the presence of PEG. The following pair of enzymes were investigated: malate dehydrogenase–glutamate dehydrogenase§ and malate dehydrogenase–citrate synthase. It is important to note that the interaction of these enzymes, which are involved in the Krebs cycle, could not be detected in buffer systems in vitro.

Finally, the third region of application of the exclusion effect, which is most important in practice, is associated with the ability of linear polymers to induce the phase separation of the system, i.e. the precipitation of other macromolecular compounds. In this case an appreciable increase of the activity coefficient of the added polymer leads to attainment of the solubility limit by the latter. Together with dextran, PEG is widely used to precipitate proteins[5].

In comparing the abilities of PEG and dextran to induce the precipitation of proteins, one may note that PEG is three times more effective than dextran, in agreement with data obtained in the study of the influence of these polymers on the kinetics of enzymatic reactions[1].

A study has been published recently[6] illustrating the ability of PEG to induce the crystallisation of proteins from aqueous solutions. It has been shown for the crystallisation of 22 proteins that PEG is the most universal reagent compared with those employed previously. The study of the morphology of protein crystals isolated from PEG solutions showed that the structure of the crystals is the same as that of the preparations obtained by the usual methods.

Inspection of the literature data on the exclusion processes occurring in the presence of different water-soluble polymers shows that the most effective exclusion agents are PEG,[1,7–11] dextran[1], and hyaluronic acid[12–14]; polyvinylpyrrolidinone and poly(vinyl alcohol) are less effective[15].

The excluded volumes in systems containing different polymers with the same "partner" can serve as the most natural criterion for the comparison and estimation of the exclusion properties of polymers; however, such data are not available in the literature. Measurement of the excluded volumes is difficult[16]. Ogston¶ and Laurent[17] succeeded in greatly simplifying this problem by considering the simplest model of the interaction of a linear polymer, which can be represented by a long thin rod, with globular particles which are assumed to be spherical (Fig. 2). The greatest exclusion effect, expressed as the excluded volume for S, referred to unit mass of R, observed for asymmetric R. The centre of the spherical particle S cannot approach R to a distance less than r_S. The excluded volume for the centre of S is equal to the volume of the cylinder bounded by dashed lines whose radius is equal to the sum of the radii $r_S + r_r$ (r_r = the radius of the rod). If the end group effect can be neglected, then the volume excluded for the sphere is $\pi l_r (r_S + r_r)^2$, where l_r is the length of the rod. If d is the density of the rod, then its mass is $\pi l_r r_r^2 d$ and the excluded volume v_{excl}, referred to unit mass of R, is

$$v_{excl} = \frac{\pi l_r (r_S + r_r)^2}{\pi l_r r_r^2 d} = \frac{1}{d}\left(\frac{r_S}{r_r} + 1\right)^2.$$

The degree of exclusion increases with increasing radius of S and with decreasing radius of R or with increasing asymmetry of the polymer.

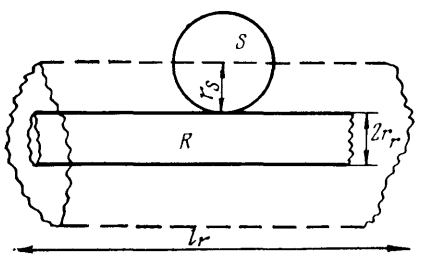


Figure 2. Scheme explaining the phenomenon of the exclusion of a spherical particle by a rodlike particle.

If a series of rods are distributed at random in space, the excluded volumes for individual rods should overlap. The expression for K_{av}, the overall volume accessible to spheres with radius r_S in the space containing randomly distributed long rods with radius r_r, is

$$K_{av} = \exp[-\pi L (r_S + r_r)^2],$$

where L is the sum of the lengths of all the rods per unit volume. We may note that the concentration of the rods (i.e. L) and the square of the radius of the sphere (r_S^2) are the only parameters which determine the accessible volume for $r_r \ll r_S$.

The fraction of the volume accessible for the given substance (K_{av}) is an extremely important parameter for the determination of the exclusion properties of the system. It is related to the excluded volume by the expression

$$v_{excl} = (1 - K_{av})/c_R,$$

where c_R is the concentration of the rods R expressed in terms of mass referred to the volume.

§L.A.Fahien, K.Kmiotek, and L.Smith, Arch.Biochem. Biophys., **192**, 33 (1979).

¶Quoted by Laurent[17].

Despite its simplicity, this theory proved to be entirely applicable to the description of the exclusion properties of certain polysaccharides, in particular dextran and hyaluronic acid[14]. It permits the calculation of K_{av} by Eqn.(5) from the values of r_S, r_r, and L. Comparison of these quantities with the experimental values obtained from gel-filtration data shows an excellent agreement. The linear hyaluronic acid is 4–5 times more effective than the branched dextran. Special experiments showed[8] that 5–10% solutions of dextran have the same exclusion properties as dextran gels at the same concentration. The values of K_{av} and hence the activity coefficients of the substances excluded by the polymer gel can therefore be used subsequently to calculate the activity coefficients of the substances present in solutions of the corresponding polymers.

The excluded volumes in three-component systems containing PEG, a globular polymer, and water, have been found by Edmond and Ogston[18] by measuring the thermodynamic parameters in systems with phase separation.

Adopting the Ogston–Laurent hypothesis as a basis for the description of exclusion effects, one should also bear in mind that polymers influence the structure of water[19–22]. It follows from NMR data for aqueous solutions of PEG that each oxygen atom in the polymer chain binds up to 16 water molecules[23]. Thus PEG has a structure-forming influence on several molecular layers of water. It may be that the structure-forming effect of PEG on water is in fact one of the causes of its appreciable exclusion properties.

One should note that the exclusion principle, which obtains in living organisms and is widely used in molecular biology, can be applied successfully also in the chemistry of high-molecular-weight compounds in order to carry out tasks such as the increase of the specificity of reactions between macromolecular components, the crystallisation of water-soluble polymers, etc.

III. THE USE OF THREE-COMPONENT POLY(ETHYLENE GLYCOL)–DEXTRAN–WATER SYSTEMS FOR PREPARATIVE AND ANALYTICAL PURPOSES

The same exclusion principle, namely the mutual displacement of polymers from part of the solution, is also responsible for phase separation in systems consisting of two polymers in a common solvent. When aqueous solutions of dextran and PEG at concentrations above the critical value are mixed, a two-phase system is formed in which PEG is contained in the upper phase and dextran in the lower phase. Such systems, which can be "buffered" and made isoosmotic, are widely used for the separation of biomacromolecules, cell particles, viruses, membranes, chloroplasts, etc. by partitioning the relative substances between different phases[24]. Together with the dextran–PEG pair, other pairs incorporating modified derivatives of these polymers are also used, for example, dextran–methylcellulose, dextran sulphate–dextran, dextran sulphate–carboxymethyldextran, etc.

The specific features of three-component systems containing two polymeric components are such that phase separation occurs even for polymers with very similar chemical structures, present in solution at low concentrations. The main application of two-phase systems consist in the separation of substances by partitioning between two polymeric phases. This method of separation is more effective than other procedures—electrophoresis and sedimentation[24].

The most remarkable property of the PEG–dextran system, containing non-ionogenic polymers, is the influence of electrolytes on the partition of substances between phases[25]. The fact that a given substance can be transferred from one phase to another simply by adding, for example, NaCl in excess relative to sodium phosphate or by substituting Li^+ ions by Na^+ ions is of interest from both theoretical and practical points of view. It has been noted[26] that negatively charged biomacromolecules have higher partition coefficients in two-phase systems containing sodium sulphate than in those containing sodium chloride; the opposite behaviour has been observed for positively charged compounds. Plots of the partition coefficients K of proteins in phases containing Na_2SO_4 and NaCl against pH consist of two curves intersecting close to the isoelectric point[24]. Such crossed curves are illustrated in Fig.3 for bovine serum albumin[27]. Using two-phase systems at different pH, Sasakawa and Walter[27] obtained the isoelectric points also for a number of other proteins and investigated the dependence of the isoelectric points of haemoproteins on the molecular weight. Blomquist[28] obtained the isoelectric points for the enolase isoenzymes. There is no doubt that this method can be used successfully also for the determination of the isoelectric points of synthetic polyelectrolytes.

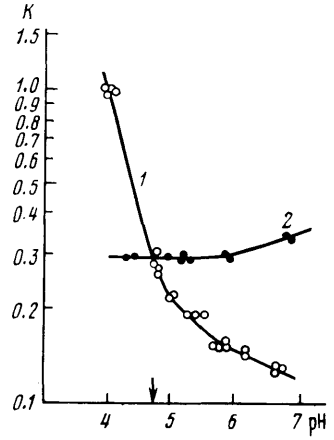


Figure 3. The cross-distribution curves for bovine serum albumin; pH dependence of the partition coefficient K in a two-phase system containing NaCl (curve *1*) and in a system containing Na_2SO_4 (curve *2*).

It is believed[24] that there is a non-uniform distribution of ions between the phases of the PEG–dextran–water system, which leads to a potential difference between the phases defined by the relation

$$U_2 - U_1 = \frac{RT}{(z^+ + z^-)F} \ln \frac{KB^{z^-}}{KA^{z^+}}, \qquad (1)$$

where z^+ and z^- are the numbers of positive and negative charges arising on partitioning the salt A_z-B_z+, F is the Faraday, and K_{Bz^-} and K_{Az^+} are the partition coefficients of the anion and cation respectively.

This potential difference influences in its turn the distribution of the polyelectrolyte or charged species, such as those of proteins and nucleic acids. As a result of the large number of charges on the biomacromolecules, the behaviour of such species in the partitioning process depends strongly on the interfacial potential even if the latter is relatively small.

The problem arises of the cause of the non-uniform distribution of different inorganic electrolytes between the phases. It is believed[25] that cations exhibit a greater affinity for PEG than for dextran, the affinity decreasing in the sequence $Li^+ > Na^+ > K^+$. At the same time, an increase of the affinity of the anions for PEG has been noted in the series of halides with decrease of their polarisability in the sequence $I^- > Br^- > Cl^-$. On the other hand, it has been found[25] that SO_4^{2-} and HPO_4^{2-} have a greater affinity for dextran. These phenomena are due to differences in the tendencies towards the formation of ion pairs in the two phases.

The introduction of charged groups at the ends of the PEG molecule has an even greater influence on the interfacial potential. Typical examples of charged PEG are bistrimethylamino-PEG and PEG-bissulphonate[29]:

$$(CH_3)_3\overset{+}{N}CH_2CH_2OCH_2CH_2O \ldots OCH_2CH_2\overset{+}{N}(CH_3)_3$$
$$^-O_3SCH_2CH_2OCH_2CH_2O \ldots OCH_2CH_2SO_3^- .$$

When these polymers are introduced into the PEG–dextran two-phase system, they move to the PEG-containing phase, as a result of which the system acquires the properties of a liquid ion exchanger.

The decisive factor in the distribution of proteins between the phases is their charge. On the other hand, the required distribution of substances could be attained either by introducing charged groups into the dextran molecule, using, for example, DEAE- or CM-dextrans, or by adding exogenous polyelectrolytes to the system. However, in this case the components of a polyelectrolyte two-phase system have such a high charge density in their molecules that, in conformity with Eqn.(7), the potential difference between the phases diminishes. Furthermore, dextran derivatives frequently migrate to the PEG-containing phase. Finally, the formation of polymeric complexes between polyelectrolyte molecules and cell particles, which are difficult to dissociate, has been noted[24]. Thus the main advantage of charged PEG is that the charges are located solely at the ends of the polymer and the macromolecules retain their affinity for the PEG-containing phase[24].

In his study of the distribution of proteins in two-phase systems, Albertson (quoted by Blomquist[28]) proposed a method which makes it possible to determine the surface charge of proteins. He derived the following equation which makes it possible to relate the partition coefficient of the protein K to the overall molecular charge z and the interfacial potential ψ:

$$\ln K = \ln K^0 + zF\psi/RT,$$

where K^0 is the partition coefficient of the protein having an overall charge of zero.

The use of two-phase systems also made it possible to discover a new method of estimating the hydrophobic properties of macromolecules and small molecules[30]. For this purpose, the end groups of PEG were modified with hydrophobic ligands, in particular, they were esterified by aliphatic acid residues. The PEG modified in this way moves to the same phase as the unsubstituted polymer and makes it less polar. By studying the distribution of a large number of compounds in the same system containing 80–95% of water, it is possible to compare their hydrophobic properties. Using this method, it is natural to adopt as a measure of the hydrophobic properties of the given substance the difference between the free energies of the transfer of 1 mole of the substance from the upper phase of the system containing unsubstituted PEG to the upper phase of another system containing the hydrophobic ligand bound to the polymer:

$$\Delta G'' - \Delta G' = -2.3\, RT\, \Delta \lg K, \qquad (2)$$

where $\Delta G''$ is the free energy of the transfer of 1 mole of the substance from one phase to another in a system containing a hydrophobic polymeric ligand and $\Delta G'$ is the corresponding quantity for a standard two-phase system containing unsubstituted PEG.[30] The quantity $\Delta \lg K$ in Eqn.(2) is defined as follows:

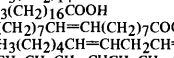
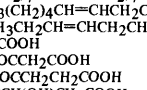
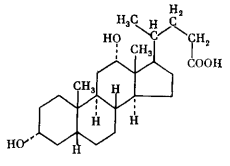
$$\Delta \lg K = \lg K_0'' - \lg K_0',$$

where K_0'' and K_0' are the distribution constants of the substance in the system containing the hydrophobic ligand and in the standard system.

This method for the determination of the hydrophobic properties of substances makes it possible to eliminate effects due to the electrostatic interactions between the molecules of the polymeric ligand and the protein. Another advantage of the method is that the hydrophobic interactions can be investigated in water, in the absence of organic solvents.

The use of hydrophobic ligands bound covalently to PEG constitutes one of the examples of the introduction of affinity ligands into PEG in order to enhance the specificity of the separation of natural products. The same principle has been used for the specific extraction of a number of proteins[31]. For example, a dinitrophenylated derivative of PEG has been used to isolate the S-23 myeloma protein from a mixture[32]. In order to purify steroid-binding proteins, such as plasma transport proteins, PEG containing oestradiol residues as end groups was synthesised as a ligand with a high affinity for the protein[33].

Table 1. Poly(ethylene glycol) esters of various acids.

Acid used to esterify PEG	No. of carbon atoms in acid residue	Degree of substitution, %
Acetic CH_3COOH	2	17
Butyric $CH_3(CH_2)_2COOH$	4	12
Caproic $CH_3(CH_2)_4COOH$	6	9
Caprylic $CH_3(CH_2)_6COOH$	8	12
Capric $CH_3(CH_2)_8COOH$	10	9
Lauric $CH_3(CH_2)_{10}COOH$	12	7
Myristic $CH_3(CH_2)_{12}COOH$	14	8
Palmitic $CH_3(CH_2)_{14}COOH$	16	9
Stearic $CH_3(CH_2)_{16}COOH$	18	11
Oleic $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	18	11
Linoleic $CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	18	6
Linolenic $CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2{=}CH{=}CH(CH_2)_7COOH$	18	6,5
Malonic $HOOCCH_2COOH$	3	15
Succinic $HOOCCH_2CH_2COOH$	4	16
Malic $HOOCCH(OH)CH_2COOH$	4	11
Tartaric $HOOCCH(OH)CH(OH)COOH$	4	6
Fumaric $HOOCCH{=}CHCOOH$	4	4
Benzoic 	7	4
Nicotinic 	6	4
Trichloroacetic CCl_3COOH	2	1
Bromoacetic $BrCH_2COOH$	2	36
Iodoacetic ICH_2COOH	2	5
Deoxycholic 	24	8

Affinity partition can also be used as an analytical method for the measurement of the binding constants and of the number of binding centres in proteins in relation to different ligands[34]. For this purpose, a number of PEG esters of carboxylic acids, both monobasic and dibasic with different numbers of carbon atoms as well as acids containing a double bond, hydroxy-groups, etc., have been synthesised (see Table 1).

Serum albumin (SA) is known to have a high affinity for aliphatic acids. This explains the significant influence of the addition of PEG esters of higher aliphatic acids to the two-phase system on the distribution of SA. In the standard system SA is displaced predominantly to the dextran-containing phase. In the presence of PEG esters, which migrate to the same phase as PEG, the aliphatic acid residues are absorbed on the SA surface.

SA is known to have seven centres which strongly adsorb long-chain aliphatic acids ($K_{ass} = 10^6-10^8$ litre mol^{-1}) and twenty centres with a much lower affinity ($K_{ass} = 10^2-10^3$ litre mol^{-1}).[34] If only strong binding is considered, it is seen that the protein can bind seven molecules of PEG esters. The resulting complex exhibits an affinity for the upper, PEG-containing phase.

An equation has been obtained[35] establishing a relation between the partition coefficient and the chemical structure of the partitioned substance; according to this equation, the introduction of a new chemical group of the given type into the molecule of the complex alters lg K by a constant amount[35]:

$$\lg K = \lg K^* + n\alpha,$$

where K is the distribution constant of the SA–PEG ester complex, K^* the distribution constant of free SA, n the number of PEG ester molecules in the complex, and α the increment in lg K following the introduction of each new ester molecule.

It has been shown[34] that the equation holds for SA–PEG ester complexes. Using different PEG esters, the increment α was determined and the values of n were calculated. In the calculations no account was taken of the decrease of the accessible surface of the protein with increasing number of bound ligand molecules. If this effect is not very great, the distribution in two-phase systems containing PEG esters can serve as a convenient method for the determination of the number of binding centres in the protein molecule. The binding curves (the dependence of lg K on the ester concentration) can be used to calculate the binding constants.

This method for the investigation of the binding of proteins to ligands is particularly convenient when it is necessary to work with small amounts of protein.

In such cases radioactive labels are used to detect proteins in solution. In this respect, the method for the investigation of binding using two-phase systems has advantages over the method of equilibrium dialysis. Another possibility of using "affinity partition" involves the determination of the type of binding centres present in biopolymers, membranes, and cells.

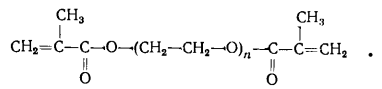
Thus the method based on the distribution of substances in two-phase systems permits not only the purification and separation of biomacromolecules but also yields much information about their various properties, about dimerisation and aggregation, about denaturation under certain conditions, and about the change in the charge of the proteins as a function of pH. The method can also be employed to determine the surface charge of the molecules, their isoelectric points, relative hydrophobic properties, the extent of binding to different ligands, etc.

IV. BIOCHEMICAL ASPECTS OF THE USE OF MONO- AND BI-FUNCTIONAL DERIVATIVES OF POLY(ETHYLENE GLYCOL)

In the description of the properties of two-phase systems the use of disubstituted PEG was already mentioned above[29, 32,33,67], although the need for specifically bifunctional derivatives was not considered.

One of the promising applications of disubstituted derivatives of PEG involves their use as cross-linking agents in the immobilisation of enzymes[36].

One study has already been made on the use of the bifunctionality of PEG in the immobilisation of enzymes[37]. In this study the PEG end groups were esterified by methacrylic acid, which yielded PEG dimethacrylate:



When PEG preparations with different molecular weights were used, polymers were obtained containing at the ends photosensitive functional groups located at the required distance from one another. Next, a mixture, containing the given polymer, enzyme, or microbial cells, was prepared and irradiated for several minutes with ultraviolet light. This yielded matrices cross-linked via their ends and containing the biological materials enclosed in them. The enzyme yeast invertase was immobilised in this way. The photosensitive polymers based on PEG have the following advantages: they form mechanically strong networks, are chemically inert, and are sufficiently permeable to the substrate and the products of the enzymatic reaction. This example by no means exhausts the possibilities of the use of PEG as a cross-linking agent.

In connection with the development of research into the synthesis of medicinal polymeric compounds (MPS), we think it would be extremely useful to synthesise and investigate the properties of such compounds based on PEG. The problem of the determination of the correlation between the structure of the MPS and its physiological activity, which is fundamental, can be solved most rigorously when only a controlled number of pharmacologically active fragments is introduced into the polymer chain. This approach can be used via the chemical modification of the end groups in macromolecules whose functionality is known beforehand.

PEG having hydroxy-groups at the ends of the chain meets these requirements fully.

On the other hand, a necessary requirement which must be met by polymeric carriers, is the immunostimulating activity of the polymer itself. This requirement is also satisfied by PEG, which exhibits the properties of an immunostimulant†.

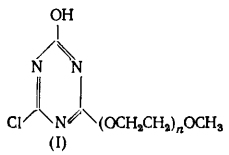
The literature data available at present on the MPS based on PEG involve only one field of application—immunology. The possibility of employing mono- and bi-functional PEG derivatives as antigens for the study of the mechanism of the antigen–antibody interaction has been studied[38]. The interaction of antibodies isolated from immunised animals, with mono- and di-substituted derivatives of 2,4-dinitrophenyl-PEG has been investigated by methods involving the quenching of fluorescence[39] and light scattering[40]. The experimental data obtained in these investigations[38–40] made it possible

†I.N.Topchieva, N.Yu.Alekseeva, V.P.Evdakov, R.V.Petrov, I.V.Savinova, E.D.Filatova, L.I.Khaustova, R.M.Khaitov, and M.B.Temchenko, "Tezisy Doklada na IV Vsesoyuznom Nauchnom Simpoziume "Sinteticheskie Polimernye Materialy Meditsinskogo Naznacheniya"" (Abstracts of Reports at the IVth All-Union Scientific Symposium "Synthetic Polymeric Materials for Medical Purposes"), Dzerzhinsk, 1979, p.5.

to observe structural differences between the binding centres of immunoglobulins, to estimate the distances between the binding centres for two types [class IgG and IgG(T)] of antibodies, and to assess the differences between their conformations in solution.

An important stage in the study of PEG derivatives containing antigenic determinants is the investigation of their activity in vivo. The 2,4,6-trinitrophenylethyl ether of PEG with a molecular weight of 40000, which exhibited a high antigenic activity, was synthesised for this purpose†.

Studies on the chemical modification of proteins with PEG derivatives, which alters the immunological properties of the former, are of great interest[41–43]. The reagent was PEG with a molecular weight of 2000, in which one end group contained the 2-chloro-4-hydroxytriazine moiety, capable of interacting with the amino-groups of the protein, while the other was a hydroxy-group converted into the methoxy-derivative:



(I)

When catalase is treated with this reagent, it is possible to substitute up to 60% of the amino-groups while retaining the enzymatic activity of the protein[41]. A higher degree of substitution of the amino-groups by the reagent reduces the enzymatic activity of catalase. A catalase preparation with a 75% degree of substitution (PEG-catalase) proved to be inactive in relation to the antiserum for native catalase, which was established by gel diffusion and complement fixation methods. The introduction of PEG-catalase into the blood of mice did not lead to the production of antibodies against both PEG-catalase and native catalase. Thus chemical modification of catalase by the PEG reagent yielded a modified enzyme without immunogenic properties. These studies constitute the first step on the way to the solution of the problem of reducing the immunogenic properties of proteins, which will make it possible to extend significantly the therapeutic applications of exogenic enzymes.

A patented method involving the reductive alkylation of the NH_2 groups of enzymes using an aldehyde-derivative of methoxy-substituted PEG and sodium tetrahydroborate was devised in a continuation of the above investigation[42]. The method makes it possible to obtain enzyme preparations with a higher activity and stability compared with those obtained previously.

Reagent (I) has been used[43] for the chemical modification of antigen E, the principal protein allergen of ambrosia pollen. The aim of this modification was to obtain an antigen derivative with a reduced allergenic activity but retaining the immunogenic properties of the native molecule. According to the generally accepted concept, the allergenic activity consists in the liberation in the cell of chemical mediators of allergic symptoms in the interaction of polyvalent antigens with immunoglobulins of class IgE. Chemical modification of antigens, leading to a decrease of the number of accessible antigenic determinants or to a decrease of the affinity for specific antibodies, should reduce their allergenic activity. By controlling the degree and type of chemical modification, it is possible to obtain mixtures of derivatives partly (but not fully) retaining the immunogenic properties of the native protein.

In the interaction of the PEG-reagent with antigen E, containing 18 lysine amino-groups, on average 11 lysine residues reacted. The study of the immunological properties of the PEG derivative of antigen E showed[43] that the latter stimulates the production of specific antibodies, although it is a weaker immunogen than the native protein. At the same time, the PEG-antigen shows a markedly reduced allergenic activity compared with the native antigen. The properties of several derivatives of antigen E, modified via their amino-groups, namely PEG and dextran derivatives, as well as two other derivatives obtained as a result of the introduction of low-molecular-weight groups (*N*-carboxymethyl and butyrimidato-) into the molecule, have been compared[43] (Table 2). Evidently the PEG derivative undergoes a greater decrease of allergenic activity compared with the dextran derivatives, despite the fact that the molecular weight of dextran significantly exceeds that of the fragment of the polyoxyethylene chain. It is of interest to note that both these derivatives have the same molecular volumes, which follows[43] from the identity of their elution volumes in gel chromatography on Sepharose 6B.

Table 2. The properties of derivatives of antigen E modified at the lysine amino-group[43].

Derivative of antigen E	Molecular weight	No. of modified lysine residues	Molecular weight of introduced group	Overall charge of modified antigen	Relative allergenic activity
Native protein	38000	0	0	−9	1
PEG derivative	53000	7	2100	−16	0.024
N-Carboxymethyl derivative	39000	16	58	−31	0.56
Butyrimidato-derivative	39000	16	72	−9	1
Dextran derivative	140000	4	25000	−9	0.15

This finding can probably be explained on the basis of the difference between the degree of compactness of the PEG and dextran macromolecules in aqueous solutions. The more compact dextran molecules are less effective as regards the steric blocking of the antigenic determinants compared with the less compact PEG groups. We are probably dealing in this instance with exclusion effects generated by different polymers, which are now bound covalently to the molecules of the antigen protein, in relation to the antibody proteins. Examination of the mechanism of the action of PEG-containing proteins from this point of view makes it clear why the modification of the protein by the PEG reagent does not affect its interaction with low-molecular-weight substrates (catalase activity) but hinders significantly the protein–protein interactions (the immunogenic and allergenic activities).

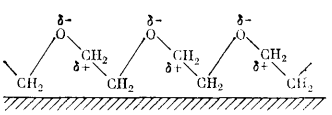
V. THE SURFACE-ACTIVE PROPERTIES OF POLY(ETHYLENE GLYCOL)

The usefulness of PEG for the immobilisation of various physiologically active compounds is also associated with its ability to exert a specific influence on the lipid layer of membranes[44]. The idea of the influence of PEG on the structure of lipids arose as a result of observations that PEG induces the merging of plant protoplasts[45], chicken erythrocytes, chicken erythrocytes with yeast protoplasts[46], and mammalian cells[47].

In order to investigate the molecular mechanism of the action of PEG on cells, a study has been made[44] of the influence of PEG on phospholipid monolayers simulating cell membranes. The authors considered how relations of the surface pressure–area and surface potential–area type vary for phosphatidylcholine and phosphatidylethanolamine monolayers when various low-molecular-weight compounds (glycerol, sorbitol, and dimethyl sulphoxide) as well as PEG specimens with different molecular weights are introduced into the aqueous phase. It was found that all the compounds tested caused considerable changes in the surface potential of the phospholipid layer in the state of dense molecular packing. However, the orders of magnitude of the concentrations of the additive causing the maximum decrease of the surface potential are significantly different for the low-molecular-weight compounds and PEG. Thus the optimum concentrations of the additives in the case of monolayers of dipaltimoylglycerylphosphorylcholine are 3.8 M glycerol, 3 M dimethyl sulphoxide, 1.5 M sucrose, and 2 M sorbitol. On the other hand, the corresponding concentrations of different PEG fractions are 4.2×10^{3} M PEG-6000, 1.5×10^{-3} M PEG-15000, 2.5×10^{7} M PEG-300000, and 1×10^{9} M PEG-5000000. Thus, together with the much greater specificity of the action of PEG, one may note a significant dependence of its influence on its molecular weight.

The authors[44] do not reach a definite conclusion concerning the molecular mechanism of the action of PEG on membranes. In order to account for its role, one should probably turn to the properties of PEG at the interface, primarily at the water–air interface. A detailed study has been made of this problem[48] and it has been shown that PEG is able to form monomolecular films on the surface of water. Depending on the contraction pressure, the polymer can exist in two conformations—a looser conformation occupying an area of 28 Å^2 per monomer unit and a compact conformation occupying an area less than 16 Å^2 per unit.

The study of the behaviour of PEG under polarographic conditions[49] showed that it is adsorbed on negatively charged surfaces in such a way that the negatively charged polar atoms of the ether oxygen are directed towards water, while the non-polar $-CH_2-CH_2$ groups are directed to the negatively charged surface of mercury:



(3)

According to Hillson's calculations[49], the area occupied by the monomeric PEG unit, adsorbed on such a surface, is 13 Å^2.

These data suggest that, when PEG interacts with lipid monolayers, type (3) dipole interactions between the PEG units and the dipoles of the polar head of the lipid also take place. If this is the case, then the range of compounds interacting with PEG and capable of forming complexes of the type resembling the polymeric complexes of PEG with polymeric acids[50] can be greatly extended; numerous surface-active compounds, capable of forming monolayers on the surface of water, should be included among them.

On the other hand, the ability of PEG to act on membranes suggests that this property should be manifested not only in the phenomenon of cell fusion but also in other subcellular processes such as endocytosis, exocytosis, etc., which is extremely important for the functioning of physiologically active compounds incorporating PEG fragments.

Interactions of the dipole–dipole type probably constitute the basis of the molecular mechanism of the action of PEG as a stabiliser of hydrophobic sols[23]. It is striking that in this case one also notes a pronounced dependence of the stabilising activity of PEG on its molecular weight.

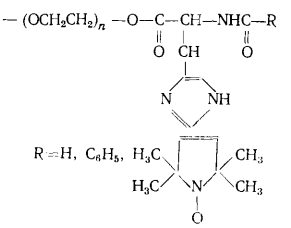
VI. THE SYNTHESIS OF DISUBSTITUTED DERIVATIVES OF POLY(ETHYLENE GLYCOL)

The great practical importance of PEG and the wide-scale employment of this substance and its derivatives in various fields of molecular biology have stimulated the development of research into the chemical modification of the hydroxy-groups at the ends of PEG. We may note that the thoroughly investigated hydroxyethylation reactions, used to synthesise non-ionic detergents[51], make it possible to obtain only monosubstituted PEG derivatives. The most rational method of synthesising bifunctional PEG derivatives consists in the chemical modification of the end groups of PEG.[51,52] Despite their apparent simplicity and triviality, these reactions have in fact many characteristic features and merit a more detailed examination.

PEG specimens with molecular weights up to 20000 are obtained mainly by the hydroxyalkylation method; they contain hydroxy-groups at their ends. Polymers of expoxyethane having a high molecular weight are obtained by other methods; as a rule, they do not contain functional groups at their ends[52].

The hydroxy-groups of PEG undergo reactions of the type usual for alcohols. Numerous PEG derivatives of the type $R-O-(CH_2-CH_2-O)_n-R$, where R = Me, Ph, CH_3CO, or C_6H_5CO, and of the type $R-(CH_2-CH_2-O)_nR$, where R = C, Br, PhS, etc., are known. The reactions between PEG and the corresponding low-molecular-weight reagents are in many cases quantitative and can therefore be used to determine the number-average molecular weight and the molecular-weight distribution[53]. Table 3 presents a list of PEG derivatives substituted in their end groups.

The specific features of the esterification of the hydroxy-groups of PEG were observed for the first time in the synthesis of polymeric derivatives of histidines having the general formula[71]



It was found that in all these cases it is impossible to achieve the complete substitution of the PEG end groups. Special experiments, whose aim was to increase the yield of the polyoxyethylene ethers by modifying the condensing agent and by altering the nature of the solvent and the order of mixing of the reactants, did not lead to a significant alteration of the degree of substitution. All these findings apparently reflect internal features, characteristic of the PEG chain, and definite structural changes occurring in the macromolecule on modification of the latter by the given substituents. The introduction of a polar group at the end of the polymer chain, for example, an imidazole or amide group, leads to structure formation, which hinders the complete modification of all the end groups.

Table 3. Poly(ethylene glycol) derivatives.

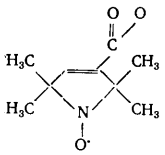
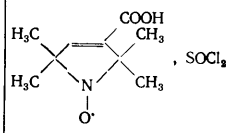
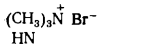
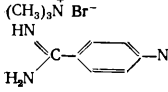
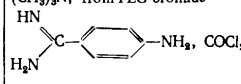
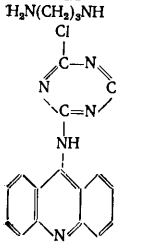
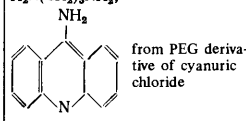
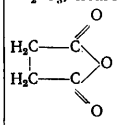
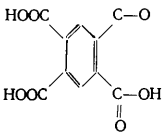
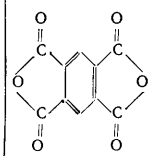
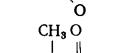
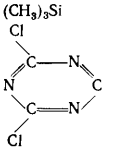
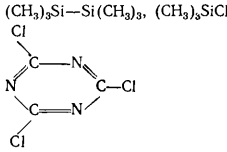
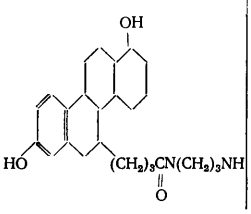
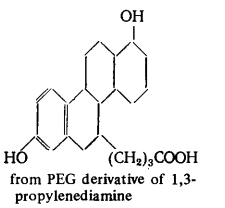
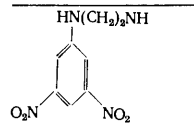
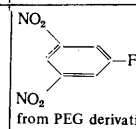
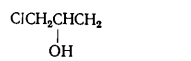
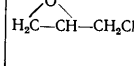
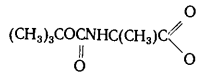
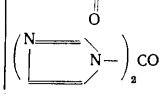
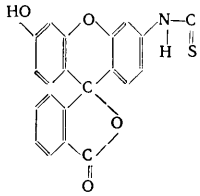
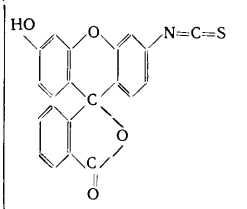
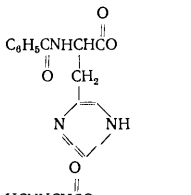
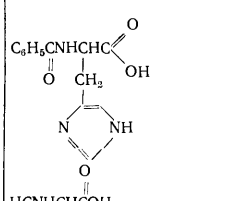
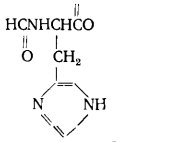
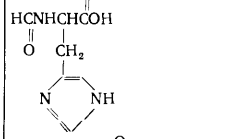
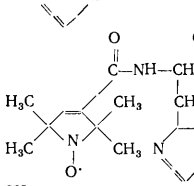
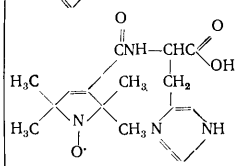
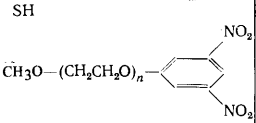
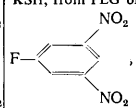
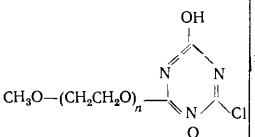
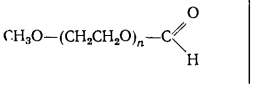
End of group of PEG derivative	Formula of reagent	Yield, %	Refs.
Br	PBr_3	quantitative	29
Cl	$SOCl_2$	quantitative	54
CH_3O	CH_3ONa, from PEG chloride	quantitative	55
C_6H_5O	C_6H_5ONa, from PEG chloride	quantitative	56
C_6H_5S	C_6H_5SNa, from PEG chloride	quantitative	56,57,58
	$(CH_3CO)_2O$	quantitative	59
	CCl_3COCl	quantitative	53
	C_6H_5COCl	quantitative	60
		quantitative	61,62
	$(CH_3)_3N$, from PEG bromide	quantitative	29
		quantitative	66
$H_2N(CH_2)_2NH$	$NH_2(CH_2)_2NH_2$, from PEG bromide	quantitative	33
$H_2N(CH_2)_3NH$	$H_2N(CH_2)_3NH_2$, from PEG bromide		
	 from PEG derivative of cyanuric chloride	quantitative	67
SO_3Na	Na_2SO_3, from PEG bromide	quantitative	29
		quantitative	68
		quantitative	68
	$C_{16}H_{33}COCl$	quantitative	34,63
		*	37
$(CH_3)_3Si$	$(CH_3)_3Si-Si(CH_3)_3$, $(CH_3)_3SiCl$	quantitative	54
		quantitative	64
	 from PEG derivative of 1,3-propylenediamine	60	33

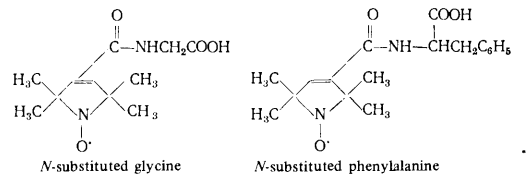
Table 3 (contd.).

End of group of PEG derivative	Formula of reagent	Yield, %	Refs.
	 from PEG derivative of 1,2-ethylenediamine	quantitative	32,38,41
		*	65
	$(CH_3)_3COCNHCH(CH_3)COOH$, 	80	70
		2	6
		37.5	71
		27	72
		8	73
SH	KSH, from PEG bromide	8	74
	 from monomethoxy- derivative of PEG	*	39
	reagent not indicated, from monomethoxy-derivative of PEG	*	41
	MnO_2, from monomethoxy-derivative of PEG	*	42

*Yield not indicated.

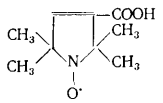
In order to analyse this problem, it is necessary to alter consecutively the nature of the substituent and to follow the changes in the yield and structural characteristics of the

resulting polymers. An attempt has been made[73] at a systematic investigation of the esterification reaction by employing a number of acids RCOOH, where R are aminoacid residues containing the iminoxy-substituent as the *N*-protecting group:



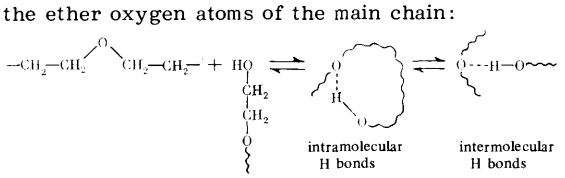
N-substituted glycine *N*-substituted phenylalanine

The simplest spin-labelled acid species, namely the 3-carboxy-2,2,5,5-tetramethylpyrrolin-1-yloxy-radical



was used as the first member of the series. It was shown[73] that the reaction involving the first member of the series goes almost to completion, in agreement with the literature[61]. On passing to the next member, a decrease of the degree of substitution to 35–40% was observed, while in the case of the PEG derivative of phenylalanine the degree of substitution fell to 8%. Thus one may conclude that the introduction of the amide group into the PEG molecule decreases significantly the reaction yield and to a greater extent the more bulky the substituent introduced into the composition of the acid residue.

In order to account for the characteristic features of the reactions described by Topchieva et al.[73], we should consider initially the modification of PEG by carboxylic acids without polar groups. As a rule, such reactions are carried out in non-polar media in which the hydroxy-end groups of the initial PEG form intra- or inter-molecular hydrogen bonds with the ether oxygen atoms of the main chain:

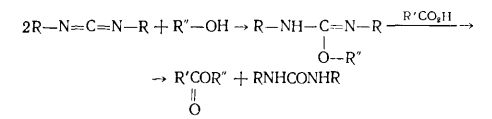


It was shown[60] that, depending on the PEG concentration, one or other type of hydrogen bonds predominate. It was natural to suppose that free hydroxy-groups are involved in the esterification reaction and, as the latter proceeds, the equilibrium shifts towards the non-associated hydroxy-groups.

On the other hand, if the polar group of the substituent is at the end of the macromolecule, then the latter, like the hydroxy-group will tend to form a hydrogen bond (intra- or inter-molecular) with the oxygen atoms of the main chain. The decrease of the degree of substitution on passing to a substituent incorporating polar groups indicates a decrease of the accessibility of the hydroxy-groups of the unreacted PEG. Presumably the hydroxy-groups of PEG, forming hydrogen bonds with the associated polymer molecules, become sterically relatively inaccessible for the reactants.

This hypothesis makes it possible to explain the experimentally observed[73] decrease of the degree of substitution following the introduction of substituents containing polar groups into the ends of the chain, on the one hand, and the dependence of the degree of substitution on the size of the terminal substituent, on the other. Indeed, the greater the bulk of the substituent the looser become the associated species and the greater the number of free hydroxy-groups which can be "entangled" within the associated macromolecules.

In this connection it is of interest to analyse data[34] on the synthesis of a number of polyoxyethylene ethers by the carbodiimide method. The authors[34] obtained an activated PEG derivative by treating it with dicyclohexylcarbodiimide and this derivative was then introduced into a reaction with a carboxylic acid:



The yields of the polymeric esters proved to be very low (Table 1). On the other hand, when palmitoyl chloride is used in the synthesis of the PEG ester of palmitic acid, then esters with a degree of substitution of approximately 80% are obtained. Preliminary activation of PEG by dicyclohexylcarbodiimide apparently leads to the formation of PEG derivatives containing the R–NH–C(=O–R′)= group, whose structure is very similar to that of the amide group, which can also form hydrogen bonds leading to the formation of associated macromolecular species. The correlation between the increase in the size of the substituents and the decrease of the degree of substitution of the esters is striking. Quantitative substitution could apparently be attained if dicyclohexylcarbodiimide was used to activate the carboxy-component with subsequent introduction of the glycol.

A considerable advance in the development of research into the chemical modification of PEG was made in studies[77,78] devoted to the synthesis of polyoxyethylene esters of aminoacids and peptides[75–78]. In the first place, using a large excess of low-molecular-weight reactants, the authors were able to obtain high yields (80–99%) of *N*-protected aminoacid esters by carrying out the reaction in an aqueous or organic solvent ("the liquid-phase method of synthesis")[77,78]. Next, as a result of the so-called crystallisation method which they developed[70], the authors were able to reduce greatly the duration of the synthesis by increasing the efficiency of the elimination of unreacted substances and impurities from the reaction products. Finally, another advantage of the use of PEG as the *C*-terminal protecting group consists in the fact that the latter facilitates the dissolution of sparingly soluble peptides in solvents of different chemical types, which makes it possible to investigate their conformational state in solutions by the method of circular dichroism[70]. We may note that the possibility of using this method in relation to PEG-peptides is due to the optical transparency of PEG in the visible and ultraviolet regions up to 190 nm.

The hydrophobic octapeptide of the myoglobin sequence 66–73 was investigated by this method[70] and the influence of the substituted or free *N*-terminal amino-group on the conformation of the peptide was observed. It was shown that the blocked octapeptide is more helical than the corresponding peptide with an unsubstituted amino-group. The conformational state of the PEG-esters of nona- and deca-alanines was studied in the same investigation in two solvents—trifluoroethanol and water—and it was shown that the peptide with the free amino-group has the β-conformation in both solvents. The corresponding peptide containing the *N*-protecting group has the helical conformation. Hence the authors[77] concluded that the terminal amino-group has a decisive influence on the formation of the β-structure of the peptide. It is striking that, following the introduction of terminal peptide fragments, capable of forming stable conformational isomers, the effects of the interaction of these groups with the main PEG chain in

organic solvents become minimal. However, in aqueous solutions of PEG-reagents containing hydrophobic end groups there is a possibility of hydrophobic interactions between the non-polar groups of the peptide fragment, leading to the formation of micellar structures in which the hydrophobic nucleus of the micelle consists of the non-polar end groups and the role of the hydrophilic surround is played by the polymeric PEG chains. Association of a similar type has been observed[71] for polyoxyethylene esters of *N*-substituted benzoylhistidines.

In conclusion we should like to emphasize that the study of the interaction of a polymer with biomacromolecules in vitro or with an organism in vivo should develop in parallel with the study of its physicochemical properties. One may hope that this approach will in fact lead to a mutual enrichment of these types of research.

REFERENCES

1. T.C.Laurent, Eur.J.Biochem., **21**, 498 (1971).
2. T.C.Laurent, B.N.Preston, and B.Carlsson, Eur. J.Biochem., **43**, 231 (1974).
3. Yu.M.Evdokimov, N.M.Akimenko, N.E.Glukhova, A.S.Tikhonenko, and Ya.M.Varshavskii, Mol.Biol., **7**, 151 (1974).
4. B.I.Kurganov, I.N.Topchieva, N.P.Lisovskaya, N.A.Chebotareva, and O.Ya.Notarius, Biokhimiya, **44**, 629 (1979).
5. P.H.Iverius and T.C.Laurent, Biochim.Biophys.Acta, **133**, 371 (1967).
6. A.McPherson, J.Biol.Chem., **251**, 6300 (1976).
7. M.Ceska, Experientia, **28**, 146 (1972).
8. M.Ceska, Experientia, **27**, 767 (1971).
9. F.W.Janssen and H.W.Ruelius, Biochim.Biophys.Acta, **151**, 330 (1968).
10. A.Polson, G.M.Potgieter, J.F.Largier, G.E.F.Mears, and E.J.Jourhert, Biochim.Biophys.Acta, **82**, 463 (1964).
11. P.W.Chun, M.Fried, and E.F.Ellis, Anal.Biochem., **19**, 481 (1967).
12. T.C.Laurent and A.G.Ogston, Biochem.J., **89**, 249 (1963).
13. T.C.Laurent, B.N.Preston, H.Pertoft, B.Gustafsson, and M.McCabe, Eur.J.Biochem., **53**, 129 (1975).
14. T.C.Laurent, Biochem.J., **93**, 106 (1964).
15. V.Jancsik and T.Keleti, J.Mol.Catal., 1, 137 (1975/1976).
16. V.N.Tsvetkov, V.E.Eskin, and S.Ya.Frenkel', "Struktura Makromolekul v Rastvorakh" (The Structure of Macromolecules in Solutions), Izd.Nauka, Moscow, 1964, p.55.
17. T.C.Laurent, "The Chemical Physiology of Mucopolysaccharides", Little, Brown and Co., 1967, p.153.
18. E.Edmond and A.G.Ogston, Biochem.J., **109**, 569 (1968).
19. F.E.Bailey and R.W.Callard, J.Appl.Polym.Sci., 1, 373 (1959).
20. G.G.Hammes and P.B.Roberts, J.Amer.Chem.Soc., **90**, 7119 (1968).
21. K.H.Ebert, Monatsh., **98**, 1128 (1967).
22. J.Goldfarb and S.Rodriguez, Makromol.Chem., **116**, 96 (1968).
23. A.A.Baran, I.M.Solomentseva, V.V.Man, and O.D.Kurilenko, Dokl.Akad.Nauk SSSR, **207**, 363 (1972).
24. P.-A.Albertsson, "Partition of Cell Particles and Macromolecules", Almqist and Wiksell, Stockholm, 1971.
25. G.Johansson, Biochim.Biophys.Acta, **221**, 387 (1970).
26. P.-A.Albertsson, Adv.Protein Chem., **24**, 309 (1970).
27. S.Sasakawa and H.Walter, Biochemistry, **11**, 2760 (1972).
28. G.Blomquist, Biochim.Biophys.Acta, **420**, 81 (1976).
29. G.Johansson, Methodological Developments in Biochemistry, **2**, 155 (1973).
30. V.P.Shandhag and C.-G.Axelsson, Eur.J.Biochem., **60**, 17 (1975).
31. C.-G.Axelsson and V.P.Shandhag, Eur.J.Biochem., **71**, 419 (1976).
32. S.D.Flanagan and S.H.Barodes, J.Biol.Chem., **250**, 1484 (1975).
33. P.Hubert, E.Dellacherie, J.Neel, and E.-E.Baulieu, FEBS Letters, **65**, 169 (1976).
34. G.Johansson, Biochim.Biophys.Acta, **451**, 517 (1976).
35. A.J.P.Martin, Biochem.Soc.Symp., **3**, 4 (1949).
36. I.V.Berezin (Editor), "Immobilizovannye Fermenty" (Immobilised Enzymes), Izd.Moskov.Gos.Univ., Moscow, 1976, Vol.1, p.116.
37. S.Fukui, A.Tanaka, T.Jida, and E.Hasegawa, FEBS Letters, **66**, 179 (1976).
38. M.P.Cooke, B.G.Archer, and H.Krakauer, Biochem. Biophys.Res.Comm., **57**, 1032 (1974).
39. B.G.Archer and H.Krakauer, Biochemistry, **16**, 615 (1977).
40. B.G.Archer and H.Krakauer, Biochemistry, **16**, 618 (1977).
41. A.Abuchowski, T.van Es, N.C.Palczuk, and F.F.Davis, Fed.Proc., **33**, 1317 (1974).
42. G.P.Royer, US P.4002531 (1977); Chem.Abs., **87**, 129550 (1977).
43. T.P.King, L.Kochoumian, and L.M.Lichtenstein, Arch.Biochem.Biophys., **178**, 442 (1977).
44. B.Maggio, Q.F.Ahkong, and J.A.Lucy, Biochem.J., **158**, 647 (1976).
45. K.N.Kao and M.R.Michayluk, Planta, **115**, 355 (1974).
46. Q.F.Ahkong, W.Tampion, and J.A.Lucy, Nature (London), **256**, 208 (1975).
47. G.Pontecorvo, Somatic Cell Genet., 1, 397 (1975).
48. R.L.Schuler and W.A.Zisman, J.Phys.Chem., **74**, 1523 (1970).
49. P.J.Hillson, J.Phologr.Sci., 11, 225 (1963).
50. I.M.Papisov, V.Yu.Baranovskii, V.Ya.Chernyak, A.D.Antipina, and V.A.Kabanov, Dokl.Akad.Nauk SSSR, **199**, 1364 (1971).
51. M.J.Schick (Editor), "Nonionic Surfactants", Marcel Dekker, New York, 1966.
52. "Encyclopedia of Polymer Science and Technology", 1967, Vol.6, p.103.
53. J.-C.Galin, M.Galin, and P.Calme, Makromol.Chem., **134**, 273 (1970).
54. L.Favretto, G.P.Marletta, and L.F.Gabrielli, J.Chromatog., **50**, 304 (1970).
55. Y.-K.Leung, Polymer, **17**, 374 (1976).
56. L.Favretto, G.P.Marletta, and L.F.Gabrielli, J.Chromatog., **46**, 255 (1970).
57. C.Calzolari, L.Favretto, and B.Stancher, J.Chromatog., **54**, 373 (1971).
58. C.Calzolari, L.Favretto, and B.Stancher, J.Chromatog., **47**, 209 (1970).
59. L.Gildenberg and J.R.Trowbridge, J.Amer.Oil.Chem. Soc., **42**, 69 (1965).
60. A.M.Affi-Effat and J.N.Hay, Polymer Letters, **9**, 651 (1971).
61. P.Törmälä, J.Martinmaa, K.Silvennoinen, and K.Vaantera, Acta Chem.Scand., **24**, 3066 (1970).

62. A.B.Shpiro, K.Baimagambetov, M.G.Gol'dfel'd, and E.G.Rozantsev, Zhur.Org.Khim., **8**, 2263 (1972).
63. V.P.Shanbhag and G.Johansson, Biochem.Biophys. Res.Comm., **61**, 1141 (1974).
64. L.Monnerie and J.Neel, Compt.rend., **256**, 1528 (1963).
65. D.V.Emerson, W.K.Laugudon, and J.Niu, Macromolecules, **9**, 667 (1976).
66. G.Takerkart, E.Segard, and M.Monsigny, FEBS Letters, **42**, 214 (1974).
67. L.Monnerie and J.Neel, Compt.rend., **258**, 4986 (1954).
68. H.Inagaki and M.Tanaka, Makromol.Chem., **74**, 145 (1964).
69. H.Tanaka, T.Janagida, A.Feramoto, and H.Fujita, J.Phys.Chem., 71, 2415 (1967).
70. M.Mutter, H.Mutter, R.Uhmann, and E.Bayer, Biopolymers, **15**, 917 (1976).
71. I.N.Topchieva, A.B.Solov'eva, B.I.Kurganov, and V.A.Kabanov, Vysokomol.Soed., **A14**, 825 (1972).
72. I.N.Topchieva, A.B.Solov'eva, and V.A.Kabanov, Dokl.Akad.Nauk SSSR, **199**, 1084 (1971).
73. I.N.Topchieva, G.F.Peker, G.B.Postnikova, B.I.Kurganov, and V.A.Kabanov, Vysokomol.Soed., **A15**, 2153 (1973).
74. I.N.Topchieva and V.A.Kabanov, Vysokomol.Soed., **12**, 542 (1970).
75. M.Mutter and H.Hagenmaier, Angew.Chem., **83**, 883 (1971).
76. E.Bayer and M.Mutter, Nature, **237**, 512 (1972).
77. E.Bayer and M.Mutter, Chem.Ber., **107**, 1344 (1974).
78. M.Mutter and E.Bayer, Angew.Chem., **86**, 101 (1974).

Faculty of Chemistry,
Moscow State University

Translated from *Uspekhi Khimii*, **49**, 518-556 (1980) U.D.C. 547.927.41 + 548.737

The Structure of Organocyclosiloxanes

V.E.Shklover and Yu.T.Struchkov

X-Ray results form the basis of a discussion of the stereochemistry of monocyclic siloxanes—monomers yielding polyorganosiloxanes—as well as the structure of higher polycyclic siloxanes, simple oligomers. A list of 105 references is included.

CONTENTS

I.	Introduction	272
II.	Monocyclic siloxanes	273
III.	Spirocyclic siloxanes	279
IV.	Cyclolinear siloxanes	280
V.	Other polycyclic siloxanes	284
VI.	Crystalline structure of organocyclosiloxanes	286
VII.	Conclusion	292

I. INTRODUCTION

The practical usefulness of two classes of polymers having inorganic main chains—polycyclosiloxanes and polyphosphazens—is firmly established. Both hetero-organic and macromolecular aspects of the chemistry of organosiloxanes and organophosphazens have been studied in some detail.

Among the main lines of attack on which investigators attempting to produce novel polymers with inorganic main chains concentrate their efforts, three are directly related to the subject of the present Review—firstly the production of polymeric molecules having a non-traditional structure (cyclolinear, spirocyclic, etc.),[1,2] secondly a transition to polymers having main chains differing in composition (polysilazanes, polyheterosiloxanes, polyphosphoxans, polysilthians, polyborazens, etc.),[1-4] and thirdly study of the influence of the framework both on the character of the bond and the conformation of the inorganic unit and on the overall properties of the polymeric product[5].

There is no doubt about the importance of structural investigations for these three lines of research. The increasing number of studies, consequent mainly on the growth in instrumental physicochemical methods, have been made at different structural levels, from the simplest molecules containing only one silicon (phosphorus, etc.) atom in the organic framework to polymeric macromolecules of molecular mass $\sim 10^6$. The investigators usually attempt to relate their structural information to the observed (or supposed) properties of the compounds. The transferability of such conclusions to real compounds depends, of course, on the level at which the structural investigation has been made. Research on the structure of polymers is "closer to life" than that on simple molecules, but the information is considerably more complicated to interpret than in the latter case. Therefore the qualitative aspect predominates in the former, and the quantitative aspect in the latter studies.

The present Review summarises results of X-ray structural investigations on organocyclosiloxanes, which have been more thoroughly studied in relation to polymers than have other types of hetero-organic monomers (although numerically organophosphazens predominate), which helps to reveal several rules useful in analysing the structure of other classes of monomers.

In analysing and comparing structures it has been borne in mind that these compounds serve either as monomers or as oligomers of polymers containing common structural units. The following restrictions must, of course, be taken into account in elucidating correlations between the properties of the lower monomeric (and oligomeric) structures and those of the polymers. (i) The properties of polymers depend on their structure at all levels, i.e. on the primary, secondary, and tertiary structures (crystal-chemical analysis of the structure of the monomer will give information only on the primary and to some extent the secondary structures). (ii) Crystal-chemical analysis applies to molecules situated in a crystal field, which may change the equilibrium conformation of the free (reacting) molecule. (iii) It is improbable that the solid-phase polymerisation of siloxanes will have a purely topochemical mechanism: it will most likely occur in amorphous zones, while the elements of the crystalline order will be retained.

These and perhaps other limitations on crystal-chemical conclusions regarding the structure of polymeric products and reactivity in the solid phase must be borne in mind by the reader of the Review. However, it appears to the Reviewers that such restrictions do not so much diminish the practical value of the crystal-chemical approach as emphasise the complexity of the problems and thereby justify the idealised approach employed in the Review.

The chemistry of organosiloxanes is largely that of organosiloxane rings. Very great variation in size is characteristic of $(SiO)_n$ rings†, which may be either isolated (monocyclic siloxanes) or fused, with extremely diverse modes of fusion (spirocyclic, cyclolinear, and other polycyclosiloxanes).[1] The natural sequence in which cyclosiloxane structures are discussed in this Review (initially monocyclic, and then more complicated fused polycyclic systems) enables the structure of complex polycycles to be analysed in terms of results for their simpler constituents.

†The existence of disiloxane rings $(SiO)_2$[6,7] has not yet been confirmed by means of X-rays. Rings $(SiO)_n$ having $n = 10$–15 are probably of practical value, although there are indications of the existence of rings with n up to 400.[8]

II. MONOCYCLIC SILOXANES

Table 1 gives the most important structural constants for trisiloxane rings D_3# in monocyclic cyclotrisiloxane derivatives investigated by X-ray structural analysis. These rings have an approximately planar structure in which the maximum divergence of atoms from the planes of the rings is $\Delta = 0.01$ Å. Such a planar structure is evidence of some steric strain in these rings. Indeed the SiOSi bond angles in trisiloxane rings (131–134°) are among the smallest known. However, disruption of the planarity of the rings would have implied a still greater decrease in these bond angles, which, as will be shown below, would have weakened the silicon–oxygen bonds and diminished the stability of the rings. Even in complicated sterically strained fused polycyclic systems the departure of atoms from the planes of the trisiloxane rings does not exceed 0.4 Å (see below).

Table 1. Data on trisiloxane rings in monocyclotrisiloxanes.

No.	Formula	l_{Si-O}, Å	α_{SiOSi}	Δ, Å	Ref.
(I)*	$(Me_2SiO)_3$	1.61	136°	0**	9
(II)	$(Ph_2SiO)_3$	—1.64	131.9°	0.07	10
(III)	*cis*-$(MePhSiO)_3$	1.65	132.3°	0.10	11
(IV)	*trans*-$(MePhSiO)_3$	1.65	132°	0.05	12
(V)	$Na_3[PhSi(O)O]_3$	1.647	133.5°	0.029	***

*Determination of this structure was inaccurate, and has been disregarded in the comparison with others.

**Molecule in a special position (see text).

***This compound crystallises as the octahydrate $Na_3(C_6H_5SiOO)_3.8H_2O$. Some of the results of this investigation have appeared in Ref. 13.

The molecule (I) has an ideally planar structure. Its great intrinsic symmetry (D_{3h}) is retained even in the crystal, where the molecules occupy unique positions (space group $R3m$, $Z = 1$). The impossibility of packing a large number of bulky phenyl substituents in a sufficiently highly symmetrical space group probably prevents realisation in the crystal of the potentially high intrinsic symmetry of molecule (II). An example of the geometrical isomerism of cyclosiloxanes is provided by molecules (III) and (IV). Organosiloxanes are often formed as mixtures of geometrical isomers. In some cases clear identification of isomers acquires practical importance, e.g. with isomers (III) and (IV), which differ sharply in their polymerisation properties[14]. Other examples of the use of X-ray structural analysis to solve problems of the identification of isomers will be found in the Review.

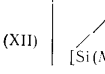
#The notation adopted for the configurations of organosiloxanes combines the symbols for the four structural units[8]

Functionality	Symbol	Unit
Mono	*M*	$R'R''R'''SiO_{1/2}$
Di	*D*	$R'R''SiO_{2/2}$
Tri	*T*	$RSiO_{3/2}$
Tetra	*Q*	$SiO_{4/2}$

The subscript following the oxygen atom denotes the number of oxygen atoms per silicon atom (e.g. $\frac{3}{2}$ indicates that the silicon atom is attached to three oxygen atoms, each of which is combined with another silicon atom).

Great interest attaches to the structure of the siloxane anion in sodium *cis*-1,3,5-triphenylcyclotrisiloxane-1,3,5-triolate (V). The distance Si–O^- to the ionised oxygen atom was first determined (on the average 1.586(2) Å). The T_3 ring in structure (V) is appreciably "flattened" in comparison with the D_3 rings in molecules (II)–(IV), and has well defined C_{3v} symmetry (crown conformation), with the plane of the three cyclic oxygen atoms located farther from the exocyclic oxygen atoms than is the parallel plane of the three silicon atoms. If the conformation of the ring can be explained by the *T* character of the cyclic silicon atoms (C_{nv} symmetry is characteristic even of larger T_n rings—see below), the great "flatness" is probably due to mutual electrostatic repulsion of Si–O^- groups. The cyclic silicon–oxygen bond lengths in (V) are the same as in other trisiloxane rings.

Table 2. Data on tetrasiloxane rings in monocyclotetrasiloxanes*.

No.	Formula	l_{Si-O}, Å	α_{SiOSi}	Symmetry of ring	Conformation of ring	Angles of fold	Ref.
(VI)	$(Me_2SiO)_4$ (β-form)	1.65	142.5	C_i	chair	31.3°	15
(VII)	$[(Me_2SiO)(Ph_2SiO)_2]_2$	1.62	148.5°	S_4	boat	27.5° и 31	16
(VIII)	*cis*-$[(MePhSiO)(Me_2SiO)]_2$	1.63	144.2°	C_2	boat	35.5°	17
(IX)	*trans*-$[(MePhSiO)(Me_2SiO)]_2$	1.622	145.2°	C_i	chair	31°	18
(X)	$(R_2SiO)_4$	1.62	149°	C_i	chair	34.2°	19, 20
(XI)	*cis*-$[(Me(OH)SiO(Ph_2SiO)]$	1.622	144°	S_4	boat	40.2°	см.*
(XII)		1.636	140°	C_i	chair	24°	см.*

*The angle of fold of the ring in (IX) is close to that found for structure (VI); the chair conformation in structure (X) differs (see text) from the chair conformation in (VI); for the structures (XI) and (XII) see Refs. 100 and 101 respectively; $R_2 = [CH_2]_4$; and $R' = CH_2.C(COOC_2H_5)_2.CH_2$.

The rings in organocyclosiloxanes $(RR'SiO)_n$ with $n > 3$ are non-planar, and hence may be expected to exist in different conformations. Table 2 gives data on structures having eight-membered tetrasiloxane rings. Comparison of Tables 1 and 2 shows§ that silicon–oxygen bonds are shorter in tetrasiloxane than in trisiloxane rings (on the average respectively 1.62 and 1.65 Å), and the SiOSi angles are larger (respectively 142–149° and 131–134°). Thus the silicon–oxygen bonds are more stable in D_4 than in D_3 rings.

Fig. 1 shows diagrammatically possible conformations of cyclic systems $(AB)_4$ comprising alternating atoms, which include tetrasiloxane rings. With the SiOSi bond angles observed in tetrasiloxanes (142–149°) all the conformations indicated in Fig. 1 (with the exception of D_{4h}) are possible, as well as conformational transitions between them.

X-Rays have been used to study the structure of the low-temperature β modification of octamethylcyclotetrasiloxane, which at −16.3 °C passes into the high-temperature α modification melting at 17.5 °C. In a crystal of the β modification

§It must be borne in mind when making the comparison that structures (I) and (VI) have not been determined with great accuracy.

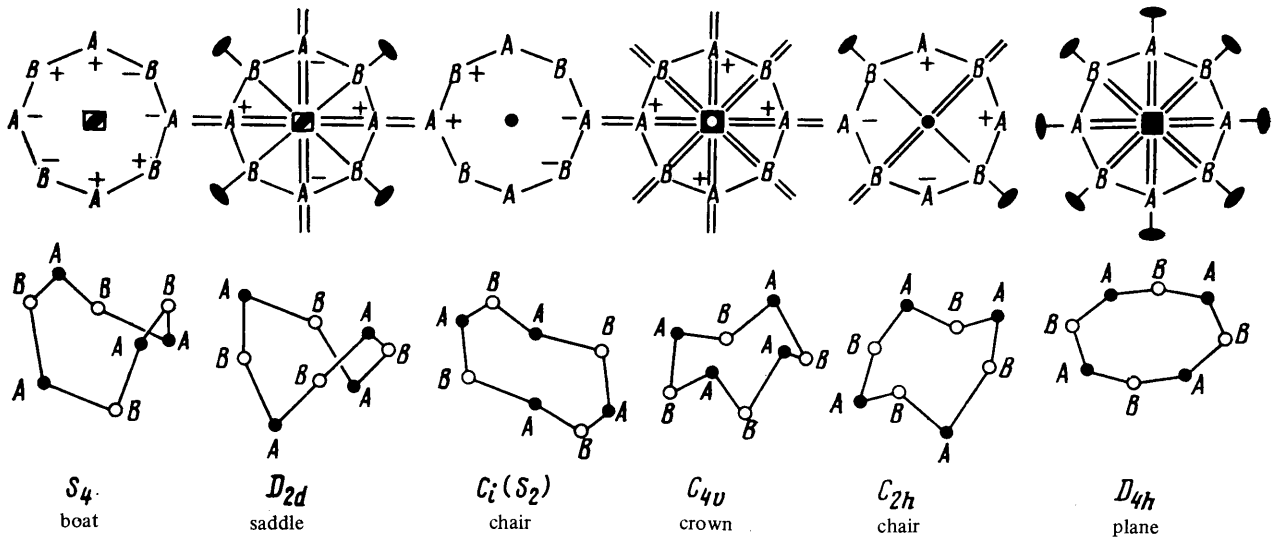


Figure 1. Possible ideal conformations of $(AB)_4$ rings comprising alternating atoms[16]. The plus and minus signs show the divergence of atoms above and below the mean plane of the ring.

the molecules are located at centres of symmetry, and the D_4 ring has a chair conformation (Fig. 1).[15] The molecule is located at a special position also in a crystal of the α modification, but now on a fourfold axis: i.e. it has a boat or saddle conformation[15]. It was supposed originally[15] that the phase transition involved the appearance of orientational disorder, since it was assumed by analogy with organic rings that the heat of transition would be too small to change the conformation of the molecule. A later spectroscopic investigation showed[21] that conversion into the high-temperature modification was a conformational transition with a change in the intrinsic symmetry of the molecule.

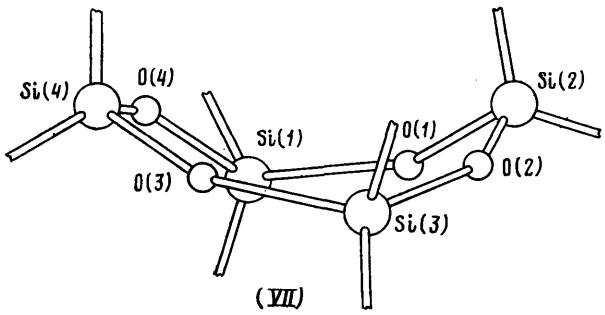


Figure 2. Conformation of D_4 ring in molecule (VII).[16]

The D_4 ring in molecule (VII) has non-crystallographic symmetry intermediate between S_4 and D_{2d} (closer to S_4), with a boat conformation (Fig. 2). The $Si_{(1)}O_{(1)}Si_{(3)}O_{(3)}$ plane, which constitutes the "bottom" of the boat, forms with the $Si_{(1)}O_{(4)}Si_{(4)}O_{(3)}$ and $O_{(1)}Si_{(2)}O_{(2)}Si_{(3)}$ planes dihedral angles of 27.5° and 31° respectively.

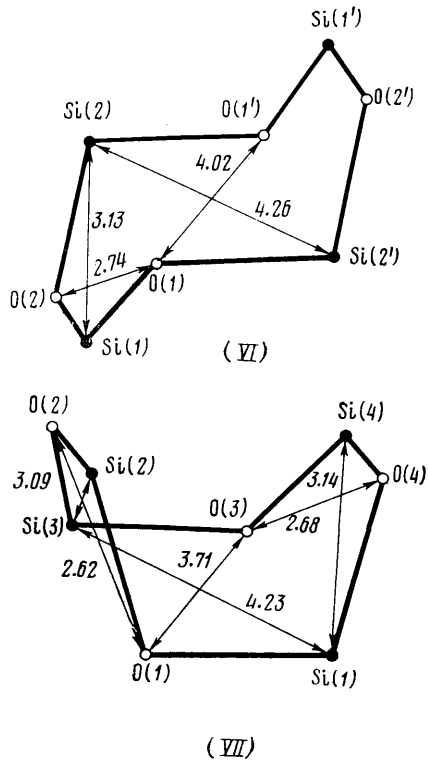


Figure 3. Non-bonded endocyclic distances in D_4 rings in molecules (VI) and (VII).[16]

Ideally chair–isomerism involves rotation of only one diatomic Si–O group relative to the remaining part of the ring. However, Fig. 3 shows that the real molecules (VI) and (VII) differ

also in the geometry of the central portion of the D_4 ring (the "bottom" of the boat). In particular, the difference between the diagonal Si...Si and O...O distances in the central portion is smaller in (VI) (4.26 and 4.02 Å) than in (VII) (4.23 and 3.71 Å). Furthermore, this portion is planar in (VI) (the molecule is situated at a centre of symmetry), whereas in (VII) the atoms forming the central four-membered portion depart by ±0.11 Å from its median plane[16].

Further discussion of the geometry of siloxane rings involves consideration of the nature of the silicon–oxygen bond in this group of compounds. These questions are not examined in detail in the present Review, since they have been covered exhaustively in several papers, cited e.g. in reviews[4,22]. Although the concept of silicon–oxygen p_π–d_π interaction has been increasingly criticised during recent years by several quantum chemists[23–25], this approach is nevertheless adopted in the present Review for the following two reasons.

(1) This approach provides a good explanation of the observed geometry even of extremely complicated organocyclosiloxane molecules. However, a serious problem for the concept of p_π–d_π interaction was presented by the $[(C_6H_5)_2Si]_2O$ molecule[28], in which the SiOSi angle had increased to 180° (the molecule was located at a centre of symmetry), while the silicon–oxygen bond had contracted only to 1.616(1) Å.¶

(2) An alternative approach, in which the silicon–oxygen bond length is assumed to be constant (the sum of the covalent radii corrected for the difference in electronegativity between silicon and oxygen atoms), and the SiOSi bond angle is explained by the separation of electron-pairs located in valency orbitals (the VSEPR method[27])†, is actually applicable only to a narrow range of compounds[27,28], in particular silicates having a Q unit as a structural element. There are other quantum-chemical treatments of the bonds formed by Group IVb elements (in particular silicon–oxygen bonds)[23,29,30], but as before the concept of p_π–d_π interaction remains the most popular for interpreting the geometry of organosiloxanes.

¶The fact that the MOM bond angles in $[(C_6H_5)_3C]_2O$ and $[(C_6H_5)_3Ge]_2O$ (128° and 135.2° respectively) are determined by non-bonded El...El interaction (where El = C, Ge) has led to surprise[26] that a linear geometry could occur in $[(C_6H_5)_3Si]_2O$. An "electronic" influence of the phenyl substituents should apparently be excluded in view of the quite long Si–C(C_6H_5) bonds (1.860–1.870 Å). Nevertheless, the Reviewers consider that steric factors are responsible for the geometry of this last molecule. Although intramolecular contacts between the phenyl groups are not critical here (the shortest C...H distance is 2.81 Å), the "pushing apart" of phenyl groups is fully able to affect the molecular geometry in such a fundamental fashion, as a consequence of the advantageous centrosymmetrical arrangement of the bulky phenyl groups and the relative ease of deformation of the SiOSi bond angles (in comparison with COC and GeOGe angles). The steric character of the factors governing the geometry of the $[(C_6H_5)_3Si]_2O$ molecule explains also the insufficient contraction (in a scheme with p_π–d_π interaction) of the silicon–oxygen bonds.

†Cases of linearity of oxy-bridges in $(R_3Si)_2O$ molecules are explained by the donor properties of the trialkylsilyl groups, which suppress the tendency of the oxygen bridge to assume a bent structure[102].

The rule of the interrelationship between the SiOSi angle and the length of the silicon–oxygen bonds forming it, which has been most sharply criticised by opponents of the hypothesis that p_π–d_π interaction is important, is well satisfied in organocyclosiloxanes, as shown below.

The set of almost isoenergetic chain conformations with bonds almost identical in character is considerably extended by the involvement in bonding of *d* orbitals of silicon atoms differently oriented relative to the axis of the siloxane chain[31], with a consequent diminished rigidity of the SiOSi bond angles and enhanced chain flexibility. This feature makes possible the appearance of geometrical isomers of siloxane chains, whose structures result from a compromise between the repulsion of non-bonded groups and the requirement of maximum p_π–d_π interaction[22,32].

The relation between the structure of the rings and the requirement of maximum p_π–d_π interaction was examined in detail by Craig and Paddock[31], who calculated the overlap integrals of *d* and *p* (or hybrid *sp*) orbitals for various conformations of the rings. They established the possibility of the existence of several energetically approximately equivalent conformations of rings formed by atoms possessing vacant *d* orbitals and atoms with lone pairs in *p* orbitals. Thus conformations of symmetry S_4, C_{2h}, C_{4v}, and D_{2d} are almost equally probable for eight-membered rings, e.g. D_4, with comparatively weak p_π–d_π interaction. The corresponding conformational transitions do not appreciably affect the degree of p_π–d_π interaction, since the silicon–oxygen bond lengths do not change with different conformations of the D_4 ring characterised by roughly the same SiOSi angles (142–149°).

This conclusion is supported also by numerous spectral investigations. Transition from the high-temperature crystalline modification of (VI) to the liquid phase is accompanied by a substantial change in spectra: the molecule acquires C_{4v} symmetry[21,32]. Electron diffraction by (VI) in the gas phase indicates S_4 molecular symmetry[33]. The conclusion that a conformation of C_{4v} symmetry is present in the liquid phase is consistent with the dipole moments of liquid cyclosiloxanes D_n with $n = 4–8$.[32] Among the types of symmetry possible for the tetramer only C_{4v} is consistent with the observed non-zero dipole moment.

Thus variation in the set of substituents, polymorphic transitions, and change in the state of aggregation may lead to a change in the conformation of the D_4 ring. Such rings in crystallographically independent molecules in the same crystal may also have different conformations, as has been observed e.g. with octamethylcyclotetrasilazane[34].

The molecule (XI) has non-crystallographic symmetry C_2 (approximately S_4 for the T_2D_2 ring—see Fig. 4). The planes of the phenyl rings $C_{(3)}...C_{(8)}$ and $C_{(21)}...C_{(26)}$ are almost parallel (dihedral angle 172.6°) and interact sterically, as is confirmed by the C...C distances between the ring atoms (3.17–3.50 Å). Such a molecular structure favours the development of activity by the *cis*-silanolic groups, since the approach of reagent molecules in solution is not subject to steric hindrance. Although the positions of the phenyl and methyl hydrogen atoms have been determined objectively, the hydrogen atoms of the silanolic groups could not be located. They probably undergo extremely vigorous thermal motion. It is interesting that the silanolic oxygen atoms have almost the same hybridisation as in the ring (mean Si–O(H) distance 1.643 Å).

Molecules (X) and (XII) are of interest in connection with the possible distorting influence on the structure of the D_4 ring of the "chelate" substituents, with ring closure at one or two silicon atoms (Figs. 5 and 6). The parameters of the D_4 ring in (X) have normal values (Si–O bond length 1.62 Å, SiOSi and OSiO bond angles 149° and 109°). The CSiC bond

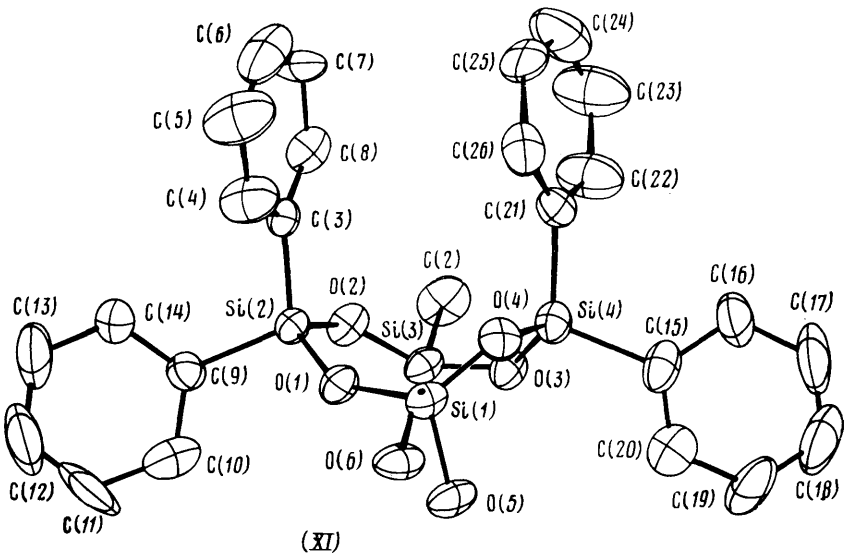


Figure 4. Structure of molecule (XI). The $Si_{(1)}$ ellipsoid shows the point of entry of the $Si_{(1)}-C_{(1)}$ bond with its methyl group.

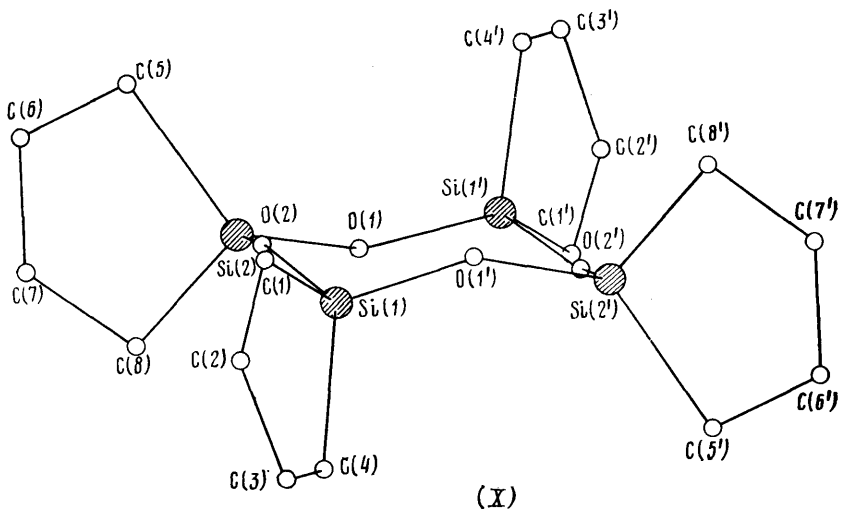


Figure 5. Structure of molecule (X) located at a centre of symmetry[20].

angles have decreased on the average to 97° owing to entry into five-membered heterocycles.

However, the D_4 conformation of the ring found in molecule (X) had not been observed for cyclotetrasiloxanes before the appearance of this recent work[19,20]. This is a particular case of the chair conformation (C_i symmetry), in which six ring atoms $[O_{(1)}Si_{(2)}O_{(2)}O_{(1')}Si_{(2')}O_{(2')}]$ are situated in the same plane (in (X) the emergence of atoms from this plane does not exceed 0.03 Å), from which the diametrically opposite silicon atoms (1) and (1') depart markedly on opposite sides (by ±0.53 Å—Fig. 5). Thus here the chair conformation is formed by the deflections of opposite triatomic groups from the remainder of the ring. The same conformation as in (X) and (XII) is exhibited by the mixed siloxazane ring of 1,3,5',7'-tetramethyl-1',3',5,7-tetraphenylcyclo-1,3,5,7-tetrasila-2,6-diaza-4,8-dioxane[35] and the silazane ring in 1,3,5',7'-tetramethyl-1',3',5,7-tetraphenylcyclotetrasilazane[36]. Both these rings have completely different sets of substituents from those in (X) and (XII).

The same conformation is found for the next D_4 derivative with "ring-closed" chelate substituents (XII), but here, instead of silicon atoms, oxygen atoms are deflected ($O_{(1)}$ and $O_{(1')}$ by ±0.69 Å) from the plane of the hexatomic fragment $Si_{(1)}Si_{(2)}O_{(2')}Si_{(1')}Si_{(2')}O_{(2)}$ (Fig. 6).

Before passing to cyclosiloxanes with >4 SiO units we note that derivatives of the D_4 ring have a special role in the

stereochemistry of organosiloxanes. These rings, which are the most frequently encountered among cyclosiloxane rings¶, form the most popular fragment in various organosiloxane polymers. Eight-membered rings based on SiO_4 tetrahedra are met quite often also among silicates (within infinite silicon–oxygen bridges, in which the silicon atoms usually have a *Q* configuration)[37].

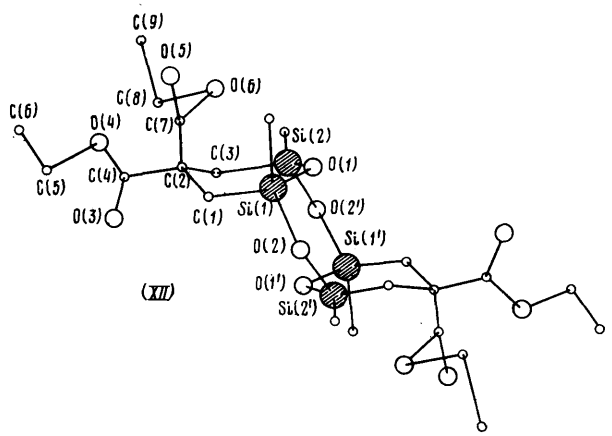


Figure 6. Structure of molecule (XII) located at a centre of symmetry.

Research on the biological activity of cyclic siloxanes of type $(C_6H_5CH_3SiO)_x[(CH_3)_2SiO]_y$ begun at the start of the 1970s has shown that several of them affect the reproductive function of mammals[38–40]. The D_4 derivatives (VIII) and $(C_6H_5CH_3SiO)_x[(CH_3)_2SiO]_3$ have proved the most active. The results of this work, which are significant from the point of view of a possible stereochemical analysis of the biological activity of organic derivatives of D_4 cyclosiloxanes, can be summarised: (1) the activity of organosiloxanes is due to the presence of arylsilicon groups; (2) the conformation and the configuration of D_4 derivatives are important (compound (VIII) has considerable oestrogenic activity, and (IX) is almost inactive); and (3) bioactivation in the animal organism does not involve conversion of chemically different organosiloxanes into chemically and (biologically) similar compounds.

Very little is known about the structure of D_n cyclosiloxanes having $n > 4$. The crystalline "octamer" $[(CH_3)_2SiO]_8$ has been examined by X-ray diffraction[32]. The molecules occupy positions having S_4 symmetry (space group $P\bar{4}2_1c$), while the conformation of the ring probably resembles that found for the D_4 ring in the α modification of (VI). Even these data indicate that the conformation of the D_8 ring may change on melting, since in the liquid phase these compounds have a non-zero dipole moment, which would be impossible with S_4 symmetry[32]. Spectral data[21] suggest that in the liquid phase the octamer molecule has C_8 symmetry.

X-Ray examination of decamethylcyclopentasiloxane $[(CH_3)_2SiO]_5$ in the liquid phase indicated[41] that the siloxane ring was buckled. However, the molecular parameters obtained (Si–O and Si–C 1.66 and 1.85 Å; SiOSi, OSiO, and CSiC respectively 145°, 115°, and 110°) suggest that this work was inaccurate (doubtful parameters are underlined).

Spectroscopic investigation shows[32] that the $[(CH_3)_2SiO]_6$ molecule can be assigned to the point groups D_{3d} and C_{6v} respectively in the crystal and in the liquid. In the crystal the dimethylsilylene groups face alternately above and below a plane perpendicular to the threefold (sixfold) axis, but in the liquid all these groups face the same direction. The diminution in symmetry from C_{6v} to D_{3d} is probably due to steric interaction of neighbouring dimethylsilylene groups. With the SiOSi angle remaining constant in C_{nv} conformations of $[(CH_3)_2SiO]_n$ molecules the distance between the methyl groups decreases with increase in *n*, and a decrease in symmetry to D_{3d} may prove energetically advantageous.

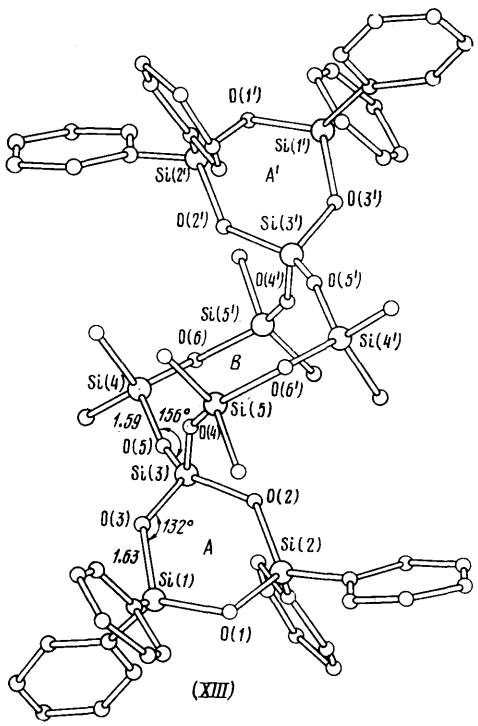


Figure 7. Structure of molecule (XIII) located at a centre of symmetry[43].

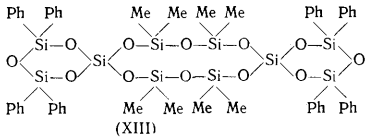
In contrast to rings in which *n* is even, the spectra of crystals with odd values of *n* differ little from those of the liquid phase: i.e. the conformation of the rings is the same in the liquid and in the crystal. Only groups D_n and C_n are consistent with the spectral data: the former can be rejected, since it has zero dipole moment, so that the molecules of pentamer and heptamer possess C_5 and C_7 symmetry, although certain features of the spectra indicate that the dimethylsilylene groups are arranged in conformity with a lower degree of symmetry.

Electron diffraction results for methyl derivatives of cyclopentasiloxane and cyclohexasiloxane in the gas phase[42] are not really consistent with any definite models. Better agreement is obtained with C_{5v} and D_{3d} symmetry respectively, with the oxygen atoms located in the same plane. Special

#See discussion at end of Section II.

attention was paid to C_5 and C_6 symmetry models, since they were based on spectral data[42]. We can pass from C_{nv} to C_n symmetry by rotating the dimethylsilylene plane relative to the corresponding OSiO fragment. However, this lower symmetry is less consistent than C_{nv} symmetry with the experimental results. It is supposed[42] that, owing to the large amplitudes of the low-frequency vibrations, molecules having large siloxane rings possess no definite conformation.

An X-ray structural investigation has been made[43] on 8,8,10,10,19,19,21,21-octamethyl-2,2,4,4,14,14,16,16-octaphenyldispiro[5,5,5,5] decasiloxane



(XIII)

whose molecule is located at a centre of symmetry and comprises three cyclosiloxane fragments (Fig.7), two six-membered (A and A') and one twelve-membered (B). The configurations of rings A and B are respectively D_2Q and D_4Q_2. The central twelve-membered siloxane ring B has the general chair conformation (symmetry C_i), with eight atoms $Si_{(4)}Si_{(5)}Si_{(4')}Si_{(5')}O_{(4)}O_{(6)}O_{(4')}O_{(6')}$ located approximately in the same plane (deviations do not exceed 0.3 Å). The deflection from it of the "chair-backs" (i.e. of the atomic planes $Si_{(3)}Si_{(4)}O_{(4)}O_{(5)}$ and $Si_{(3')}Si_{(4')}O_{(4')}O_{(5')}$) is 78°.

A most interesting feature of the structure of ring B is a sharp increase in the SiOSi angles (to an average of 156°) in comparison with e.g. eight-membered siloxane rings (Table 2). This value also exceeds the SiOSi angle of 149.6° in $[(CH_3)_2SiO]_6$ found by electron diffraction in the gas phase[42]. The increase in the angles leads to enhanced mobility of the oxygen atoms[43], which correlates with their larger temperature factors (7.6–9.6 Å^2) relative to the oxygen atoms in ring A (5.5–6.2 Å^2), in which the SiOSi angles are on the average 132°.

Structural comparison of the minerals bustamite $(Ca,Mn)SiO_3$ and wollastonite $CaSiO_3$ reveals a similar feature[32]. Both crystals are constructed of infinite chains $[SiO_3O_{9/2}]_\infty$ containing three silicon–oxygen tetrahedra in a repeating unit. The three non-equivalent SiOSi angles in the chain have the values

(Ca, Mn) SiO_3 : 161°, 135°, 137°;
$CaSiO_3$: 149°, 139°, 141°.

In the bustamite molecule the isotropic temperature factor of the oxygen atom in the grouping with the SiOSi angle straightened out to 161° was double that for the remaining oxygen atoms. In the wollastonite chain the temperature factor of the corresponding oxygen atom only slightly exceeded the mean value for all the remaining atoms[32].

In the structure of thortveitite $Sc_2Si_2O_7$ [44] the isotropic temperature factor of the bridging oxygen atom with the SiOSi bond angle 180° (the pyrosilicate group is located at a centre of symmetry) is almost double those for the terminal oxygen atoms (respectively 0.98, 0.55, and 0.65 Å^2), which are involved in the coordination of scandium atoms. The silicon–oxygen distance is shorter to the oxygen bridge than to the terminal atoms (respectively 1.605(1) and 1.629(1) Å).

In structures with abnormally large oxygen bond angles (>150°) the retardation of internal rotation in ElOEl bridges is weakened[32]. This is favoured firstly by increase in the distance between substituents attached to the El atoms and secondly by decrease in the potential barrier to internal rotation due to increasing overlap of d orbitals of the element El with p orbitals of oxygen, whose nodal plane is perpendicular to the ElOEl plane. In the limiting case, with an ElOEl angle of 180°, rotation about the ElOEl bond is probably entirely free and will depend only on steric interaction of the framing groups.

Quantum-chemical examination of these problems showed[45] that the barriers to internal rotation are zero in the chains of organic cumulenes $H_2C{:}C{:}...{:}C{:}CH_2$, and only the relative rotations of the two terminal groups can be fixed: this distinguishes a system of cumulative bonds fundamentally from a system of conjugated bonds, where internal rotation is retarded. However, in such cumulative systems in which the chain has a framework (as in many polymers having an inorganic main chain) internal rotation may be hindered by the repulsion of atoms in the framing groups. Although it was considered[45] that such retardation could not be essential (since not every atom carries substituents), it may play a large part with bulky (e.g. phenyl) substituents. Furthermore, spectral data[32] indicate that, in structures with ElOEl angles close to 180°, slight retardation of internal rotation is accompanied by diminished rigidity of these angles, so that a considerable increase in mobility of the oxygen atoms can be expected both in the ElOEl plane (perpendicular to the El...El axis) and perpendicular to it.

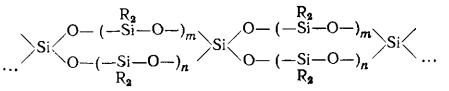
The flexibility of the SiOSi fragments entails a general conformational non-rigidity of the ring B [(XIII)], which probably accounts for the higher temperature factors of the silicon atoms than in the ring A (respectively 5.1–6.7 and 5.0–5.1 Å^2).[43] Flexibility of the ring B is promoted also by the packing of the molecules in the crystal. Of a total of 29 independent intermolecular contacts < 4 Å some 25 are formed by phenyl groups, i.e. by substituents in rings A and A'. Four methyl groups are completely uninvolved in intermolecular contacts < 4 Å. Thus the conformation of ring B is almost completely determined by intramolecular interactions, with methyl groups situated in the "rarefied" (with respect to intermolecular contacts) zone along the periphery of the central ring.

The specific packing combined with the large free displacement of oxygen atoms in structures having "abnormally" large SiOSi angles leads to enhanced mobility of fragments of the molecule (including substituents attached to the silicon atoms) relative to the Si...Si axes. This may explain also the high temperature factors (11–17 Å^2) of the methyl carbon atoms in (XIII). In this compound, as in comparable silicate structures, enhanced mobility of the oxygen atoms characterises SiOSi bridges with the largest SiOSi angles together with the shortest silicon–oxygen interatomic distances, which indicate increased bond orders.

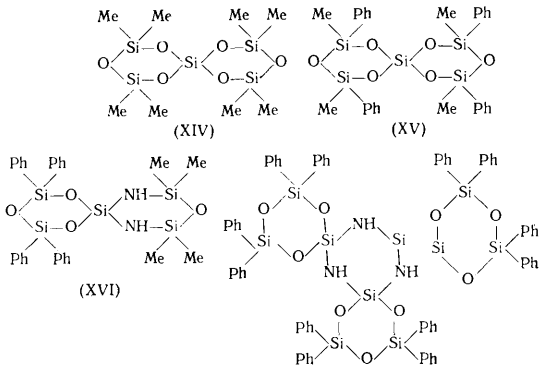
The conclusion that silicon–oxygen bonds are more stable in D_n rings with $n>4$ than in a D_4 ring is consistent with a study of the polymerisation⇌depolymerisation (cyclisation) equilibrium of dimethylsiloxanes, which indicated that the concentration of D_4 is higher than those of all other cyclic dimethylsiloxanes present in the mixture. Indeed, the lower content of more flexible and stable rings with higher values of n can be explained by the smaller probability of their closure than with the shorter D_4 chains. The greater abundance of D_4 than of D_3 rings is attributed to some strain in the latter[2,3], as well as to greater instability of their silicon–oxygen bonds (Tables 1 and 2). The advantage of eight-membered Q_4 rings in silicates has been mentioned by O'Keefe and Hyde[24], who have analysed a large number of structural investigations of silicates and concluded that the conformations of silicon–oxygen fragments in them are determined by non-bonded Si...Si interaction with almost constant silicon–oxygen bond lengths. The Si...Si distances have their most favourable values (3.08–3.10 Å) in Q_4 rings.

III. SPIROCYCLIC SILOXANES

Organospiropolycyclosiloxanes, a novel class of organopolysiloxanes[1,46], have the general formula



Structures have been determined for the five spirocyclosiloxanes (XIII)–(XVII)



whose geometrical parameters are given in Table 3. Like D_3 rings (Table 1) the D_2Q rings present in spirocyclosiloxanes have an approximately planar structure. According to Table 3 the silicon–oxygen bonds in the spiro-units of the D_2Q rings are somewhat shorter, which indicates that they are more stable than the usual siloxane bonds§. Such contraction is due to more complete involvement of the central silicon atom (than of the silicon atoms in ordinary siloxanes) in π coupling with the four surrounding oxygen atoms; the polarising effect of the latter leads to the appearance of a positive charge on the silicon atom, which diminishes the energy of its 3*d* orbitals. Such an explanation has been used, for example, in analysing the character of the bonds in siloxanes[22].

When the oxygen atoms forming the spiro-environment of silicon atoms are replaced by the less electronegative nitrogen atoms, of course, the positive charge on the silicon atoms diminishes, and the remaining silicon–oxygen bonds become weaker. As a result, for example, the D_2T spiro-ring in the molecule (XVI) has the same parameters as have D_3 rings. On passing to compound (XVII), however, the difference in the silicon–oxygen bond lengths again becomes appreciable. This indicates that in mixed siloxane–silazane polycycles the silicon–oxygen bonds in the spiro-units are stronger than the remaining silicon–oxygen bonds provided that the spiro-units involve silicon atoms of an inner silazane ring. The molecule (XVII) (Fig.8) exhibits a fairly sharp difference in planarity of the trisiloxane rings (Table 3): the $Si_{(9)}$ atom emerges markedly (by 0.43 Å) from the plane of the remaining five atoms of the ring $Si_{(3)}O_{(10)}Si_{(8)}O_{(11)}Si_{(9)}O_{(12)}$.

§The absence of this effect in the molecule (XIV) is probably due to inaccuracy in the investigation[47].

The presence of spiro-silicon atoms should enhance not only the three-dimensional rigidity¶ but also the thermal stability of the organopolycyclosiloxane chain. Two modes of construction of such chains are of interest in connection with the molecular mechanism of deformation. The first involves a chain of spiro-linked siloxane rings with a small number (3 or 4) of SiO units in each. Such chains should be characterised by strong intramolecular organisation and great rigidity. The second method incorporates into the general spirocyclolinear molecule siloxane rings with >4 SiO (or linear siloxane links with >4 SiO). The strengthening in such molecules of the silicon–oxygen bonds involving spiro-silicon atoms is combined with enhanced stability of the other silicon–oxygen bonds as a consequence of their entry into long siloxane chains, distinguished by stronger p_π–d_π interaction[32,45].

Table 3. Data on spirocyclic siloxanes (d_1 and d_2 are the mean Si–O bond lengths within and outside the spiro-group in the D_2Q ring, Δ_{max} is the maximum divergence of atoms from the D_2Q plane, and α is the mean SiOSi bond angle in the D_2Q ring).

No.	d_1, Å	d_2, Å	Δ_{max}, Å	α	Ref.
(XIII)	1.61 (1)	1.64 (1)	0.11	132°	43
(XIV)	1.64	1.64	0*	132.3°	47,22
(XV)	1.611 (6)	1.634 (6)	0.11	132.5°	48
(XVI)	1.637 (6)	1.638 (6)	0.11	132.6°	49
(XVII)	1.62 (1)	1.64 (1)	0.07; 0.11; 0.20***	132.5°	см.**

*Molecule located in the special position 42*m*.
**See Ref.103; some of the results will be found in Ref.50.
***The divergence is given separately for each of the D_2Q rings in the (XVII) molecule.

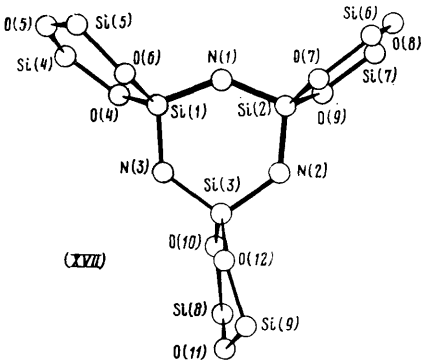
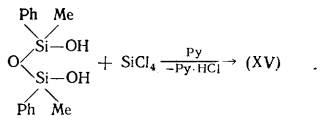


Figure 8. Tetracyclic fragment of molecule (XVII).

¶As already remarked, the rigid spiro-units in the molecule (XIII) stabilise the conformation of the inner twelve-membered siloxane ring, which enables single crystals of this compound to be obtained.

Organopolysiloxane chains of the second type, while retaining the rigidity inherent in organospirocyclosiloxanes, should possess better chemical and thermal stability. Phenyl substituents enhance the rigidity and the crystallisability of both types of organopolysiloxanes[51]. On the other hand, the presence of sterically rigid segments diminishes the thermal mobility of the molecular skeleton, with a consequent impairment of, for example, the resistance of the polymer to thermal oxidation. However, this adverse effect can be suppressed by incorporating into the general polyspirocyclosiloxane system extremely flexible extended polysiloxane segments (large rings).

The compound (XV) can exist as five stereoisomers depending on the orientation of the substituents relative to the planes of the siloxane rings (Fig. 9). Reaction with the *meso*-form of the diol accompanied by retention of configuration[52] gives the *cis,cis*-isomer of (XV) as a racemic mixture of the two enantiomers (XVa) and (XVb), for which the only element of molecular symmetry is a twofold axis:



The methyl groups in each of the siloxane rings of these enantiomers are diastereotopic, as is confirmed by the nuclear magnetic resonance spectra, in which two separate signals are observed from methyl protons. Reaction with silicon tetrachloride of the optically active forms *SS* and *RR* of the diol, and also of their racemic mixture†, should lead to formation of the *trans,trans*-isomer of (XV) as a mixture of the enantiomers (XVe) (conventionally the *d*-isomer) and (XVf) (conventionally the *l*-isomer) and the diastereomeric *meso*-form (XVg) (in the proportions 1 : 1 : 2). The molecules (XVe) and (XVf) have D_2 symmetry, i.e. three twofold axes, while the *meso*-form (XVg) has a fourfold inversion axis, and is thus optically inactive. When the reaction mixture contains both the *meso*-form and the *SS* and *RR* forms of the diol the isomers (XVc) and (XVd) may appear[48].

One of the *trans,trans*-forms of (XV) was isolated. The n.m.r. spectra did not distinguish whether this compound was a *trans-meso*-isomer (XVe) or (XVf), the racemate (XVe) + (XVf), or the *meso*-form (XVg). X-Ray structural analysis showed that the form of (XV) isolated was the *trans,trans-dl*-isomer (Fig. 10). Since the compound crystallised in the non-enantiomorphic space group $P2_1/a$, both optical antipodes (XVe) and (XVf) were present in the crystal[48].

IV. CYCLOLINEAR SILOXANES

The structure of cyclolinear organopolysiloxanes# (Fig. 11)[1] can be represented by various combinations of *cis*- and *trans*-linkings of tetrasiloxane rings. Structure (*b*), for example, has an alternation of *cis,trans,trans* linkages, whereas structure (*c*) has *trans,trans,trans*. From a study of the properties of solutions, X-ray powder data, and infrared spectra Brown[53] demonstrated the *cis*-syndiotactic structure of each $Si_{(1)}Si_{(2)}$... strand of the double chain of cyclolinear organopolysiloxanes corresponding to polymer (*c*), which is usually termed ladderlike. In such polymers, containing silsesquioxane fragments in a chain unit, every third silicon atom of each of the two chains repeats translationally the first (in structure (*b*) the first, fifth, ninth, etc. atoms are repeated).

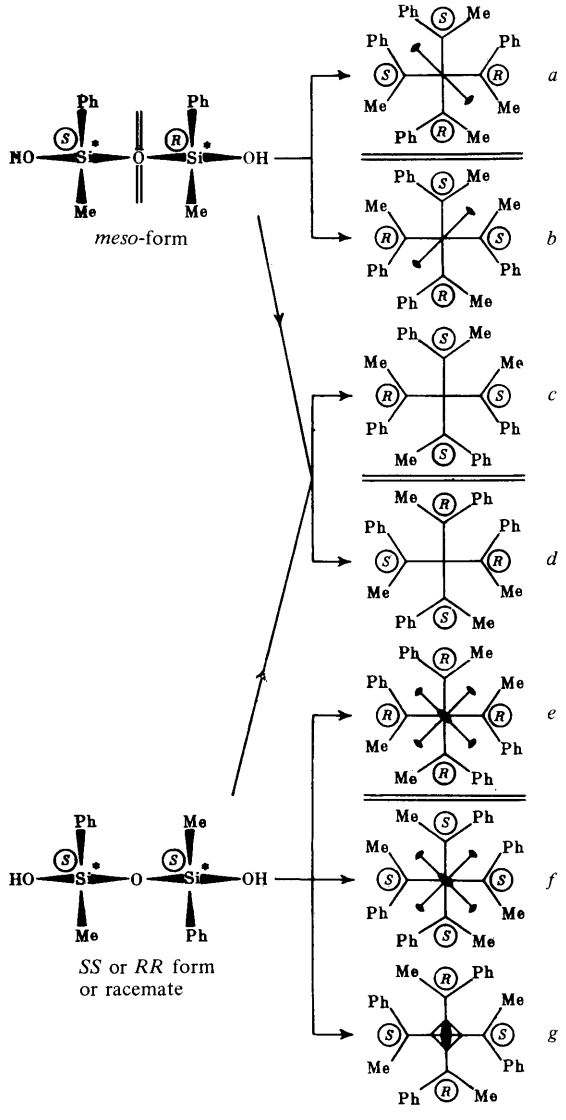


Figure 9. Possible stereoisomers of (XV). The molecules are shown diagrammatically (only substituents and their bonds with the ring, represented by a vertical or horizontal line) as a projection along the straight line passing through the spiro-atom and the two oxygen atoms most remote from it; *R* and *S* denote the configurations of the substituted silicon atoms. The symmetry elements of the molecules are indicated, as well as the mirror plane between the optical antipodes (by a pair of parallel lines).[48]

†Actually the reaction has been conducted only with the racemate of the diol.

#Such cyclolinear structures, in contrast to monocyclic structures, contain *T* units, and are usually termed silsesquioxanes.

Cyclolinear polyphenylsilsesquioxanes comprise semi-rigid macromolecules (persistent length§ 200–900 Å). The flexibility of such macromolecules is due to small fluctuations in torsional and bond angles, in contrast to flexible macromolecules (persistent length ~10–20 Å), e.g. polymethylphenylsiloxane, the mechanism of whose flexibility involves rotational isomerism[55].

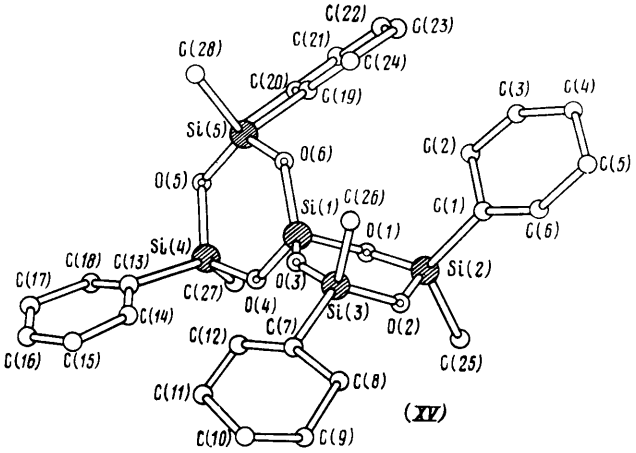
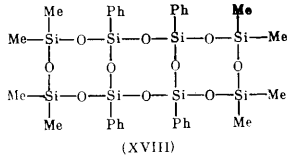
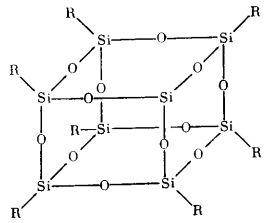


Figure 10. Structure of molecule (XV).[48]

An important factor in the study of the preparation and properties of ladderlike organopolysiloxanes is their lowest oligomers, the octa(organosilsesquioxanes) $(RSiO_{1.5})_8$ (Fig.11*d*), which are formed as by-products[56] and can also serve as starting materials for the synthesis of macromolecular polyorganosilsesquioxanes[57,58]. Table 4 gives data on the T_4 rings in the series of cyclolinear organocyclosiloxanes (XVIII)–(XXIII)

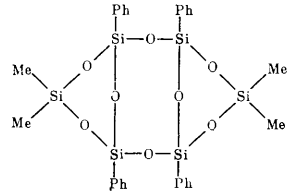


(XVIII)



(XIX), R = H; (XX), R = Me; (XXI), R = Ph; (XXII), R = C_2H_3

§This quantity characterises the rigidity of a polymer chain. A strict definition will be found in Ref.54.



(XXIII)

The structure of (XVIII) is disordered[59,60]: silicon atoms 2, 3, 6, and 7, together with their methyl substituents, can each occupy two positions with approximately equal probability (Fig.12). Passage from one position to the other can be effected by rotation of the dimethylsilylene group through an angle Ω about an axis passing through the oxygen atoms, whose positions remain unchanged. For the four dimethylsilylene groups the angle Ω has a mean value of 60°, which corresponds to displacement of the silicon atoms along an arc ~1.0 Å in length, while the attached methyl carbon atoms move ~3.0 Å.

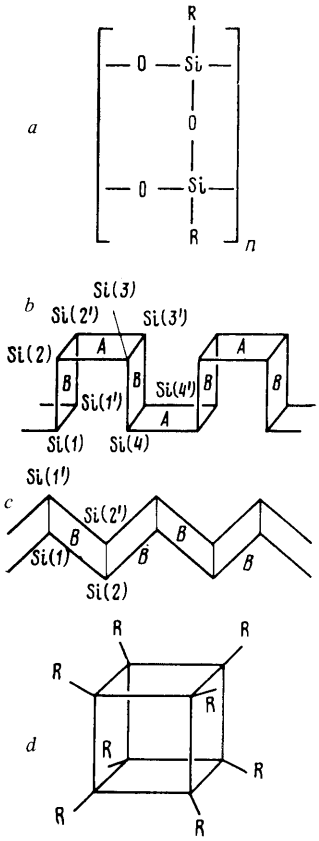


Figure 11. General formulae of: *a*) polyorganosilsesquioxane; *b*,*c*) two possible structures of a cyclolinear organopolysiloxane (a segment of a straight line corresponds to one tetrasiloxane ring; organic substituents are not shown); *d*) diagram of molecule of octa(silsesquioxane).[60]

Of the sixteen possible conformations (on the assumption that the four dimethylsilylene groups can each occupy two positions independently of the others) fourteen are forbidden because they would involve short intramolecular contacts (denoted in Fig.12 by the symbol ↓‾↓) between methyl groups attached to different silicon atoms. Thus the molecule has only two energetically equivalent conformations of its silicon atoms, i.e. 1–2–3–4–8–7–6–5 and 1–2′–3′–4–8–7′–6′–5¶.

Table 4. Data on T_4 rings in structurally studied simple cyclolinear polysiloxanes (α = mean SiOSi bond angle; d = mean Si–O bond length; and Δ_{max} = maximum emergence of O atoms from plane of four Si atoms).

No.	α	d, Å	Symmetry of ring	Conformation of ring	Δ_{max}, Å	Ref.
(XVIII)	151.7 (3)°	1.609 (6)	S_4	saddle*	0.37	59,60
(XIX)	—	—	C_{4v}	crown	—	61
(XX)	145.3°	1.61	C_{4v}	crown	0.34	62
(XXI)	149.2 (4)°	1.614 (7)	C_{4v}	crown	0.30	63
(XXII)	150°	1.609	C_{4v}	crown	—	64
(XXIIIa)	127.5 (4)** 145.5 (4)°	1.618 (7)** 1.638 (7)	S_4	boat	0.72	65
(XXIIIb)	132.5	1.626 (6)	C_i	chair	0.56	104

*The four silicon atoms are almost coplanar.
**Relates to the SiOSi fragment common to the DT_2 and D_2T_2 rings.

In a free state (solution) the molecule (XVIII) may perform frequent transitions, under the influence of thermal vibrations, from one conformation to the other. This view is supported by the very prolate character and appropriate orientation of the ellipsoids representing the thermal vibrations of the atoms of disordered dimethylsilylene groups (Fig.12). Each conformational transition can be regarded as a simultaneous change in direction of twist of the two lateral D_2T_2 rings, which can be twisted only to one side in each of the permitted conformations.

The disorder of structure (XVIII) is interesting in connection with Brown's hypothesis on the condensation of cyclosiloxanes that identical functional groups attached to mobile portions of molecules, and therefore structurally non-equivalent, differ in reactivity[56]. The principle of equal reactivity of identical functional groups, on which the statistical theory of polycondensation is based, does not apply to such systems.

Fig.13 shows that, after initial formation of a dimer (*3*), condensation of the tetraol (*1*) can occur either intramolecularly to give (*4*) and (*5*) or intermolecularly in the sequence (*3*) → (*6*) → (*7*). The statistics of intermolecular vibrations, suggested as the decisive factor in intermolecular cyclisation[56], is probably less important in the present case owing to the relatively small number of degrees of freedom in each successive primary act of intermolecular condensation with formation of a polymeric cyclolinear structure, e.g. (*7*).

¶These conformations have intrinsic (non-crystallographic) symmetry C_2 and form a pair of optical antipodes.

If the compound differing from the tricyclic derivative (*3*) in the presence of methyl instead of phenyl groups in the lateral D_2T_2 rings is assumed to have the same type of disorder as the molecule (XVIII), the smaller steric interactions between substituents will result in preferential conversion of (*3*) into (*4*) instead of (*6*). This is explained by the shorter Si...Si distances, greater frequency of collisions (as shown by analysis of the thermal ellipsoids), and hence greater probability of chemical interaction along the lines $Si_{(2)}...Si_{(6)}$ (as well as $Si_{(2')}...Si_{(6')}$—Fig.12) and $Si_{(3)}...Si_{(7)}$ (and $Si_{(3')}...Si_{(7')}$) than along the lines $Si_{(2)}...Si_{(7)}$ (and $Si_{(2')}...Si_{(7')}$) and $Si_{(3)}...Si_{(6)}$ (and $Si_{(3')}...Si_{(6')}$), corresponding respectively to edges and two-dimensional diagonals of the silsesquioxane cube (Fig.13). The presence in compounds (*1*)–(*3*) of phenyl instead of methyl groups changes the mobility of the D_2T_2 rings and leads to greater probability of process (*3*) → (*6*) than of (*3*) → (*4*), i.e. to formation of a polymer of high molecular weight (the yields of the products are indicated in Fig.13).

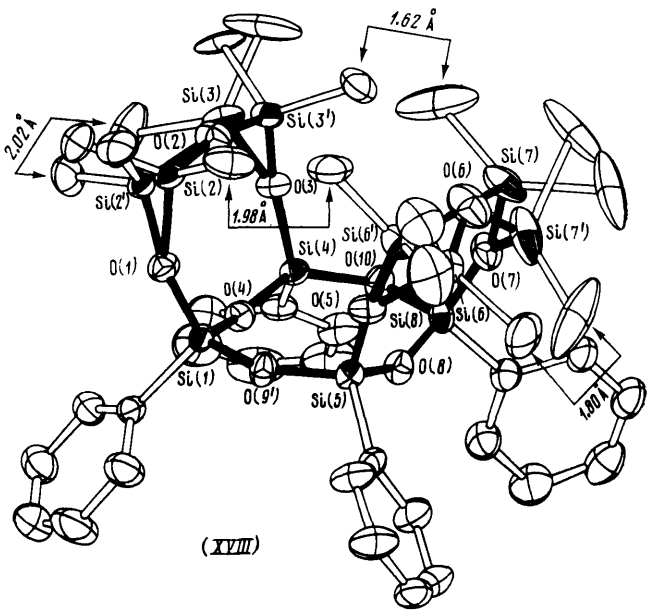


Figure 12. Structure of (XVIII) molecule[60] (explanation in text).

Neither of the "structurally" confirmed mechanisms of the deformation of tetrasiloxane rings [rotation of diatomic Si–O fragments or twisting of triatomic fragments in (XVIII)] explains the conformational transition (*a*) → (*b*) of T_4 rings (Fig.14 and Table 4). On the other hand, both mechanisms revealed for D_4 rings or the *D* portions of D_2T_2 rings, i.e. for siloxanes, involve the displacement of substituted silicon atoms, which is difficult to envisage in the more rigid silsesquioxanes. Conformational rearrangements probably have different mechanisms in D_4 and in T_4 rings. The conformational transitions of T_4 rings can be represented as the displacement of two *trans*-oxygen atoms. Such a mechanism of the conformational transition $S_4 \rightarrow C_{4v}$ had been suggested earlier (though in D_4 rings) in a spectroscopic paper[21].

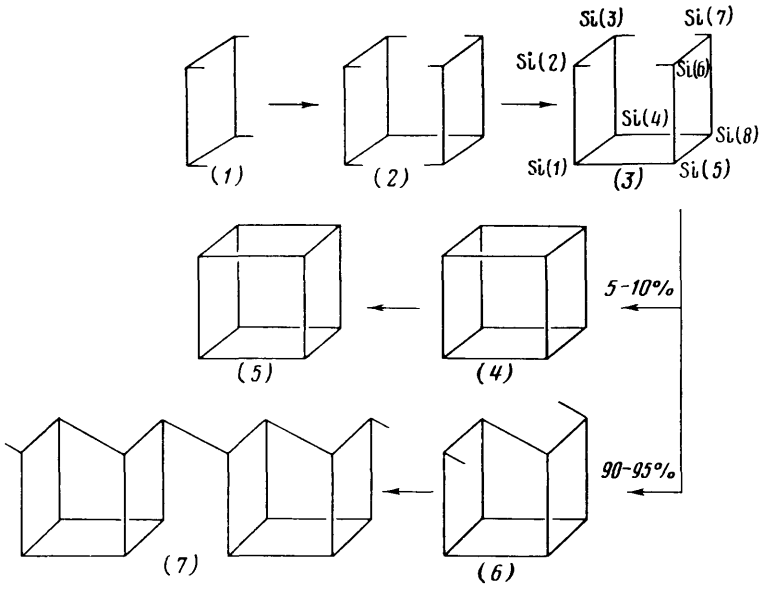


Figure 13. Scheme of condensation[56] of the tetraol (*1*) (tetraphenylcyclotetrasiloxanetetraol) via the tricyclic compound (*3*) into an octa(silsesquioxane) (*5*) and via the tetracyclic compound (*6*) into a poly(silsesquioxane) (*7*). The structures of (*3*) and (*5*) have been confirmed by X-ray examination[60,63]. Products (*4*) and (*6*) can exist as epimers with a different orientation of hydroxy-groups.

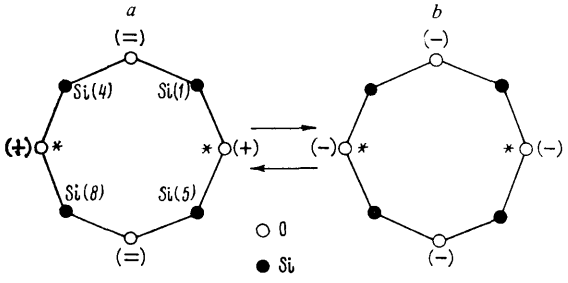


Figure 14. Scheme illustrating the differences and interrelationship between conformations of T_4 rings in the molecules: *a*) (XVIII), approximate symmetry S_4; *b*) (XXI), C_{4v}.[60] For simplicity the silicon atoms are shown in (XVIII) as lying in the same plane; the symbols (+), (−), and (=) indicate the positions of oxygen atoms above, and below, and in this plane. Asterisks denote oxygen atoms whose movements are perpendicular to the plane of the diagram and essentially determine the transitions (*a*) ⇌ (*b*). The silicon atoms are numbered in conformity with Fig. 12.

The two conformers of (XVIII) are characterised by closely similar dihedral angles of deflection of the planes of the lateral D_2T_2 eight-membered rings from that of the central T_4 ring (on the average 108°). As was to be expected, the silicon–oxygen bonds are shorter in silsesquioxane *T* units than in siloxane *D* units (on the average 1.606(3) and 1.621(6) Å respectively). Yet the difference in the mean silicon–oxygen bond lengths in T_4 and D_2T_2 rings is small (respectively 1.609(3) and 1.614(6) Å), just like the difference in mean SiOSi bond angles in these rings (151.7(2)° and 148.1(3)°).

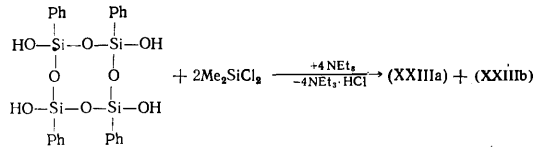
Since the conformation of the siloxane ring (infrared spectra[66]) remains unchanged when the polymer chain is extended, the parameters (bond lengths and angles) of the T_4 ring are probably maintained even in the corresponding cyclolinear polymer.

Conformational analysis has been used to determine the most probable angular parameters for *cis*-syndiotactic poly(phenylsilsesquioxane)[67]. The SiOSi angles in the "strand" (along an infinite polysiloxane chain) are 145–150°, rather smaller than the 155–170° in the "binder" (the cross-link between the polysiloxane chains). Experimental X-ray structural data[60] indicate that in the T_4 ring of (XVIII) the SiOSi angles are also somewhat smaller in the strand than in the binder (on the average 148.7° and 154.7° respectively).

As a consequence of the inductive effect the addition of aromatic substituents to the silsesquioxane cube [conversion of (XIX) and (XX) into (XXI)] strengthens appreciably the π interaction, which is apparent in an increase in the SiOSi angles in (XXI) and also in a "flattening" of the T_4 rings forming the cube (the mean emergence of the T_4 cyclic oxygen atoms from the plane through the four silicon atoms is respectively 0.34 and 0.30 Å in (XX) and in (XXI)—Table 4). This "flattening" should diminish the dipole moment of the T_4 ring and enhance d_π–p_π interaction in the silicon–oxygen bonds, but the lengths of the latter are closely similar in the T_4 rings in (XX) and in (XXI) (Table 4).

Passage from (XX) to (XXI) should be accompanied by a decrease in stability of the silsesquioxane skeleton towards radical reagents and an increase towards ionic reagents, as well as an enhancement of thermal stability. This is important in the choice of conditions for the polymerisation of octa(organosilsesquioxanes).

Compound (XXIII) is a cyclolinear oligosiloxane containing DT_2 as well as T_4 rings. Its preparation involves the isolation[65] of two products—(XXIIIa) and (XXIIIb)—differing in yield, melting point (respectively 162–163 and 222–223 °C), solubility, and physical properties:



Data have been published on (XXIIIa),[56,68,69] but (XXIIIb) has been isolated for the first time. A conformational difference is assumed between them. X-Ray examination indicates that (XXIIIa) is a *cis*-isomer of the D_2T_4 tricyclic system, and (XXIIIb) a *trans*-isomer (Fig.15).

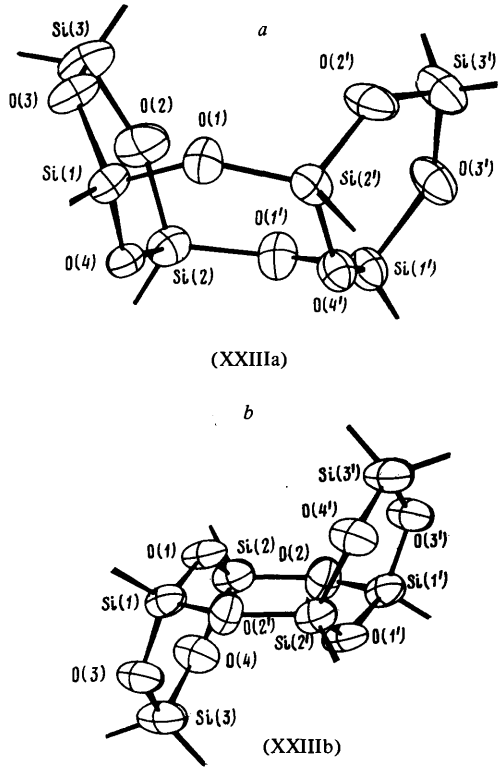


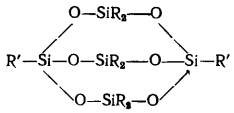
Figure 15. Structures of D_2T_4 tricyclic siloxane systems (Table 4) in the molecules: *a*) (XXIIIa)[65]; *b*) (XXIIIb).

The structure of (XXIIIa)† is characterised by "anomalous" parameters of its tetrasiloxane and trisiloxane (T_4 and DT_2) rings (Fig.15): (i) the $Si_{(1)}O_{(4)}Si_{(2)}$ and $Si_{(1')}O_{(4')}Si_{(2')}$ bond angles are 127.5°, unusually small for tetrasiloxanes (cf. Tables 2 and 4), so that the T_4 ring in (XXIIIa) is considerably more strongly deformed than, for example, the T_4 ring in (XVIII), which has a similar chemical environment and the same symmetry S_4 (Table 4); and (ii) steric interaction of methyl groups attached to $Si_{(3)}$ and $Si_{(3')}$ (C...C distance 3.713 Å) leads to deformation of the DT_2 rings (departure of the cyclic atoms from their mean planes reaches 0.33 Å—cf. D_3 rings in Table 1). Furthermore, as a consequence of this steric interaction the angle of deflection of the lateral DT_2 rings in (XXIIIa) from the central ring (115°) exceeds that in (XVIII) (108°); the ideal symmetry C_{2v} of the tricyclic siloxane system in (XXIIIa) degenerates to C_2.[65]

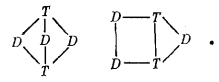
In the *trans*-isomer (XXIIIb), the molecule is located at a centre of symmetry in the crystal, the lateral DT_2 rings have a more planar structure than in (XXIIIa) (departure of the atoms from the plane of these rings does not exceed 0.1 Å), and they conform approximately to C_{3v} symmetry. The eight-membered T_4 ring has a general chair conformation (symmetry C_i); the atoms $Si_{(1)}$ and $Si_{(1')}$ deviate by ±0.56 Å on opposite sides of the general plane of the ring. The SiOSi bond angles in the T_4 ring of (XXXIIIb) have a mean value of 132.5°, markedly smaller (by ~10°) than in other derivatives of eight-membered siloxane rings (Tables 2 and 4). The dihedral angle between the planes of DT_2 and T_4 rings is 82.4°.

V. OTHER POLYCYCLIC SILOXANES

Structures have been determined for two bicyclo[3,3,3]pentasiloxane D_3T_2 derivatives



(in (XXIV) $R = C_6H_5$ and $R' = CH_2.CH$ (Fig.16)[70]; in (XXV) $R = R' = CH_3$ (Fig.17)[71]) obtained in different ways. Whereas the structure (XXIV) alone is possible for the D_3T_2 product of the reaction between vinyltrichlorosilane and diphenylsilanediol[72], the D_3T_2 product of the thermal decomposition of branched polydimethylsiloxanes may have the two structures[71]



However, X-ray examination indicates that the two products have the same siloxane skeleton. These molecules are characterised by a non-crystallographic threefold axis passing through the silsesquioxane silicon atoms, but the silicon–oxygen skeleton has the overall non-crystallographic symmetry $\bar{6}2m$.

The three tetrasiloxane D_2T_2 rings in (XXIV) and (XXV) exhibit considerably greater "non-planarity" than do D_4 and T_4 rings. For example, in (XXIV) the mean dihedral angle between tetratomic fragments of D_2T_2 rings is 44° (in D_4 rings it is 27.5–40.2°, Table 2). As a consequence the mean SiOSi angle is 14°, smaller than in D_4 rings (142.5–149°). The considerable deformation of D_2T_2 rings in (XXIV) prevents development of their silsesquioxane nature, i.e. strengthening of silicon–oxygen bonds; the mean silicon–oxygen distance in (XXIV) is 1.63 Å, but no differences in length are observed between siloxane and silsesquioxane bonds[70].

Because of the smaller bulk of the substituents the D_2T_2 rings are less deformed in (XXV) than in (XXIV), but the mean SiOSi angle (145.6°) corresponds to this value in the D_4 rings, while being smaller than the SiOSi angles in T_4 rings. The silicon–oxygen distance (1.618 Å) is close to those found in T_4 rings (above). Yet the non-bonded diagonal Si...Si distances in (XXIV) and (XXV) are closely similar. Diagonals of type $Si_{(3)}...Si_{(5)}$ in (XXIV) (Fig.16) and of type $Si_{(2)}...Si_{(4)}$

†The molecule is located on a twofold axis.

in (XXV) (Fig.17) are respectively 4.21–4.26 and 4.236–4.256 Å, while the Si...Si distances along non-crystallographic threefold axes in (XXIV) and (XXV) ($Si_{(1)}...Si_{(2)}$ in Fig.16 and $Si_{(1)}...Si_{(3)}$ in Fig.17) are 3.71 and 3.76 Å. Thus a silicon–oxygen "skylight" of this type is "compressed" along an approximate threefold axis.

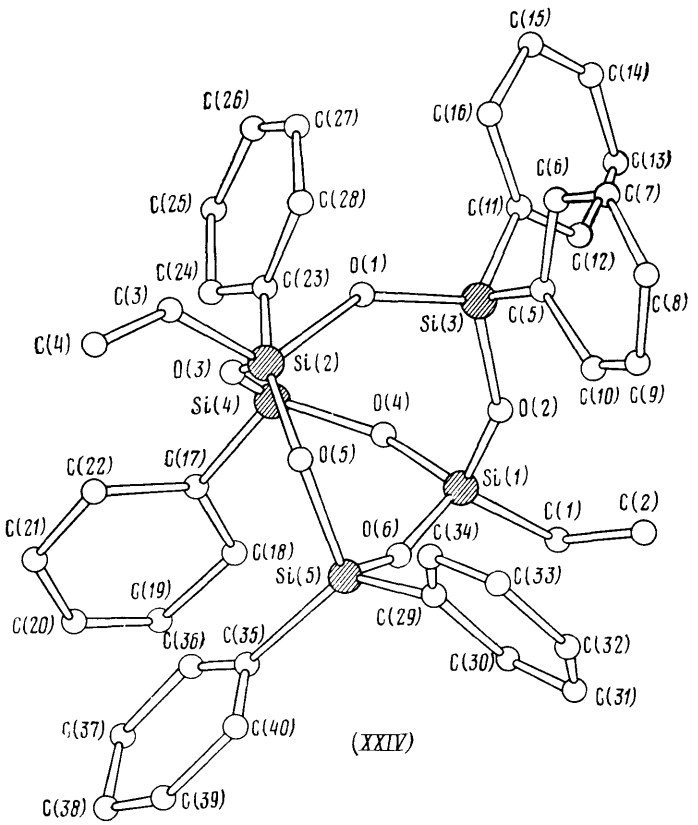


Figure 16. Structure of molecule (XXIV).[70]

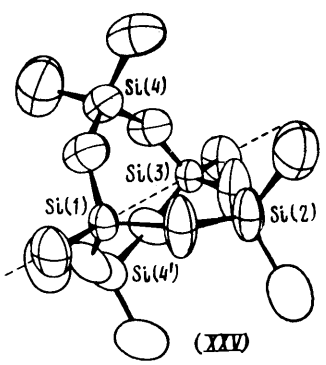


Figure 17. Structure of molecule (XXV).[71] The broken line shows the approximate threefold axis.

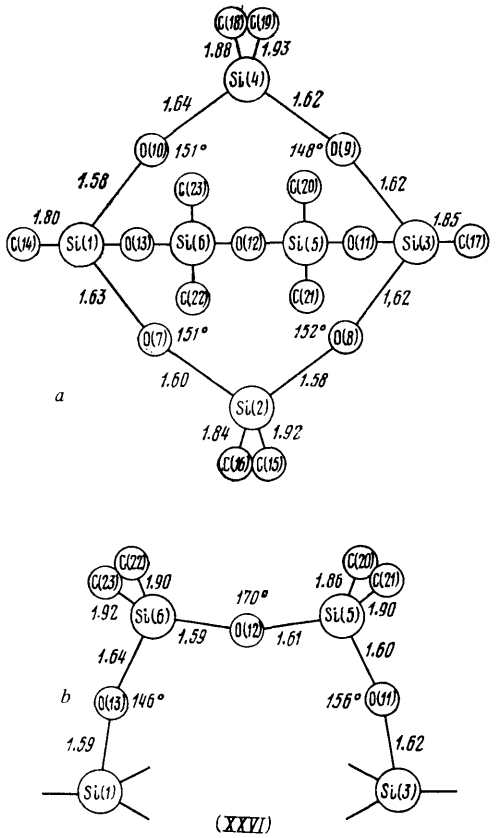
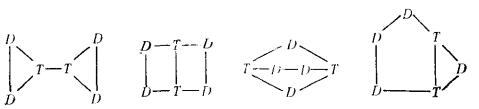


Figure 18. Structure of: *a*) molecule (XXVI); *b*) "semicircle".[73]

The thermal decomposition of branched polydimethylsiloxanes has led to the chromatographic isolation of three products (*a*)–(*c*) having the configuration D_4T_2, for which the structures



are possible[8]. X-Ray examination of one of the products has confirmed the suggested structure (*c*), i.e. (XXVI) in Fig.18.[73] In the molecule with approximate C_{2v} symmetry one D_2T_2 tetrasiloxane ring and two D_3T_2 pentasiloxane rings can be distinguished. The D_2T_2 ring has approximate D_{2d} symmetry (saddle conformation), with the atoms emerging rather less (up to 0.30 Å) from the plane of this eight-membered ring than in isolated D_4 rings, e.g. 0.49 Å in (XI). The atoms forming the "semicircle" $Si_{(1)}O_{(13)}Si_{(6)}O_{(12)}Si_{(5)}O_{(11)}Si_{(3)}$ lie to within 0.13 Å in the same plane, which is approximately perpendicular (dihedral angle 84.9°) to the mean plane of the D_2T_2 ring. The planarity of the "semicircle" $Si_{(1)}...Si_{(3)}$ and also the unexpectedly large SiOSi bond angle (170°) at the $O_{(12)}$ atom are the most interesting stereochemical features of the molecule (XXVI).[73]

The molecule (XXVII) (Fig.19) represents a completely different type of polycyclic organosiloxane[74]. It is located at a centre of symmetry and contains two D_2T rings joined by an extended siloxazane bridge. In a D_2T ring the mean

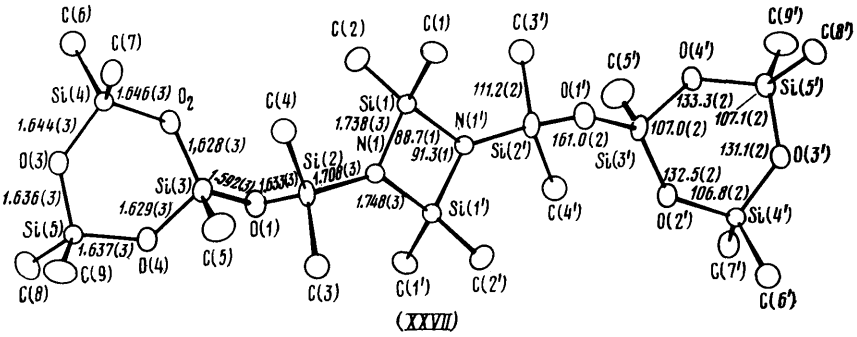


Figure 19. Structure of molecule (XXVII).[74]

silicon–oxygen distance in the *T* unit 1.628(3) Å is shorter than in the *D* units (on the average 1.641(3) Å) or in D_3 rings (Table 1). The maximum departure of atoms from the plane of the D_2T rings (0.08 Å) is of the same order as in D_3 rings. The bond lengths and angles (Fig.19) indicate an interesting strengthening of the linear bonding between siloxane and silazane rings due to intensified p_π–d_π interaction particularly in these parts of the molecule. Hence these siloxazane bridges should be not only the most stable energetically but also the most resistant to the action of ionic reagents. The silazane ring in (XXVII) has the usual geometry#.

VI. CRYSTALLINE STRUCTURE OF ORGANOCYCLOSILOXANES

Crystals of organosiloxanes usually have loose packing and weak intermolecular interaction[51]. Nevertheless, the some thirty crystalline structures known for organosiloxanes include several non-trivial examples related to the stereochemical peculiarities of such compounds and important from the point of view of their practical application.

In a crystal comprising conformationally disordered molecules of (XVIII) the methyl groups of identical§ conformers, the molecules of which are related by the translation *c* and also a centre of symmetry at ½,½,0, are separated by C...C distances of 3.58 (translation *c*), 3.52, 3.52, and 3.64 Å (centre at ½,½,0).[60]

The van der Waals radius of the methyl group is generally assumed to be ~2 Å.[9,75] However, in a crystal of *DL*-*N*-chloroacetalanine[76], for example, with a $C(CH_3)...C(CH_3)$ distance of 3.72 Å between molecules related by centres of symmetry, the H...H distances (the hydrogen atoms have been identified objectively) between these methyl groups are 2.88 Å, i.e. ~0.5 Å greater than double the van der Waals radius of the hydrogen atom[77]. If it is supposed that, with the shortened $C(CH_3)...C(CH_3)$ distances found in a crystal of (XVIII), orientations of the methyl groups are possible for which the H...H and C...H distances are not shortened, a random distribution of conformers of (XVIII) may occur in the crystal: i.e. both identical and different conformers may be neighbours. If, however, such orientations are impossible, some of the intermolecular contacts between identical conformers are forbidden. Unfortunately, X-ray structural analysis has not yet answered the question of the possible juxtaposition of conformers of the same or different types, or indicated the character of the disorder (statistical or dynamic) in a crystal of (XVIII). This requires investigations at low temperatures with location of the hydrogen atoms.

Two problems in organic crystal chemistry—the crystallisation of molecules with porous packing and the chemical interaction of molecules densely packed in a crystal—have special significance for crystals of organocyclosiloxanes. In a crystal of (XXI) cavities of volume ~150 Å³¶ have been observed around symmetry centres 0,½,0 (Fig.20). Clearly, the shape of molecules of (XXI) permits only two-dimensional dense packing: compact superposition of layers is impossible, and the above cavities, which may be filled with small solvent molecules, appear in the crystal. Indeed, differential synthesis of electron density has revealed in the cavities several peaks of electron density corresponding to disordered small molecules of solvents used in preparation and crystallisation[63].

The high temperature factors for atoms present in a solvent molecule are consistent with results obtained for clathrates. For example, the atoms of the dioxan molecules in the clathrate complex $Cd(NH_3)_2.Ni(CN)_4.2C_4H_8O_2$ have isotropic temperature factors of 23 and 14 Å².[78] The volume of a cavity considerably exceeds the molecular volume[80] of the solvents used in the preparation of (XXI) (pyridine 91 Å³, *o*-dichlorobenzene 100 Å³)†, so that the packing coefficient in the cavities is low ($k \approx 0.63$). Then, of course, the (XXI)...Solv intermolecular distances exceed the sum of the van der Waals radii. This explains the possible disorder in the arrangement of solvent molecules in the cavities[63]. When the occluded solvent molecules are taken into account, good agreement is obtained between calculated and measured densities of a crystal of (XXI). If, however, the occupation of the cavities is ignored, the calculated value is smaller than the measured density (1.29 and 1.34 g cm^{-3}), as for the second (not studied structurally) monoclinic modification[79].

#We intend to survey the structure of cyclosilazanes in a subsequent review.

§Corresponding distances between different conformers are considerably longer than 3.8 Å.

¶This quantity has been determined by means of a special programme of search for the positions and volumes of cavities in a crystal, established by L.M.Borisanova (Faculty of Chemistry, Moscow State University, 1976).

†Molecular volumes were calculated from the contributions by atomic groupings[80].

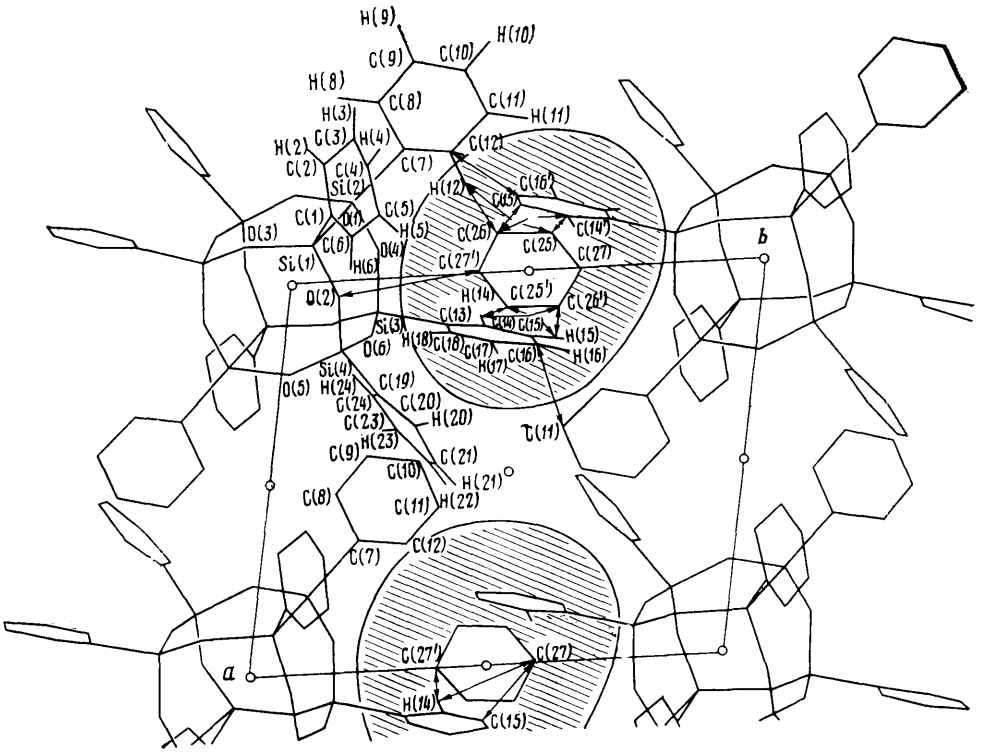


Figure 20. Projection [001] of structure (XXI). The arrows show distances between (XXI) and solvent molecules. Cross-sections of the cavities made by the plane of projection are shaded[63].

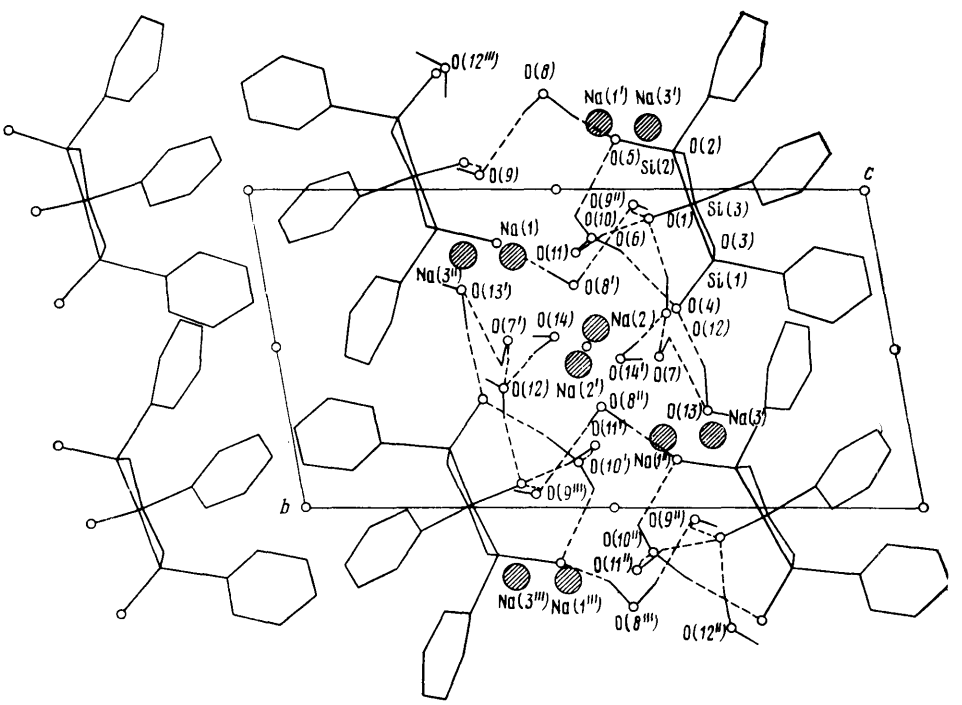


Figure 21. Projection on the face *bc* of the packing of molecules in a crystal of (V). Hydrogen bonds O–H...O are shown by broken lines[105].

Molecules of (XVII) also crystallise with porous packing. Centres of symmetry $0,\frac{1}{2},0$ (the crystals belong to space group $P\bar{1}$) are located in cavities filled with solvent (benzene) molecules. As with crystals of (XXI), the volume of a cavity exceeds that of a benzene molecule, so that the latter is slightly "disordered", which is evident in somewhat increased isotropic temperature factors (~50% larger than for phenyl substituents in the (XVII) molecule).[50]

Among all the crystalline structures of organosiloxanes investigated (around thirty have been determined) voids have been found only in crystals of (XVII) and XXI), which differ from other organocyclosiloxanes in a rigid silicon–oxygen skeleton and from siloxanes having such a skeleton [e.g. from the methyl derivative (XX)] in the presence of bulky phenyl substituents. These latter, by sharply increasing distances between siloxane skeletons, diminish the polar interaction inherent in, for example, crystals of octa(silsesquioxanes) with small substituents[61], as well as promoting the formation of cavities in the crystal.

The ability of several large skeletal siloxane molecules with bulky framing groups to pack with the formation of cavities acquires special interest in the light of the specific gas-permeability of certain cyclolinear organosiloxanes, which has found practical application[81–83]. Although the character of the system of cavities in crystals of (XXI) excludes the possibility of migration of even the simplest molecules from one cavity to another, it may be expected in principle that, by varying the substituents, we shall be able to obtain monolayers or double layers (and perhaps even three-dimensional structures) possessing the necessary permeability.

Many chemical reactions of siloxanes involve intermediate ionic structures. Interest therefore attaches to the results of the first X-ray structural investigation of the ionic sodium salt (V) of a siloxane[13]. The siloxane rings of the anions form layers parallel to the plane *ab*. The gaps between the layers are filled alternately with phenyl groups of the anions (van der Waals interaction between layers) and with sodium cations and water molecules (ionic interaction and hydrogen bonds) (Fig. 21). Interlayer spaces of the second type are characterised by strong electrostatic interaction, which is not found in ordinary molecular crystals of organosiloxanes. The coordination of the sodium ions and their distribution relative to charged fragments of the anion in a crystal of (V) are important for understanding the initial stages in the reactions of organosiloxanes in hydrophilic alkaline media.

Chemical reactions (including polymerisation) of molecules densely packed in a crystal have begun to be studied relatively recently. Several important papers on the crystal chemistry of these processes have been cited in a review[84]. A necessary condition for the occurrence of topochemical solid-phase reactions is that shifts in the equilibrium positions of atoms in the reactant molecules should be minimal with fairly intense vibrational thermal motion of the atoms. This is the fundamental principle of lattice-controlled reactions formulated

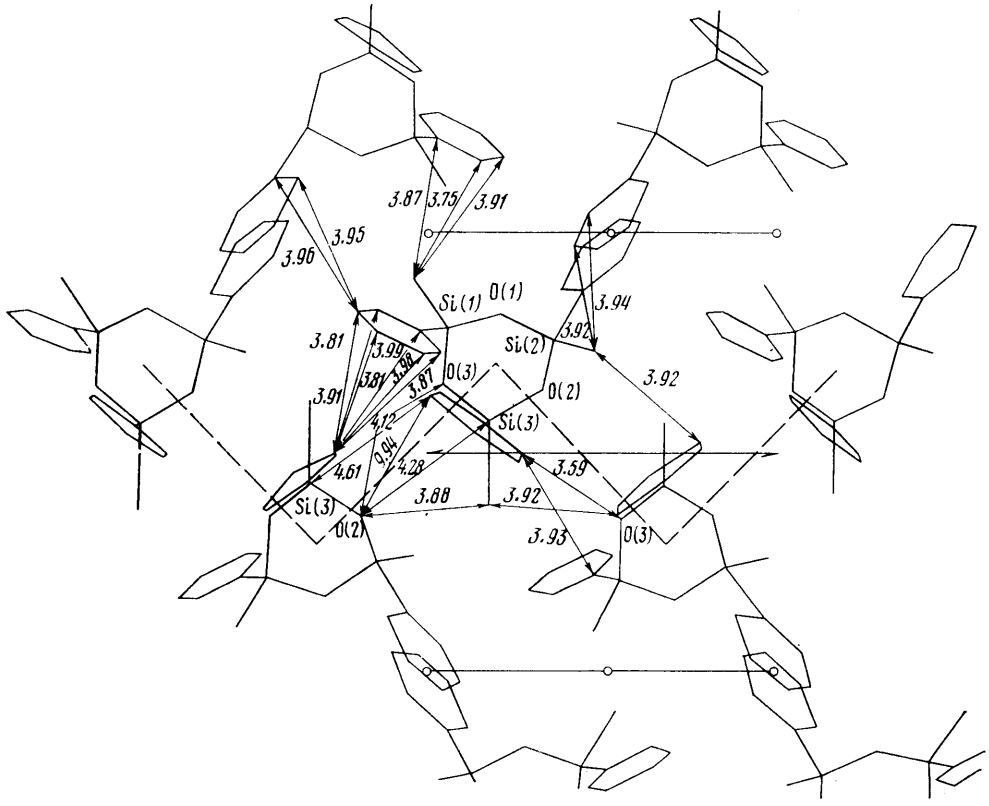


Figure 22. Arrangement of molecules in a layer in structure (IV). The broken lines join centres of D_3 rings in molecules forming chains. The numerals indicate intermolecular distances[12].

by Schmidt[85,86]. In application to solid-phase polymerisation this principle was formulated by Kargin and Kabanov[87].

Derivatives of D_3 rings—(I), (III), and (IV)— are capable of solid-phase polymerisation at room temperature or above in the presence of potassium trimethylsilanolate as initiator[88]. X-Ray examination of compounds (I)–(IV)[9–12] has led to several interesting conclusions on the possibility and the mechanism of the polymerisation of D_3 derivatives in the solid phase. Unfortunately, in contrast to, for instance, oligomers of formaldehyde, for which a molecular mechanism of polymerisation is based on numerous experimental confirmations of the formation of an oriented crystalline polyoxymethylene[89–91,84], results on the formation of ordered polysiloxanes by solid-phase polymerisation have not yet been obtained. Therefore discussion of the mechanism of the solid-phase polymerisation of siloxanes is tentative in character.

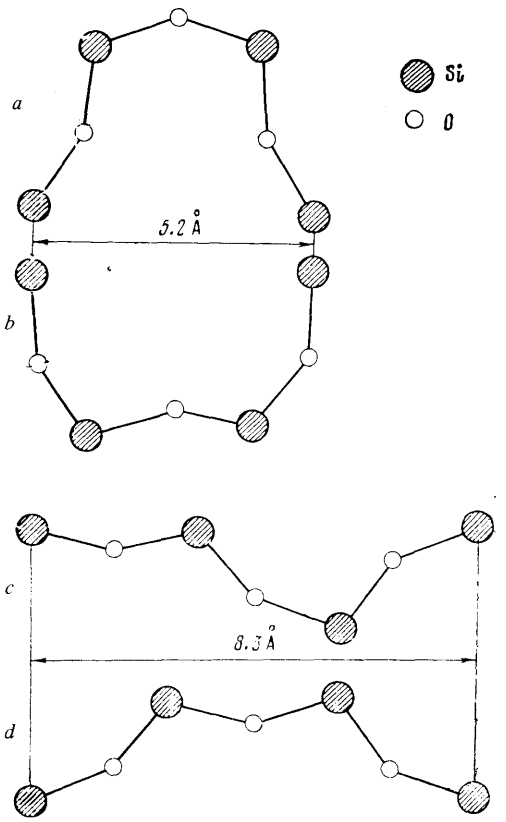


Figure 23. Some possible conformations of a planar monomeric unit in a polysiloxane chain: *a*) *trans,cis,cis,trans*; *b*) *cis,trans,trans,cis* ("shortest" units); *c*) *trans,trans,cis, trans*; *d*) *trans,trans,trans,trans* ("longest" units)[11,12].

In a crystal of (IV)[12] layers of molecules can be clearly distinguished, whose siloxane rings are very accurately coplanar. These layers have an interplanar spacing of 9.52 Å and are parallel to the $(1\bar{2}0)$ face. Fig.22 shows that a layer in turn contains distinct chains of molecules connected by a screw axis lying in the plane of the layer (e.g. 2_1 [$\frac{1}{2}$ $\frac{1}{4}$ z]). Within the layers the distances between silicon and oxygen atoms of neighbouring molecules in the same chain (4.28 and 4.61 Å) are appreciably shorter than the distances between chains (5.46 and 5.63 Å).

The structure of (III)[11] also contains distinct layers of molecules, parallel to the (100) face, but in contrast to (IV) the planes of the D_3 rings are non-coplanar, forming an angle of 27.5° with the plane of the layer. The Si...O distances between the rings of molecules in a layer are 5.46–7.54 Å (no well defined chains present), and those between rings in molecules of neighbouring layers ~9 Å.

In a crystal of (I) the molecules have a disordered distribution, which indicates that their number in a cell is anomalous (space group $R3m$, $z = 1$) with strong diffuse scattering on the X-ray photographs[9]. Layers having $z = 0$, $\frac{1}{3}$, and $\frac{2}{3}$ prove to be identical but displaced statistically one relative to the other along $\mathbf{a}\sqrt{3}/3$ vectors. In the layers the Si...O distances between the initial and each of the six neighbouring siloxane rings have been determined as 4.62 Å; the distance between layers is 6.4 Å.[9]

The packing of molecules of (II), which does not polymerise in the solid state[10], exhibits the following features: (i) all distances between atoms of siloxane rings in neighbouring molecules exceed 7 Å; (ii) although shorter intermolecular contacts are present in the structure of (II) than in that of (IV), they are all effected by atoms of the framing phenyl substituents (only one short C...O contact, of 3.38 Å, is present); (iii) the phenyl groups are so oriented that they shield siloxane rings in neighbouring molecules from each other; and (iv) the coplanar arrangement of D_3 rings in neighbouring molecules characteristic of the structure of (IV) is not observed in the crystal.

A layered distribution of D_3 rings, which in all cyclotrisiloxanes[9–12] have a somewhat strained planar configuration, is especially significant. Indeed, with such an arrangement the framing substituents are distributed between the layers and do not prevent interaction of siloxane rings within layers during polymerisation, which is especially important with such bulky substituents as phenyl. Thus a layered arrangement of D_3 rings favours the solid-phase polymerisation of an organocyclotrisiloxane monomer. Therefore compound (II), for example, whose crystals do not have a layer structure, does not polymerise in the solid phase. Consequently the scheme of polymerisation of cyclic monomers[92], suggested in particular for (I), according to which molecules are arranged in stacks in a crystal of the monomer, and polymerisation occurs with ring opening and formation of extended helices of a crystalline polymer, does not apply to D_3 rings.

The possibility of the polymerisation of a cyclic monomer in a given crystallographic direction can sometimes be assessed by comparing the distance between neighbouring rings in this direction with the length of a unit formed topochemically on opening of the rings. In view of the inevitable increase# in SiOSi angles from 132° to ~160° when a D_3 ring is opened, the resulting polysiloxane chain acquires a planar conformation, and the length of a unit in this chain, formed from a single ring, will vary from ~5.2 Å (*trans,cis, cis,trans*- or *cis,trans,trans,cis*-conformation) to ~8.3 Å (*trans,trans,cis,trans*- or *trans,trans,trans,trans*-conformation) (Fig.23). The distances between centres of siloxane rings corresponding to these limits are (*a*) in structure (IV)[12] respectively ~6.9 and ~8.1 Å between neighbouring molecules

#Since the SiOSi angles in D_3 rings are considerably smaller (~130°) than those in siloxanes with a large number of units, where these angles vary between 140° and 160°, polymerisation with ring opening should be accompanied by an increase in the angles.

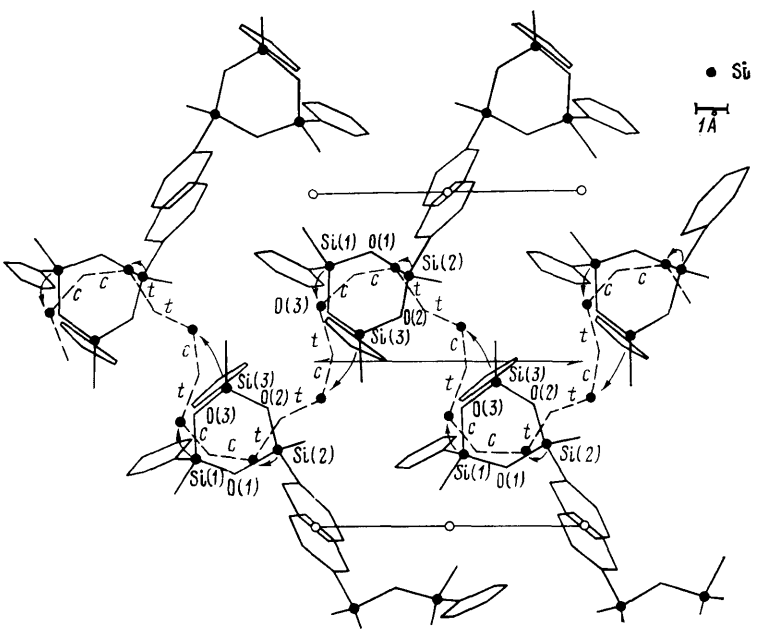


Figure 24. A layer in structure (IV). The broken line shows a planar polysiloxane chain which may be formed on the cleavage of rings at $Si_{(3)}-O_{(2)}$ bonds and the closure of $Si_{(3')}-O_{(2')}$ intermonomer bonds at the sites of the shortest intermolecular Si...O contacts (the arrows indicate the displacement of atoms on polymerisation). The letters *c* and *t* denote units in the polymer chain having *cis* and *trans* conformations respectively. The polymer chain formed has a *cis,cis,trans, trans,cis,trans* conformation of the monomeric unit[11,12].

in the chain and between molecules of neighbouring chains in the same layer related by centres of symmetry 0,0,0, (*b*) in structure (III)[11] ~8.6 and ~8.5 Å between molecules in the same layer related by translations *b* and *c*§, and (*c*) in structure (I) respectively ~7.6 and ~6.4 Å between neighbouring molecules in a layer and between molecules in neighbouring layers¶. The OSiO bond angles in mono- and poly-organosiloxanes are approximately constant and differ from the tetrahedral angle (109.5°) by at most 2–3°.

In relation to the solid-phase polymerisation of (IV) the main condition of topochemical polymerisation (retention by most atoms of their approximate positions during polymerisation[84]) leads to the requirement of maximum similarity of the configuration of the resulting polymer chain to that of the siloxane rings of the monomer. Fig. 24 shows that this requirement is met by a *cis,cis,trans,trans,cis,trans*-conformation of the monomeric unit in a polymeric chain constructed by changes in the SiOSi bond angles with the OSiO angles constant. It must be emphasised that this polymer chain is formed by opening the rings at the $Si_{(3)}-O_{(2)}$ bonds, which in a crystal of (IV) corresponds to the shortest intermolecular distance $Si_{(3)}...O_{(2')}$ (4.28 Å) of all the Si...O distances in the chain of molecules. Thus the suggested scheme of formation of the polymer chain satisfies both the condition of topochemical polymerisation and the condition of closest spatial proximity of chemically interacting atoms. It should lead to considerable compression of the crystal in the direction of the polymer chain. Actually the distance between the centres of siloxane rings in adjacent monomeric molecules in the chain is 6.9 Å, while the length of a unit in the resulting polymer chain (i.e. the distance between the centres of gravity of the trios of silicon atoms from one former ring) is ~5.9 Å.[11,12]

Thus analysis of the packing shows that the distances between the centres of neighbouring siloxane rings in structural layers of (I), (III), and (IV) probably permit chemical interaction of the rings with formation of polymer chains. The structure of (IV) is more favourable to the propagation of polymerisation in chains of molecules, which may lead (with a topochemical mechanism) to formation of an oriented polymer. In a crystal of (III) polymerisation in layers is most likely, while the direction of chain growth within a layer may vary, with formation of different macrocycles D_n. In contrast to a crystal of (IV), polymerisation in layers in (I) and (III) requires considerable three-dimensional rearrangement in the crystals of these monomers.

With regard to a possible mechanism for the initiation of polymerisation it is reasonable to assume[11,12] that deposition of the initiator on crystal faces parallel to the planes of layers of siloxane rings in crystals of (I), (III), and (IV), i.e. respectively on the faces (001), (100), and ($1\bar{2}0$), would lead to rapid two-dimensional polymerisation in these planes, leaving deep-seated portions of the crystal unaffected. Deposition of the initiator on faces perpendicular to the layer planes, however, will lead to development of polymerisation

§ A difference of ~0.3 Å from the upper limit is insignificant and "surmountable" by the thermal motion of the atoms at ordinary temperatures[80].

¶ The absence from a crystal of (I) of preferred directions (in the chain and in the layer) is consistent with the formation of an amorphous polymer by its solid-phase polymerisation[88].

in all densely packed layers of molecules, i.e. to the spread of polymerisation throughout the crystal†.

In a crystal of (XXVII) the D_2T rings in chains of molecules related by centres of symmetry $0,\frac{1}{2},\frac{1}{2}$ are significantly closer together (Fig.25). The $Si_{(4)}...O_{(3')}$ and $Si_{(4')}...O_{(3)}$ distances between these molecules are 4.12 Å, considerably less than any other Si...O intermolecular distance, the shortest of which is 5.46 Å. The layers are situated in $(01\bar{1})$ planes. The Si...O distances between D_2T rings in different layers exceed 7 Å.[74,94] The question arises whether the localisation of deformation of D_2T rings in the structure of (XXVII) and the relative weakening of $Si_{(4)}-O_{(3)}$ bonds are not caused by the observed closer approach of these particular parts of neighbouring molecules in the crystal. Such approach is probably due to electrostatic interaction of the antiparallel $Si_{(4)}-O_{(3)}$ and $Si_{(4')}-O_{(3')}$ dipoles.

It must then be ascertained whether such specific interaction of the molecules in the crystal does not affect the mechanism of polymerisation. If solid-phase polymerisation of (XXVII) is possible, this intermolecular interaction may lead to a polymer having a cyclolinear structure of alternating disilazane and D_4T_2 rings joined by trimeric siloxazane bridges with the polymer chain extended along the [011] direction of the monomer crystal (Fig.25).[94]

It follows from the crystal and molecular structure of (XXVII) that, if local attack by a nucleophilic species (with substantial initiation of solid-phase polymerisation) takes place at silicon–oxygen bonds in D units of the cyclic portion of a molecule located on the crystal surface, leading to cleavage of the siloxane ring and migration of the active centre to the oxygen atom, then rupture of a silicon–oxygen bond in an adjacent molecule (related to the initial centre of symmetry $0,\frac{1}{2},\frac{1}{2}$) should be facilitated. However, further transfer of the active centre to the other end of the molecule is impossible because of its great length, and all other distances between rings in the crystal are too large for topochemical interaction. "Chemical" intermolecular interactions other than the above interaction of D units are possible only in lattice defects.

In fact[74] solid-phase polymerisation in the presence of an ammonium catalyst involves 6–7% formation of an insoluble product, but >90% of the initial compound remains unchanged. In benzene solution at the same temperature (~50 °C) a polymer of predominantly network structure is formed together with a gel fraction (62%). Polymerisation goes similarly in the melt at higher temperatures#.

A crystal of (XXIV) contains infinite chains of molecules in contact at their vinyl side-chains with C...C distances of ~4 Å (Fig.26).[70] At such distances molecules are able to

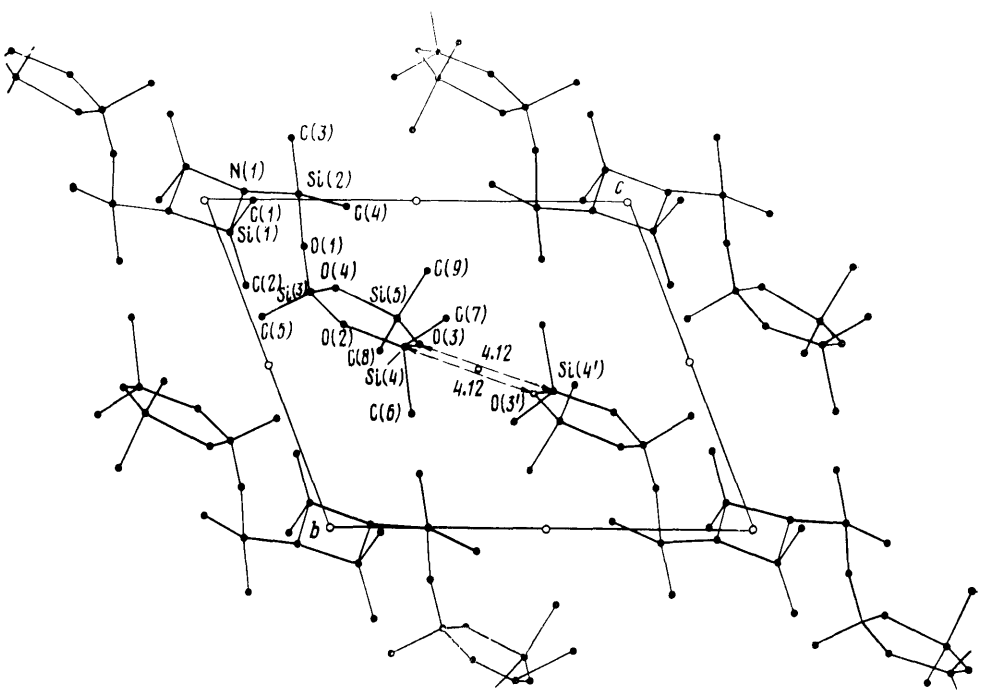


Figure 25. Projection (100) of structure (XXVII).[94]

†An analogous mechanism of initiation was suggested and confirmed by polarisation data and electron microscopy, as well as by measurements of infrared dichroism, for the solid-phase polymerisation of *p*-acetamidostyrene and *p*-benzamidostyrene, whose crystals also have a layer structure[93].

#A study is now being made of the possibility of radiation-induced solid-phase polymerisation of (XXVII), which would eliminate difficulties associated with the transfer of active centres: on exposure they are generated throughout the crystal.

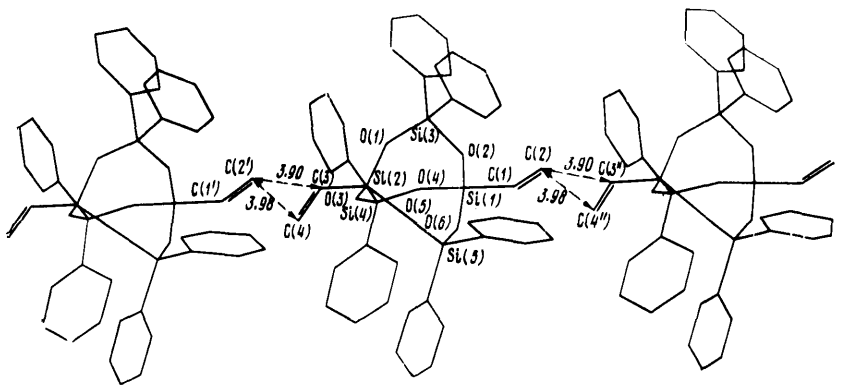


Figure 26. Diagram of chain of molecules in a crystal of (XXIV). Contacts C...C between vinyl groups in neighbouring molecules are indicated.

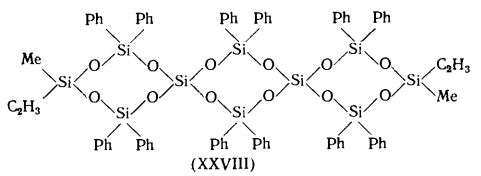
interact in the crystal by a topochemical mechanism[84]. It was therefore suggested[70] that (XXIV) is able to polymerise in the crystal through the vinyl groups with formation of a "bead" type of polymer. An attempt is now being made to confirm experimentally this crystal-chemical conclusion.

VII. CONCLUSION

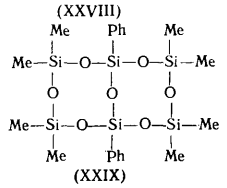
It may be concluded not so much from the quantity of papers published on the crystal structure of organocyclosiloxanes (though it is quite convincing) as from the character of the problems tackled and the importance of several of the findings that X-ray structural (and physicochemical in general) investigation of this class of compounds is being vigorously pursued. Although it is difficult to expect the preparation of novel monomers in this field, while synthetic work is aimed mainly at improving and modifying known structures, the growth in the number of structural investigations on organocyclosiloxanes is undoubtedly justified, since it not only promotes further successful development of this field of macromolecular hetero-organic chemistry but also leads to the accumulation of the valuable factual and procedural information required for the analysis of novel or little-studied classes of hetero-organic monomers.

---o0o---

During the preparation of this Review for publication structural information has appeared on the spirocyclic siloxane (XXVIII),[95] the bicyclic siloxane (XXIX),[96]



(XXVIII)



(XXIX)

and also a tetragonal modification (XXX)[97] of octa(phenylsilsesquioxane) $(C_6H_5SiO_{1.5})_8$. The form of the tetrasiloxane rings in (XXVIII) and (XXIX) has been described by the Cremer–Pople method[98] and specified by the Hendrickson method[99].

In the centrosymmetric molecule (XXVIII) the outer D_3Q rings form dihedral angles of 83.2° with the plane of the inner D_2Q_2 ring. The latter ring has a form close to *LC*, and the outer rings are intermediate between *B* and *BB*. As in other spirocyclosiloxanes (Section III) the mean distance between a spiro-silicon atom and an oxygen atom (*Q* units) is 1.598(8) Å, rather less than the remaining silicon–oxygen distances (*D* units, 1.62(1) Å). The terminal vinyl groups, *trans* with respect to the tricyclic silicon–oxygen system, are disordered[95].

The form of the D_2T_2 rings constituting the molecule (XXIX) is close to *BB*, with a dihedral angle of 125.9°. The silicon–oxygen bond lengths in *D* and *T* units differ little (on the average they are respectively 1.630(8) and 1.62(1) Å).[96]

The $(C_6H_5SiO_{1.5})_8$ molecules in a crystal of (XXX) are situated on fourfold axes (in (XXI) at centres of symmetry). The mean silicon–oxygen and silicon–carbon distances (1.613 and 1.833 Å), and also the SiOSi bond angle (148.5°), are closely similar to those found in a crystal of the triclinic modification of (XXI). As in the latter compound, disordered solvent (acetone) molecules are found in a crystal of (XXX), which do not escape from the crystal in air, despite the absence of specific intermolecular interaction. The packing of molecules in a crystal of (XXX) is fairly free, with a shortest intermolecular C...C distance of 3.752 Å.[97]

REFERENCES

1. V.V.Korshak and A.A.Zhdanov, Uspekhi Khim., **44**, 468 (1975) [Russ.Chem.Rev., No.3 (1975)].
2. H.R.Allcock, "Phosphorus–Nitrogen Compounds" (Translated into Russian), Mir, Moscow, 1976.
3. H.R.Allcock, "Heteroatom Ring Systems and Polymers" (Translated into Russian), Mir, Moscow, 1970.
4. K.A.Andrianov, "Polimery s Neorganicheskimi Glavnymi Tsepyami Molekul" (Polymers with Inorganic Main Chains of Molecules), Izd.Akad.Nauk SSSR, 1962.
5. H.R.Allcock, Angew.Chem., **89**, 153 (1977).

6. I.Dubois, G.Herzberg, and R.D.Verma, J.Chem. Phys., **42**, 2496 (1964).
7. K.A.Andrianov, T.V.Vasil'eva, N.M.Katashuk, T.V.Snegireva, and B.I.D'yachenko, Vysokomol. Soed., **18A**, 1270 (1976).
8. G.Garzo and J.Tamas et al., Acta Chim.Acad.Sci. Hung., **69**, 273 (1971).
9. G.Peyronel, Struct.Rept., **18**, 682 (1954).
10. N.G.Bokii, G.N.Zakharova, and Yu.T.Struchkov, Zhur.Strukt.Khim., **13** (291) (1972).
11. V.E.Shklover, N.G.Bokii, Yu.T.Struchkov, K.A.Andrianov, B.G.Zavin, and V.S.Svistunov, Zhur.Strukt.Khim., **15**, 841 (1974).
12. V.E.Shklover, N.G.Bokii, Yu.T.Struchkov, K.A.Andrianov, B.G.Zavin, and V.S.Svistunov, Zhur.Strukt.Khim., **15**, 96 (1974).
13. I.P.Dubchak, V.E.Shklover, M.M.Levitskii, A.A.Zhdanov, and Yu.T.Struchkov, in "Tezisy Dokladov II Vsesoyuznogo Soveshchaniya po Kristallokhimii" (Abstracts of Papers at Second All-Union Conference on Organic Crystal Chemistry), Zvenigorod, 1978, p.79.
14. K.A.Andrianov, S.E.Yakushkina, V.S.Svistunov, and B.D.Lavrukhin, Dokl.Akad.Nauk SSSR, **138**, 345 (1969).
15. H.Steinfink, B.Post, and J.Fankuchen, Acta Cryst., **8**, 420 (1955).
16. V.E.Shklover, A.E.Kalinin, A.I.Gusev, N.G.Bokii, Yu.T.Struchkov, K.A.Andrianov, and I.M.Petrova, Zhur.Strukt.Khim., **14**, 692 (1973).
17. D.Carlstrom and G.Falkenberg, Acta Chem.Scand., **27B**, 1203 (1973).
18. M.Soderholm and D.Carlstrom, Acta Chem.Scand., **31B**, 193 (1977).
19. A.I.Gusev, D.Yu.Nesterov, N.V.Alekseev, V.V.Zverev, M.B.Lotarev, D.V.Nazarova, N.E.Rodzevich, and M.V.Sobolevskii, in "Tezisy Dokladov I Vsesoyuznogo Simpoziuma 'Stroenie i Reaktsionnaya Sposobnost' Kremniiorganicheskikh Soedinenii'" (Abstracts of Papers at First All-Union Symposium on "Structure and Reactivity of Organosilicon Compounds"), Irkutsk, 1977, p.56.
20. D.Yu.Nesterov, A.I.Gusev, N.V.Alekseev, and M.B.Lotarev, Zhur.Strukt.Khim., in the press.
21. A.N.Lazarev and T.F.Tenisheva, Izv.Akad.Nauk SSSR, Ser.Khim., 1168 (1964).
22. N.G.Bokii and Yu.T.Struchkov, Zhur.Strukt.Khim., **9**, 722 (1968).
23. D.A.Bochvar, N.P.Gambaryan, and L.M.Epshtein, Uspekhi Khim., **45**, 1316 (1976) [Russ.Chem.Rev., No.7 (1976)].
24. M.O'Keefe and B.G.Hyde, Acta Cryst., **B32**, 2923 (1976).
25. C.Glidewell, Inorg.Chim.Acta Rev., **7**, 69 (1973).
26. C.Glidewell and D.C.Liles, Acta Cryst., **B34**, 124 (1978).
27. C.Glidewell, Inorg.Chim.Acta, **12**, 219 (1975).
28. M.O'Keefe, Acta Cryst., **B34**, 27 (1978).
29. M.E.Dyatkina and N.M.Klimenko, Zhur.Strukt. Khim., **14**, 173 (1973).
30. C.G.Pitt, J.Amer.Chem.Soc., **61**, 49 (1970), [sic.].
31. D.C.Craig and N.L.Paddock, J.Chem.Soc., 4118 (1962).
32. A.N.Lazarev, "Kolebatel'nye Spektry i Stroenie Silikatov" (Vibrational Spectra and Structure of Silicates), Nauka, Leningrad, 1968.
33. H.Oberhammer, W.Zeil, G.Fail, and G.Fagarasi, J.Mol.Structure, **18**, 309 (1973).
34. G.S.Smith and L.E.Alexander, Acta Cryst., **16**, 1015 (1963).
35. V.E.Shklover, N.G.Bokii, Yu.T.Struchkov, K.A.Andrianov, A.B.Zachernyuk, and E.A.Zhdanova, Zhur.Strukt.Khim., **15**, 850 (1974).
36. V.E.Shklover, Yu.T.Struchkov, B.I.Astapov, and K.A.Andrianov, Zhur.Strukt.Khim., **20**, 102 (1979).
37. G.B.Bokii, "Kristallokhimiya" (Crystal Chemistry), Nauka, Moscow, 1971.
38. K.J.Olson, Toxicol.Appl.Pharmacol., **21**, 12 (1972).
39. D.R.Bennett, S.J.Gorzinski, and J.E.LeBeau, Toxicol.Appl.Pharmacol., **21**, 55 (1972).
40. D.R.Bennett and B.Aberg, Acta Pharmacol.Toxicol., **36**, Suppl.III (1975).
41. A.F.Skryshevskii, V.P.Klochkov, and Yu.V.Pasechnik, Zhur.Strukt.Khim., **2**, 140 (1960).
42. H.Oberhammer, W.Zeil, and G.Fogarasi, J.Mol. Structure, **18**, 309 (1973).
43. V.E.Shklover, N.G.Bokii, Yu.T.Struchkov, K.A.Andrianov, and A.B.Zachernyuk, Zhur.Strukt. Khim., **15**, 857 (1974).
44. Yu.I.Smolin, Yu.F.Shepelev, and A.P.Titov, Kristallografiya, **17**, 857 (1972).
45. E.M.Shustorovich, Zhur.Strukt.Khim., **4**, 773 (1963).
46. K.A.Andrianov and A.B.Zachernyuk, Vysokomol. Soed., **16A**, 1435 (1974).
47. L.W.Roth and D.Harker, Acta Cryst., **1**, 34 (1948).
48. V.E.Shklover, Yu.T.Struchkov, K.A.Andrianov, and A.B.Zachernyuk, Zhur.Strukt.Khim., **19**, 116 (1978).
49. V.E.Shklover, Yu.T.Struchkov, G.V.Solomatin, A.B.Zachernyuk, and K.A.Andrianov, Zhur.Strukt. Khim., **20**, 315 (1979).
50. V.E.Shklover, G.V.Solomatin, A.B.Zachernyuk, and Yu.T.Struchkov, see Ref.13, p.78.
51. M.G.Voronkov, V.P.Mileshkevich, and Yu.A.Yuzhelevskii, "Siloksanovaya Svyaz'" (The Siloxane Bond), Nauka, Novosibirsk, 1976.
52. K.A.Andrianov, A.B.Zachernyuk, and B.D.Lavrukhin, Dokl.Akad.Nauk SSSR, **207**, 593 (1972).
53. J.F.Brown, L.H.Vogt, and P.I.Prescott, J.Amer. Chem.Soc., **86**, 1120 (1964).
54. V.N.Tsvetkov, V.E.Eskin, and S.Ya.Frenkel', "Struktura Makromolekul v Rastvorakh" (Structure of Macromolecules in Solution), Nauka, Moscow, 1964.
55. T.M.Birshtein, Vysokomol.Soed., **16A**, 54 (1974).
56. J.F.Brown, J.Amer.Chem.Soc., **87**, 4317 (1965).
57. K.A.Andrianov, G.A.Kurakov, F.F.Sushchentseva, V.A.Myagkov, and V.A.Avilov, Dokl.Akad.Nauk SSSR, **166**, 855 (1966).
58. A.Katchmann, US P.3 162 614 (1964).
59. V.E.Shklover, A.N.Chekhlov, Yu.T.Struchkov, N.N.Makarova, and K.A.Andrianov, Dokl.Akad. Nauk SSSR, **234**, 614 (1977).
60. V.E.Shklover, A.N.Chekhlov, Yu.T.Struchkov, N.N.Makarova, and K.A.Andrianov, Zhur.Strukt. Khim., **19**, 1091 (1978).
61. K.Larsson, Arkiv Kemi, **16**, 215 (1960).
62. K.Larsson, Arkiv Kemi, **16**, 203 (1960).
63. V.E.Shklover, Yu.T.Struchkov, N.N.Makarova, and K.A.Andrianov, Zhur.Strukt.Khim., **19**, 1107 (1978).
64. I.A.Baidina, N.V.Podberezskaya, T.N.Martynova, S.V.Borisov, A.N.Kanev, and Yu.V.Vasikhin, see Ref.19, p.239.

65. V.E.Shklover, Yu.T.Struchkov, I.Yu.Klement'ev, V.S.Tikhonov, and K.A.Andrianov, Zhur.Strukt. Khim., **20**, 308 (1979).
66. B.Z.Volchek, A.V.Purkina, and V.N.Nikitin, Vysokomol.Soed., **18A**, 1203 (1976).
67. A.N.Goryunov and T.M.Birshtein, Vysokomol.Soed., **18A**, 2466 (1976).
68. K.A.Andrianov and N.N.Makarova, Izv.Akad.Nauk SSSR, Ser.Khim., 2046 (1972).
69. K.A.Andrianov, N.N.Makarova, and N.V.Chizhova, Izv.Akad.Nauk SSSR, Ser.Khim., 2554 (1975).
70. V.E.Shklover, N.G.Bokii, Yu.T.Struchkov, K.A.Andrianov, M.N.Ermakova, and N.A.Dmitricheva, Zhur.Strukt.Khim., **15**, 864 (1974).
71. G.Menczel and J.Kiss, Acta Cryst., **B31**, 1214 (1975).
72. K.A.Andrianov, M.N.Ermakova, N.A.Dmitricheva, V.E.Shklover, N.G.Bokii, and Yu.T.Struchkov, Dokl.Akad.Nauk SSSR, **220**, 1321 (1975).
73. G.Menczel, Acta Chim.Acad.Sci.Hung., **92**, 9 (1977).
74. V.E.Shklover, P.Ad'yaasuren, Yu.T.Struchkov, E.A.Zhdanova, V.S.Svistunov, G.V.Kotrelev, and K.A.Andrianov, Dokl.Akad.Nauk SSSR, **241**, 377 (1978).
75. P.J.Wheatley, J.Chem.Soc., 1721 (1962).
76. F.E.Cole, Acta Cryst., **B26**, 622 (1970).
77. Yu.V.Zefirov and P.M.Zorkii, Zhur.Strukt.Khim., **15**, 118 (1974).
78. E.Kendy and D.Ulku, Z.Krist., **144**, 91 (1976).
79. K.Larsson, Arkiv Kemi, **16**, 209 (1960).
80. A.I.Kitaigorodskii, "Molekulyarnye Kristally" (Molecular Crystals), Nauka, Moscow, 1971.
81. A.V.Nikiforov, A.D.Sobolevskaya, Yu.V.Zherdev, A.Ya.Korolev, and B.A.Kiselev, Vysokomol.Soed., **17B**, 238 (1975).
82. V.P.Budtov, V.P.Vorob'ev, and P.I.Sozhin, Vysokomol.Soed., **11A**, 2586 (1974).
83. J.Marchaud, Rev.gén.Caoutchoucs Plast., **50**, 929 (1973).
84. V.E.Shklover, N.G.Bokii, and Yu.T.Struchkov, Uspekhi Khim., **46**, 1368 (1977) [Russ.Chem.Rev., No.8 (1977)].
85. M.I.Cohen and G.M.J.Schmidt, J.Chem.Soc., 1996 (1964).
86. G.M.J.Schmidt, "Reactivity of the Photoexcited Molecule", Interscience Publ., London, 1967, p.227.
87. V.A.Kargin and V.A.Kabanov, Zhur.Vses.Khim. Obshch.Mendeleeva, **9**, 602 (1964).
88. K.A.Andrianov, V.A.Temnikovskii, L.M.Khananashvili, B.G.Zavin, A.G.Kuznetsov, S.A.Golubtsov, and V.I.Ivanov, Vysokomol.Soed., **9B**, 637 (1969).
89. Y.Chatani, T.Uchida, H.Tadokoro, K.Nayashi, M.Nishii, and S.Okamura, J.Macromol. Sci., Phys., **B2**, 567 (1968).
90. Y.Chatani, K.Kitahama, H.Tadokoro, T.Yamuauchi, and Y.Miyake, J.Macromol.Sci., Phys., **B4**, 61 (1970).
91. Y.Chatani, T.Ohno, T.Yamauchi, and Y.Miyake, J.Polymer Sci., **A-2**, 11, 369 (1973).
92. G.Wegner, A.Munoz-Escalona, and E.W.Fischer, Ber.Bunsengesellschaft, Phys.Chem., **74**, 909 (1970).
93. S.Z.Jakabhazy, H.Morawetz, and N.Morosoff, J.Polymer Sci., Polymer Symp., **4**, 805 (1964).
94. V.E.Shklover, P.Ad'yaasuren, Yu.T.Struchkov, E.A.Zhdanova, V.S.Svistunov, G.V.Kotrelev, and K.A.Andrianov, Zhur.Strukt.Khim., in the press.
95. A.A.Zhdanov, E.V.Khynku, N.A.Kurasheva, and V.E.Shklover, Dokl.Akad.Nauk SSSR, in the press.
96. V.E.Shklover, Yu.T.Struchkov, N.N.Makarova, and A.A.Zhdanov, Cryst.Struct.Comm., in the press.
97. M.A.Hossain, M.B.Hursthouse, and K.M.A.Malik, Acta Cryst., **B35**, 2258 (1979).
98. D.Cremer and J.A.Pople, J.Amer.Chem.Soc., **97**, 1354 (1975).
99. J.B.Hendrickson, J.Amer.Chem.Soc., **89**, 7047 (1967).
100. V.E.Shklover, I.L.Dubchak, Yu.T.Struchkov, V.P.Mileshkevich, T.A.Nikolaev, and Yu.V.Tsyganov, Zhur.Strukt.Khim., in the press.
101. I.L.Dubchak, V.E.Shklover, Yu.T.Struchkov, E.A.Kashutina, O.I.Shchegolikhina, and A.A.Zhdanov, Dokl.Akad.Nauk SSSR, **246**, 1133 (1979).
102. C.Glidewell, Inorg.Chim.Acta, **29**, L283 (1978).
103. V.E.Shklover, Yu.T.Struchkov, G.V.Solomatin, A.B.Zachernyuk, and A.A.Zhdanov, Zhur.Strukt. Khim., in the press.
104. V.E.Shklover, Yu.I.Klement'ev, and Yu.T.Struchkov, Dokl.Akad.Nauk SSSR, **250**, 881 (1980).
105. I.L.Dubchak, V.E.Shklover, M.M.Levitskii, A.A.Zhdanov, and Yu.T.Struchkov, Zhur.Strukt. Khim., **21**, in the press.

Institute of Hetero-organic Compounds,
USSR Academy of Sciences, Moscow

RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

April 1980

Translated from *Uspekhi Khimii*, 49, 561-587 (1980)

U.D.C. 541.124

Auto-oscillations in the Rates of Heterogeneous Catalytic Reactions

M.G.Slin'ko and M.M.Slin'ko

Experimental data on the auto-oscillations in the rates of heterogeneous catalytic reactions are surveyed and the physicochemical principles of the origin of this phenomenon are examined. It is shown that the auto-oscillations can be due to a change in the properties of the catalyst under the influence of adsorbed reactants or reactants dissolved in a thin surface layer of the catalyst. Kinetic models of the reaction of hydrogen with oxygen on nickel and platinum catalysts, the phase plots of which contain limiting cycles, are examined in detail and models are presented for the auto-oscillations in the rate of reaction of oxygen with carbon monoxide on platinum catalysts. The importance of the auto-oscillations in the reaction rate for the development of the theory of heterogeneous catalysis is discussed.
The bibliography includes 69 references.

CONTENTS

I.	Introduction	295
II.	Experimental data	295
III.	Physicochemical basis of the auto-oscillations in the rate of reaction	300
IV.	Mathematical models	301
V.	Conclusion	307

I. INTRODUCTION

A necessary condition for the occurrence of auto-oscillations is the presence in the system of a sufficiently strong feedback. It ensures the supply to the system of sufficient energy which is regulated by the movement of the oscillating system itself. The theory of bifurcations in dynamic systems constitutes the mathematical basis of the theory of auto-oscillations[1,2].

Heterogeneous catalytic systems have all the characteristic features of non-linear dynamic systems, so that under certain conditions there is a possibility of auto-oscillations in the rate of a heterogeneous catalytic reaction. Since the auto-oscillations are very sensitive to the structure and properties of the system, they are of considerable interest for the understanding of the detailed mechanism of chemical reactions and for the establishment of the general features of reactions involving various types of catalysis: homogeneous, enzymatic, and heterogeneous. The auto-oscillations in the rates of reaction in homogeneous chemical and biological systems have been vigorously studied recently and there are a number of fairly complete reviews[3-8]. This review gives an account of studies devoted to the auto-oscillations in heterogeneous catalytic systems alone.

II. EXPERIMENTAL DATA

The oxidation of carbon monoxide on platinum catalysts is one of the first heterogeneous catalytic systems where auto-oscillations in the reaction rate were observed in the kinetic

region. This reaction has been studied[9] in a flow-circulation apparatus; the catalyst consisted of a platinum mesh prepared from wire 0.04 mm in diameter and having 3600 apertures per square centimetre. The reaction mixtures contained a large excess of air. At very low carbon monoxides pressures in air stable stationary states were observed in the system and the reaction was of second order with respect to carbon monoxide. With increase of carbon monoxide pressure, stable oscillations appeared. If the partial pressure of carbon monoxide rose, the amplitude and frequency of the oscillations increased, the average rate of reaction reaching a maximum. A further increase in the partial pressure of carbon monoxide led to a sharp fall of the rate of reaction and to the disappearance of the oscillations.

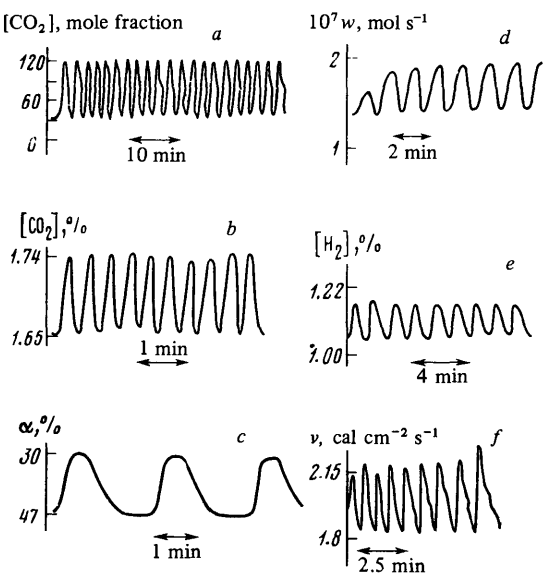


Figure 1. The overall form of the auto-oscillating processes in various heterogeneous catalytic systems: *a*) auto-oscillations in the rate of oxidation of carbon monoxide on a porous grain of platinised γ-alumina (180 °C; 1% CO; air)[10]; *b*) auto-oscillations in the rate of oxidation of CO on a Pt catalyst deposited on α-Al_2O_3;[11] *c*) auto-oscillations in the rate (degree of conversion α) of oxidation of CO on a Pt foil catalyst in an ideal mixing reactor (239 °C; 1.08% CO; air)[14]; *d*) auto-oscillations in the rate (*w*) of oxidation of hydrogen on a nickel foil (245 °C; 0.8% O_2; 99% H_2);[55] *e*) auto-oscillations in the rate of oxidation of hydrogen on a platinum wire (221 °C; 3.48% H_2; air)[53]; *f*) auto-oscillations in the rate of heat evolution in the oxidation of ethylene on a platinum wire (390 °C; 2% C_2H_4; 98% O_2).[24]

A similar dependence of the rate of reaction of carbon monoxide with oxygen on the carbon monoxide concentration in the gas phase was observed in another study[10] of this reaction on a catalyst grain containing 0.3% Pt deposited on γ-Al_2O_3. The reaction was carried out in a flow reactor in a stream of air containing small amounts of carbon monoxide. Fig. 1*a* illustrates the stable oscillations of the reaction rate observed in the region of the rate maximum. The period of the oscillations was several minutes. As in the oxidation of carbon monoxide on the platinum mesh, the amplitude of the oscillations increased with increase of the CO concentration in the initial mixture. As the catalyst temperature rose, the frequency of the oscillations increased and their amplitude fell. Above 250 °C the oscillation vanished. The authors[10] noted the high sensitivity of the characteristics of the oscillations to the properties of the catalyst. On passing from one catalyst grain to another, a change in the amplitude and period of the oscillations was noted.

McCarthy et al.[11] also investigated the reaction of CO and O_2 on a deposited catalyst containing 0.035% of platinum. At catalyst temperatures below 260 °C the dependence of the rate of reaction on the carbon monoxide concentration which they observed had a maximum corresponding to less than 0.5% of carbon monoxide in oxygen†; in the region of this maximum the author observed oscillations in the rate of reaction with a period of the order of 20 s (Fig. 1*b*).

In the study of the influence of the adsorption of carbon monoxide in oxygen on the contact potential difference (CPD) between the platinum electrode and the silicon reference electrode[12] a sharp change of CPD was noted for [CO] = 2%. The authors[12] showed that the maximum in the rate of reaction of CO with O_2 at 200 °C corresponds to this composition of the reaction mixture. In order to observe the auto-oscillations in the rate of this reaction, the authors employed two methods. In the first case CO was oxidised on a platinum wire 0.03 mm in diameter. The amplitude of the oscillations in the resistance of the wire induced by the oscillations in the rate of reaction corresponded to a change in the catalyst temperature by 5 °C. The oscillations were observed in a stream of oxygen containing 2% of carbon monoxide. In the second method CO was oxidised on an electrode made of *n*-type silicon on which a thin layer (100 Å) of platinum had been deposited. At 170 °C and [CO] = 1% the authors[12] observed oscillations in the photocurrent with a period of ~20 s, induced by the oscillations in the composition of the adsorbed layer in the oxidation of carbon monoxide on the platinum catalyst. It has been shown[13] that the amplitude of the oscillations reaches a maximum when the reactants distributed on the catalyst surface are in stoichiometric proportions.

The reaction of CO with O_2 on a platinum foil has been investigated[14]. It was carried out at atmospheric pressure in the temperature range 200–250 °C in a flow reactor free from temperature and concentration gradients. The authors investigated the dependence of the degree of conversion of carbon monoxide on the flow rate of the reaction mixture. The carbon monoxide concentration in air was varied from 1 to 4%. Depending on the experimental conditions, the establishment of either stable stationary states or auto-oscillations in the reaction rate was observed (Fig. 1*c*). The amplitude and period of the auto-oscillations increased with decrease in the degree of conversion at a constant CO pressure in the initial mixture. An analogous increase of the period and amplitude of the oscillations was observed with increase of the CO concentration in the initial mixture. As the temperature rose, the period and amplitude of the oscillations fell.

Virtually simultaneously with the auto-oscillations in the rate of oxidation of carbon monoxide on platinum catalysts, auto-oscillations were observed in the reaction of hydrogen with oxygen on a nickel foil[15,16] (Fig. 1*d*). The temperature

†Here and henceforth the concentrations of the reactants in the initial mixture are expressed in percentages by volume.

of the foil was kept constant to within 0.02 °C by means of a special thermoregulator. Above 180 °C, auto-oscillations in the rate of reaction were observed with a period ranging from 3 to 60 s. The reaction mixture contained a large excess of hydrogen and the oxygen concentration did not exceed 1 vol.%. With increase of temperature to 350 °C, an increase of the amplitude and frequency of the oscillations as well as an expansion of the range of pressures at which oscillations took place were observed. The maximum amplitude of the oscillations was 40% of the average rate of reaction. Simultaneously with the auto-oscillations in the rate of reaction, the authors[17] observed and investigated oscillations in the contact potential difference (CPD) for a nickel plate. Above 200 °C, oscillations were observed both in the reaction rate and in the CPD with a period ranging from 12 to 120 s. The amplitude and the frequency of the CPD oscillations were independent of the linear rate of flow of gases through the reactor.

Auto-oscillations in the reaction rate have also been found in the oxidation of hydrogen on platinum catalysts[18] (Fig. 1*e*). Owing to the difference between the types of influence of platinum and nickel catalysts on different reactants, the auto-oscillations in the rate on platinum catalysts were observed for other component ratios in the reaction mixture (in the presence of an excess of oxygen and small amounts of hydrogen). During the reaction on a platinum wire, auto-oscillations in the rate were observed at a catalyst temperature exceeding 135 °C for a reaction mixture containing 21.5% O_2 and >0.5% H_2. With increase of temperature from 160° to 200 °C, a decrease was observed in the amplitude and period of the auto-oscillations, the latter varying in the range from 220 to 6 s.

When hydrogen was oxidised on a platinum foil, oscillations in the CPD were noted simultaneously with oscillations in the reaction rate[18]. Auto-oscillations in the reaction rate were observed in the temperature range 85–130 °C for the same compositions of the reaction mixture as for the platinum wire. With increase of the hydrogen concentration in the reactor, the amplitude and period of the oscillations also increased, to maximum values, and then fell. When the temperature of the catalyst was varied in the range 85–130 °C, the period of the oscillations changed from 60 to 2 min.

Other workers[10,19] also observed auto-oscillations in the rate of oxidation of hydrogen on a catalyst grain containing 0.4% of platinum but under non-isothermal conditions. The period of the oscillations of the temperature of the centre of the platinum grain was 60 min and its amplitude was 60 °C. (about a mean value of 170 °C). The temperature of the gas stream, consisting of a mixture of air and 3.14% of hydrogen, was kept at 53 °C. The authors concluded that, despite the non-isothermal experimental conditions, the auto-oscillations are not associated with the characteristics of the interaction of the mass and heat transfer involving the catalyst grain. This conclusion was reached in the light of the long period of the oscillations and the absence of phase shift between the oscillations in the catalyst temperature and the concentration of the water formed.

The auto-oscillations in the rate of oxidation of ethylene by oxygen on a platinum wire have been studied[20] by the method of compensation electrothermography. The auto-oscillations in the rate were noted at a catalyst temperature exceeding 275 °C (Fig. 1*f*) in the presence of an excess of oxygen. The amplitude of the oscillations increased with increasing ethylene concentration and with decreasing catalyst temperature.

Auto-oscillations have been observed also in the rates of oxidation of cyclohexane on NaX, LiY, and KY zeolites[21,22] and of propene on the surfaces of CoO–MgO solid solutions[23]. The period of the auto-oscillations of the rate of oxidation of cyclohexane was ~0.5–10 min, the concentrations of the reactants and temperature varying periodically through the oscillations. Compounds of the peroxy-type were detected by infrared spectroscopy on the surface of the zeolite in the course of the reaction. The authors suggest that the oxidation of cyclohexane takes place by a heterogeneous-homogeneous mechanism.

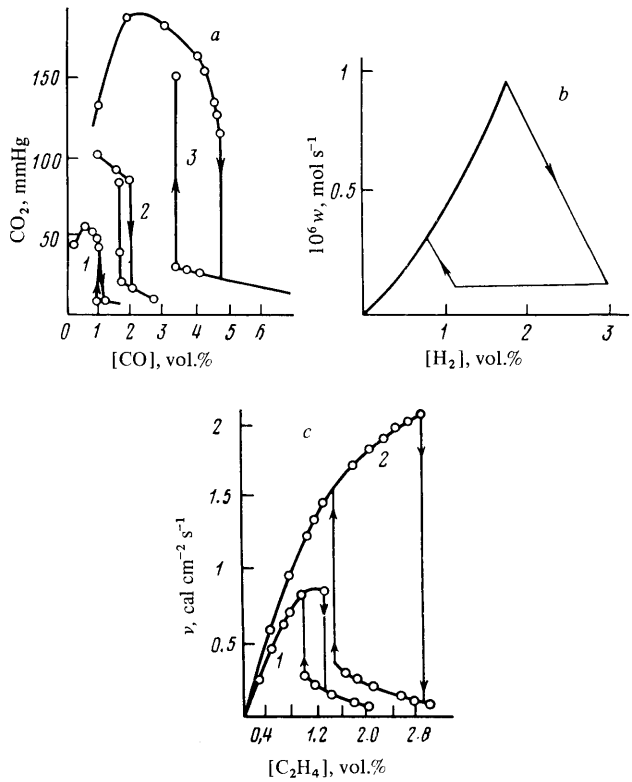


Figure 2. Dependence of the rate of reaction on the composition of the initial mixture for different heterogeneous catalytic systems: *a*) oxidation of CO on a deposited Pt catalyst[19] at different temperatures [temperature (°C): 1) 192; 2) 217; 3) 242]; *b*) oxidation of hydrogen on a platinum foil at 135 °C;[53] *c*) oxidation of ethylene on a platinum foil at different temperatures [temperature (°C): 1) 354; 2) 406].[20]

The data presented above show that auto-oscillations in the rate of reaction are observed in most cases in catalytic systems consisting of reactants differing sharply in their oxidation-reduction properties and containing a catalyst which is resistant to the formation of new bulk phases for a specified composition of the reaction mixture. For a number of heterogeneous catalytic systems, periodic conditions arise in the region of an uncertain dependence of the rate of reaction on the composition of the reaction mixture for a cyclic variation of the latter (i.e. in the region of hysteresis). Such phenomena have been observed in the oxidation of CO on platinum catalysts[9,10,19], in the oxidation of ethylene on a platinum wire[20], and in oxidation on a platinum

foil[53]. Fig.2 illustrates the dependence of the rates of the above reactions on the composition of the reaction mixtures; all the relations are similar. With increased concentration of a component which is present in the reaction mixture in a deficient amount, a gradual increase of the reaction rate is observed; above this the rate falls sharply. A decrease in the concentration of carbon monoxide, ethylene, or hydrogen leads to an increase of the rate of reaction, which, however, occurs at another (lower) concentration of the component present in a deficient amount.

Auto-oscillations in the rate have been observed either along the ascending branch or in the region of the maximum in the relation between the rate of reaction and the composition of the reaction mixture. Hysteresis has been observed[14] in the rate of oxidation of CO for a cyclic variation of the rate of flow of the reaction mixture through the reactor. The concentration of carbon monoxide at the inlet to the reactor was kept constant. Periodic changes in the rate of reaction have also been observed in the region of non-unique stationary states about an upper unstable stationary state.

Measurements of the contact potential difference in the course of the catalytic reaction have shown that the regions of maximum reaction rates and a multiplicity of stationary states are characterised by a high sensitivity of the activity of the catalyst to the composition of the gas phase and the surface layer. The marked influence of the composition of the adsorbed layer on the rate of the catalytic process is apparently one of the principal causes of the non-linear kinetic relations between the rate of reaction and the composition of the gas phase. Such complex relations, involving regions of non-unique stationary states, have been observed in reactions of carbon monoxide with hydrogen on a nickel catalyst[24] and in the oxidation of ammonia on platinum catalysts[25,26].

Fig.1 shows that the form of the oscillations observed in various reactions varies within wide limits from nearly harmonic to the form of relaxation oscillations (relaxation oscillations are characterised by an alternation of rapid and slow movements in the course of a single cycle). There is also a possibility of more complex oscillations. Fig.3*a* illustrates complex oscillations in the rate of oxidation of hydrogen on a platinum wire[53]. Fig.3*b* presents complex oscillations in the rate of heat evolution in the oxidation of ethylene on a platinum wire[20]. Complex irregular dynamic conditions in the oxidation of hydrogen on a platinum wire, illustrated in Fig.4, have also been observed[54]. Evidently oscillations with a small amplitude and a short period can be replaced by oscillations with larger values of these parameters (Fig.4*a*). After unequal time intervals, the oscillatory conditions can also be disturbed by a sharp decrease of the rate of reaction and can then return to the initial state (Fig.4*b*).

The auto-oscillations in the rates of heterogeneous catalytic reactions have been observed in reactors of different types on both deposited and metallic catalysts. In the study of the oxidation of CO on platinum catalysts this phenomenon was observed in flow reactors[10,12,13,19], in a gradient-free reactor

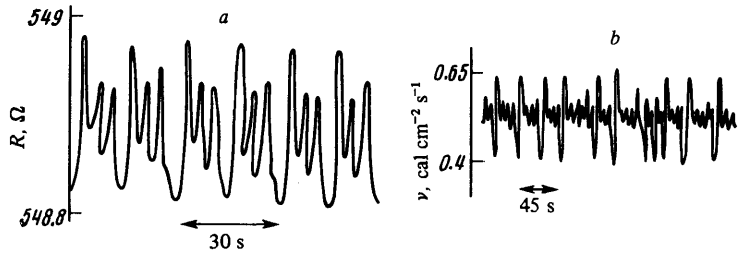


Figure 3. The form of the oscillations observed on platinum wire catalysts: *a*) variation of the resistance of the platinum wire R during the oxidation of hydrogen (2.8% H_2; 17.5% O_2; 79.7% N_2);[53] *b*) oscillations in the rate of heat evolution ν during the oxidation of ethylene (0.5% C_2H_4; 99.5% O_2).[20]

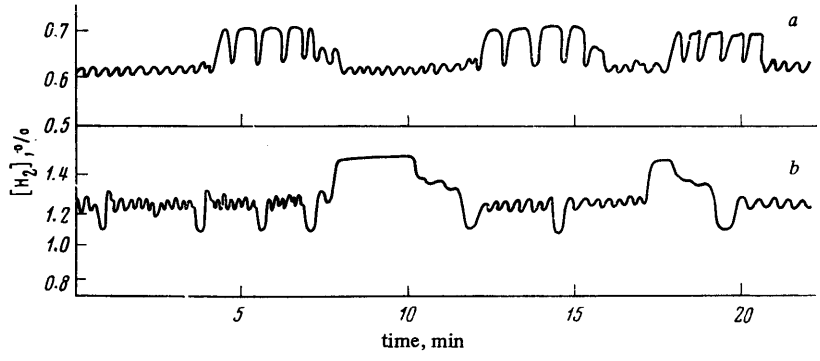


Figure 4. Complex oscillatory conditions observed on a platinum wire during the oxidation of hydrogen: *a*) 202 °C; 2.13% H_2, 21.5% O_2; *b*) 216 °C, 1.74% H_2, 15.6% O_2.[53]

with recycling[9], in a Carberry reactor[11], and in an ideal mixing reactor[14]. The auto-oscillations in the rates of oxidation of hydrogen on nickel and platinum catalysts[18], of ethylene on a platinum wire[20], and of cyclohexane on zeolite catalysts[21] have been studied in flow reactors.

In most cases auto-oscillations were detected under isothermal conditions or with a slight change in the catalyst temperature in the course of the oscillations. Thus, when CO was oxidised on a deposited catalyst, the temperature of the platinum grain changed by 2 °C [10,19] and in the study of the auto-oscillations in the rate of the same reaction on platinum catalysts in the form of a foil[14] and a wire[12] the change was by 3° and 5 °C respectively. Auto-oscillations in the rate of reaction of hydrogen with oxygen have been observed on a nickel foil whose temperature was kept constant in the course of the oscillations to within 0.02 °C.[16] This shows that the auto-oscillations in the rates of the above reactions are not associated with the influence of heat and material transport processes on the rate of reaction.

The nature of the observed auto-oscillations is determined by the catalyst temperature, the composition of the reaction mixture, and the composition of the catalyst surface. For all the oxidation reactions on metallic catalysts investigated, an increase of the rate of auto-oscillations with increasing temperature and the concentration of the component present in excess has been found. The frequency of the auto-oscillations depends much more on the concentration of the component present in the reaction mixture in a smaller amount. An increase of the period of the auto-oscillations in the rate of oxidation of carbon monoxide with increasing carbon monoxide concentration has been reported[11,14]. However, a decrease of the period of the auto-oscillations in the reaction rate for this process has been observed[9] with increase of the content of carbon monoxide in the initial mixture.

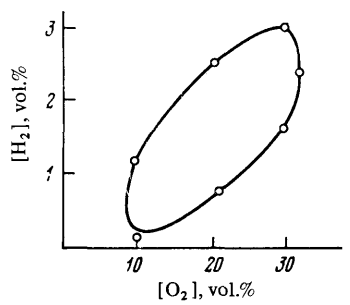


Figure 5. The region of the existence of auto-oscillations in the rate of oxidation of H_2 on a platinum foil in the plane corresponding to the variation of the hydrogen and oxygen concentrations at 85 °C.[18]

The variation of the period of the auto-oscillations in the rate of the hydrogen oxygen–reaction on a platinum foil with the initial concentration of hydrogen has a maximum whose height depends on the temperature[18]. With increase of the catalyst temperature, the amplitude of the auto-oscillations in the rate of reaction of hydrogen with oxygen on platinum catalysts fell. An analogous dependence of the amplitude of the oscillations in the rate on temperature has been noted in all studies of the reaction of carbon monoxide with oxygen.

On the other hand, on nickel catalysts an increase of the amplitude of the auto-oscillations in the rate of oxidation of hydrogen was observed with increase of temperature to 350 °C. The amplitude of the auto-oscillations depends also on the composition of the reaction mixture. With increase of the CO pressure, the amplitude of the auto-oscillations in the rate of oxidation of CO on a platinum catalyst increased. On nickel and platinum catalysts, a maximum has been observed in a number of experiments in the dependence of the amplitude of the auto-oscillation in the rate of oxidation of hydrogen on the composition of the reaction mixture. On a platinum foil, a closed region of auto-oscillations was found in the plane corresponding to changes in the concentrations of hydrogen and oxygen, illustrated in Fig.5.[18] The presence of critical concentrations of the reactants and a catalyst temperature for which auto-oscillations in the rate appear and vanish as well as the dependence of the amplitude and the frequency of the auto-oscillations on these parameters indicate the chemical nature of the observed phenomenon. A periodic variation of the contact potential difference, which was observed simultaneously with the auto-oscillations in the rate of reaction, indicates a change in the composition of the adsorbed layer. Fig.6 illustrates the auto-oscillations in the rate of reaction of hydrogen with oxygen on nickel (*a*) and platinum (*b*) catalysts measured simultaneously with the contact potential difference. Evidently the oscillations in the CPD have the same form and period as those in the rate of reaction. On a nickel catalyst, these quantities vary out of phase, while on a platinum foil there is no phase shift between the oscillations in the CPD and in the rate of reaction.

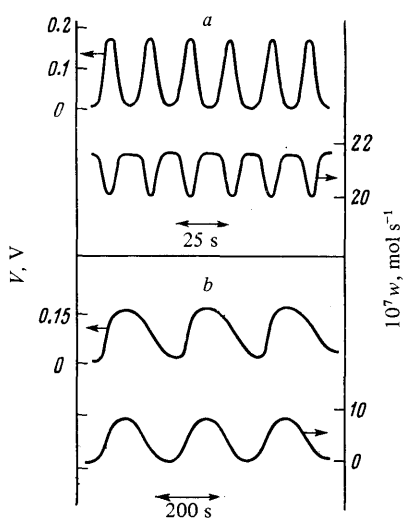


Figure 6. Auto-oscillations in the rate of oxidation of hydrogen on nickel (*a*) and platinum (*b*) catalysts recorded simultaneously with measurement of the changes in the CPD.[18]

Analysis of the CPD oscillations is difficult owing to the non-linear variation of the electron work function with the concentration of the adsorbed substances. However, it is known that the adsorption of oxygen on nickel and platinum leads to an increase of the electron work function and that this influence on the work function is stronger when the

influence of the hydrogen or carbon monoxide concentration is larger. Consequently, the form of the auto-oscillations in the rate of oxidation of hydrogen and in the CPD leads to the conclusion that an increase of the degree of surface coverage of nickel by oxygen and a decrease of the oxygen concentration on the platinum surface entail a decrease of the rate of reaction. The variation of the CPD between platinum and silicon with the ratio of carbon monoxide and oxygen in the reactor at different temperatures has been published[13]. It was shown that an increase of [CO] entails an increase of the CPD and a decrease of the rate of oxidation of CO. The form of the oscillations of the photocurrent, noted during this reaction on a platinum electrode, is analogous to the form of the oscillations of the CPD during the oxidation of hydrogen on a platinum foil. The rapid decrease in the amount of carbon monoxide or hydrogen on the surface, which leads to an increase of the rate of reaction, is replaced by a slower stage involving a return of the composition of the surface to the initial state.

III. PHYSICOCHEMICAL BASIS OF THE AUTO-OSCILLATIONS IN THE RATE OF REACTION

Auto-oscillating systems are well known in physics, engineering, and biology. Auto-oscillations are used particularly widely in radio-engineering, mechanics, and the control of technological processes. It is known from the theory of oscillations[2] that in most cases an auto-oscillating system should contain four fundamental elements: a constant (non-oscillating) source of energy or substance; an oscillating system, a device regulating the supply of energy or substance from the source to the oscillating system and feedback between the oscillating system and the regulating device (regulator), which acts by controlling the supply of the energy or substance. Auto-oscillating systems with a special feedback controlling the operation of a valve are called systems with an external feedback. External feedback can be absent and the valve can be controlled directly by the oscillating system. Such auto-oscillating systems are referred to as systems with internal feedback.

Auto-oscillating systems are divided into virtually harmonic systems and discontinuous or relaxation systems. The former have a high quality factor, a relatively small amount of energy is supplied during the period of the oscillation, and the energy in the oscillating system is exchanged between its elements. In systems of the second type dissipative forces play a significant role. In an oscillating system there exists one energy accumulator which either stores it or dissipates it. The period of the relaxation oscillations can frequently be divided into stages differing sharply in the rate of change of the state of the system. The boundary between the relaxation and harmonic auto-oscillations is not sharp and they can be regarded as a single physical phenomenon.

Auto-oscillatory conditions are impossible in linear systems and can arise only when there is a non-linearity in the system. In most cases the feedback is the source of the non-linearity. However, the presence of a feedback is not a sufficient condition for the occurrence of auto-oscillations; a definite force of this feedback is required.

In homogeneous chemical systems the feedback is determined by the auto-catalytic and inhibitory overall stages[5], as a result of which a closed sequence of stages appears in the system. Degn[6] indicated four possible types of feedback in homogeneous chemical systems. The presence of even one feedback in the system leads to the appearance of kinetic features different from the Law of Mass Action. However, Korzukhin[27] showed that, for any change in the concentrations of some of the reactants over a finite time interval, it is possible to construct a chemical system consisting of elementary stages whose rates are described by the Law of Mass Action.

The feedback in biochemical systems is in most cases achieved as a result of the influence of the substrate of the product on the activity of the enzyme and its properties[28].

Heterogeneous catalytic systems have many features in common with enzymatic systems. The reactants adsorbed on the catalyst surface can also exert a major influence on its catalytic properties. By considering the catalyst and the reaction medium as a single heterogeneous catalytic system, it can be shown that under certain conditions the heterogeneous catalytic system contains all the elements of an auto-oscillating system. The stationary flow of reactants entering the reactor in the direction of the catalyst surface constitutes a constant non-oscillating source of material. The oscillating system consists of a collection of adsorbed substances whose concentrations can vary periodically with time. By controlling the accumulation and consumption of the adsorbed substances as a result of adsorption and the reaction, the catalyst behaves as a regulator and the influence of the reactants on the properties of the catalyst can serve as the internal feedback from the system to the regulator.

In order to achieve non-decaying oscillations in the rate, it is necessary for accumulation to take place at each stage of the cycle, i.e. the rate of chemisorption of substances must exceed the rate of reaction, while in another stage the rate of reaction must be higher than the rate of accumulation. The catalyst as a regulator fulfills in this instant alternately the role of a source of negative and positive feedback. This is possible if the activity of the catalyst depends on the concentrations of the reactants on the catalyst surface. The application of the diffraction of slow electrons (LEED) in the study of catalytic systems made it possible to observe structural changes in the catalyst under the influence of the reactants in the course of adsorption and the reaction[29,30]. Such changes include a rearrangement and formation of new faces on the catalyst surface, the reconstruction of the surface with formation of mixed ordered surface layers containing the catalyst and reactant atoms, and the displacement of the positions of the atoms of the catalyst as a result of the formation of chemical bonds with the reactants. The formation of structures on the surface of platinum has been observed on different faces in the course of the adsorption of carbon monoxide[31] and hydrogen[32], while the adsorption of oxygen did not alter the surface structure of pure platinum up to complete saturation[31,33]. On the other hand, ordered surface structures were observed on nickel during the adsorption of oxygen[29,34,35] as a function of the face and the surface concentration, while hydrogen is capable of forming an ordered structure only on the (110) face of the nickel single crystal[36].

A period of increasing rate of reaction with decrease of the surface coverage by oxygen has been observed on the (110) and (100) faces of a nickel single crystal[37]. The authors[37] suggest that the development of the reaction requires the generation of "islands" of the pure nickel phase and that the rate of reaction is determined by the length of the boundary between these islands. An analogous topochemical type of reaction has been proposed[38] to account for the interaction of hydrogen with oxygen preadsorbed on the (110) nickel face and in another study[39] for the oxidation of hydrogen on a platinum catalyst.

The change in the properties of the catalyst as a result of adsorption in the reaction can be explained within the framework of the electron gas theory developed by Temkin[40]. According to this theory, the energetic properties of the surface are determined by the number of electrons in the surface layer of the catalyst and hence by a number of atoms adsorbed on the catalyst surface which supply and remove these electrons. A change in the amount of adsorbed substance entails a linear change in the activation energies for the adsorption process and the reaction on the catalyst surface. When substances with different donor–acceptor properties are adsorbed, the properties of the electron gas change, and this is reflected in the influence of the adsorption of one substance on that of the other. Thus the adsorption of carbon monoxide can alter the reaction properties of the hydrogen adsorbed on platinum[41]. In its presence a change in the rate of adsorption of oxygen on a platinum catalyst was also observed[31]. The influence of oxygen on the strength of the bond formed by hydrogen and carbon monoxide with the platinum surface has been observed[42]. With increase of the surface coverage by adsorbed oxygen, an increase of the amount of hydrogen or carbon monoxide, adsorbed in a state with much higher bond energies than on a clean surface, has been noted.

IV. MATHEMATICAL MODELS

The modelling of auto-oscillating systems is based mathematically on the general theory of oscillations, according to which auto-oscillations arise in non-linear systems with feedback. In order to elucidate the mechanism of the influence of feedback in heterogeneous catalysis, it is necessary to have an idea about the changes in the concentrations of the reactants on the catalyst surface during the reaction. In the studies discussed above such measurements could not be made and the construction of a detailed mathematical model is therefore difficult. One of the first mechanisms suggested for the operation of feedback in heterogeneous catalytic systems was one where the reactants influence the activity and properties of the catalyst[16]. The possibility of this mechanism of feedback is indicated by experimental data for the adsorption and reactions of a number of substances on metallic catalysts, which were described in the previous section. This type of feedback has been used[18] to construct a mathematical model of the reaction of hydrogen and oxygen on nickel and platinum catalysts.

The mathematical model of the oxidation of hydrogen on an element of the catalyst surface must reproduce the principal features of the process: the adsorption of hydrogen and oxygen and the interaction of the adsorbed substances, without specifying further the details of the mechanism:

$$\begin{gathered} O_2 + 2[M] \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2[M{-}O], \\ H_2 + 2[M] \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} 2[M{-}H], \\ [M{-}O] + 2[M{-}H] \xrightarrow{k_3} 3[M] + H_2O. \end{gathered} \tag{1}$$

where [M] is a free site on the catalyst surface, [M–O] and [M–H] represent the oxygen and hydrogen adsorbed on the free catalyst site, and k_i ($i = \pm 1$, ± 2, or ± 3) are the rate constants for the corresponding reaction stages.

Experimental studies of this reaction showed that there is only a slight dependence of the characteristics of the auto-oscillations on the rate of flow of the reactants through the reactor. Oscillations in the CPD have been observed for a relatively small change in the composition in the gas phase. Consequently one may claim that the auto-oscillations in the rate of reaction are due to periodic processes on the catalyst surface. This made it possible to treat the hydrogen and oxygen pressures as constant and to assume that they are equal to the average values for the period.

The kinetic model describing the changes in the surface concentrations of adsorbed oxygen (θ_O) and hydrogen (θ_H) is of the following type:

$$\begin{gathered} \frac{d\theta_O}{dt} = k_1 p_{O_2} (1 - \theta_O - \theta_H)^2 - k_{-1}\theta_O^2 - k_3\theta_O\theta_H^2 = Q(\theta_O, \theta_H), \\ \frac{d\theta_H}{dt} = k_2 p_{H_2} (1 - \theta_O - \theta_H)^2 - k_{-2}\theta_H^2 - 2k_3\theta_O\theta_H^2 = P(\theta_O, \theta_H), \end{gathered} \tag{2}$$

where p_{O_2} and p_{H_2} are the oxygen and hydrogen pressures in the gas phase.

Eqns.(2) do not entail limiting cycles in the phase plane, since the Bendickson criterion holds for it: if the expression $\partial P/\partial x + \partial Q/\partial y$ has a constant sign in a single-phase region of the phase plane, then there are no closed contours in this region. It is readily seen that throughout the θ_O and θ_H phase plane the expression $\partial Q(\theta_O, \theta_H)/\partial P(\theta_O, \theta_H)/\partial\theta_H$ is always negative. In this case there is a unique stable stationary state of the type of a node or focus in system (2) for all values of the parameters. Auto-oscillations of the rate are impossible in the system, since one of the fundamental elements of an auto-oscillating system, namely the feedback, is absent.

The feedback arising from the influence of the reactants on the activity and properties of the catalyst can be expressed by the dependence of the activation energy for the adsorption and reaction stages on the hydrogen and oxygen concentrations on the catalyst surface. We shall analyse the simplest case where the concentrations of the adsorbed substances influence only the rate of the surface interaction of the reactants, the activation energy for this stage varying linearly with the degree of surface coverage by oxygen and hydrogen in accordance with the equation

$$E_3 = E_{30} + \alpha_1\theta_O + \alpha_2\theta_H. \tag{3}$$

The rate constant for the third stage can then be formulated as follows:

$$k_3 = k_{30}\, e^{(\mu_1\theta_O + \mu_2\theta_H)},$$

where the parameters $\mu_1 = \alpha_1/RT$ and $\mu_2 = \alpha_2/RT$ can be both greater and smaller than zero.

The variation of the rate of oxidation of hydrogen on nickel catalysts under the conditions of an excess of hydrogen and low oxygen concentrations in the gas phase can be due to the variation of the amount of adsorbed oxygen[37]. If the rate constant for the third stage varies with the degree of surface coverage by oxygen in accordance with the expression

$$k_3 = k_{30}\, e^{-\mu_1\theta_O}, \tag{4}$$

where $\mu_1 > 0$ and $\mu_2 = 0$, then, when account is taken of Eqn.(4), Eqns.(2) can be written as follows:

$$\begin{gathered} \frac{d\theta_O}{dt} = k_1 p_{O_2} (1 - \theta_O - \theta_H)^2 - k_{-1}\theta_O^2 - k_{30}\theta_O\theta_H^2\, e^{-\mu_1\theta_O} = Q(\theta_O, \theta_H), \\ \frac{d\theta_H}{dt} = k_2 p_{H_2} (1 - \theta_O - \theta_H)^2 - k_{-2}\theta_H^2 - 2k_{30}\theta_O\theta_H^2\, e^{-\mu_1\theta_O} = P(\theta_O, \theta_H). \end{gathered} \tag{5}$$

Here the functions $Q(\theta_O, \theta_H)$ and $P(\theta_O, \theta_H)$ have been determined in the region $G = \{(\theta_O, \theta_H): \theta_O + \theta_H \leq 1;\ \theta_O \geq 0;\ \theta_H \geq 0\}$ and all the $k_i > 0$ ($i = \pm 1$, ± 2, or ± 3).

Eqns.(5) have been studied[55] by the phase plane method. Relations were found between the parameters for which a single unstable stationary state surrounded by stable limiting cycle is possible in the system. The following theorem was used to find periodic solutions of Eqns.(5).

Suppose that C is a cycle without contact and F is the region bounded by it. There exists at least one stable cycle if the following conditions are fulfilled: (1) all the trajectories intersecting C with increasing t enter F; (2) in the region F there is a single unstable stationary state of the type of a node or focus.

Linearisation of Eqns.(5) in the vicinity of the stationary state with θ_O^S and θ_H^S leads to algebraic expressions of the following type:

$$\frac{d\theta_O}{dt} = a_{11}(\theta_O - \theta_O^S) + a_{12}(\theta_H - \theta_H^S),$$
$$\frac{d\theta_H}{dt} = a_{21}(\theta_O - \theta_O^S) + a_{22}(\theta_H - \theta_H^S),$$

where

$$a_{11} = \left(\frac{\partial Q}{\partial \theta_O}\right)_{\theta_O^S, \theta_H^S}, \quad a_{12} = \left(\frac{\partial Q}{\partial \theta_H}\right)_{\theta_O^S, \theta_H^S},$$
$$a_{21} = \left(\frac{\partial P}{\partial \theta_O}\right)_{\theta_O^S, \theta_H^S}, \quad a_{22} = \left(\frac{\partial P}{\partial \theta_H}\right)_{\theta_O^S, \theta_H^S}$$

The stability of the stationary state is determined by the roots of the following characteristic equation:

$$\lambda^2 - (a_{11}+a_{22})\lambda + (a_{11}a_{22} - a_{12}a_{21}) = \lambda^2 - \sigma\lambda + \Delta = 0 . \quad (6)$$

A sufficient condition for the existence of a unique stationary state throughout the region of the parameters is

$$\frac{dQ(\theta_O, \theta_H)}{d\theta_O} < 0. \quad (7)$$

When the above condition holds, the following inequality is always valid: $\Delta(\theta_O, \theta_H) > 0$ along the curve

$$P(\theta_O, \theta_H) = 0 \quad (8)$$

Denoting the transport of oxygen to the surface by $k_1 p_{O_2}(1 - \theta_O - \theta_H)^2 - k_{-1}\theta_O^2 = G_O$ and the rate of reaction by $k_{30}\theta_O\theta_H^2 e^{-\mu_1\theta_O^2} = w$, condition (8) can be formulated thus:

$$\frac{dG_O}{d\theta_O} < \frac{dw}{d\theta_O}. \quad (9)$$

The physical significance of condition (9) is that in the stationary state the variation of the rate of reaction with oxygen concentration on the surface should be greater than the variation of the rate of transport of the latter to its surface. Condition (9) is valid when the following inequality holds:

$$2k_{-1} > k_{-2}(\mu_1 - 1). \quad (10)$$

In order that limiting cycles should arise in the system defined by Eqns.(5), the condition $\sigma(\theta_O^S, \theta_H^S) > 0$ must be fulfilled together with condition (10). This is achieved for $\mu_1 > 30$. The high values of μ_1 for which auto-oscillations in the rate of reaction arise in system (5) show that there must be a strong influence by the adsorbed substances on the properties of the catalyst.

System (2) has also been studied in the presence of various functional types of influence of the concentrations of the reactants on the properties of the catalyst. The form of the feedback was specified by the function $f_i(\theta_O)$ in the expression for the change in the rate constant for the third stage as a function of the degree of surface coverage by oxygen:

$$k_3 = k_{30} f_i(\theta_O).$$

For auto-oscillations to arise in system (2) with $f_1(\theta_O) = (1 - \theta_O)^{\mu_1}$ it is necessary that $\mu_1 > 20$, and for a feedback of the type $f_2(\theta_O) = (1 + \theta_O)^{-\mu_1}$, it is necessary that $\mu_1 > 37$.

A detailed study of a system of type (2) with the above types of feedback has been carried out in a general form for a system taking into account the different orders of the adsorption and desorption reactions of the reactants and its results can be used to find the conditions for the occurrence of auto-oscillations in kinetic models of both the hydrogen oxidation reaction on nickel and platinum catalysts and the carbon monoxide oxidation reaction on platinum catalysts.

The mathematical model of an auto-oscillating heterogeneous reaction of type (5) has many features in common with the system of differential equation describing the behaviour of a non-isothermal ideal mixing reactor[43]. The identical structure of the differential equations entails the similarity of the dynamic behaviour of the processes in the ideal mixing reactor and on a surface element of the catalyst. A detailed study of the properties of an ideal mixing flow reactor[44] revealed a multiplicity of phase plots observed in this system. The decisive parameters are the kinetic criterion and the adiabatic heating criterion, the Damköhler number, and the rate of removal of heat by the cooling unit. Depending on the values of these parameters, nine types of phase plots are possible, on five of which stable limiting cycles are possible. The cause of the auto-oscillations is the presence of a feedback via the influence of the temperature of the reaction mixture on the rate of reaction. This influence of the temperature is analogous to auto-catalysis. With increase of temperature, there is a sharp increase of the rate of reaction relative to the rate of supply of the reactants, which entails a decrease of the concentrations of the reactants in the reactor and a lowering of the temperature, which in its turn gives rise to a sharp fall of the rate of reaction relative to the rate of supply of the reactants. On subsequent increase of the amount of reactants in the reactor up to the critical concentration, a sharp increase of the rate begins again.

Condition (11), the fulfillment of which over the entire range of parameters guarantees a unique stationary state, is well known for thermokinetic oscillations:

$$\frac{dG_T}{dT} > \frac{dw}{dT}, \quad (11)$$

where G_T is the transport of heat to the reactor and w the rate of reaction. Conditions (9) and (11) are analogous in form and differ only by their signs due to the different influences of the adsorbed substances and temperature on the rate of reaction.

In an adiabatic ideal mixing reactor auto-oscillations of the rate of reaction are impossible. Additional removal of heat by the cooling unit is necessary for auto-oscillations to occur. Similarly additional removal of oxygen from the surface of the catalyst by desorption is essential for the auto-oscillations of the rate of reaction of hydrogen with oxygen on a nickel catalyst.

Sets of parameters for which limiting cycles arise have been found for system (5).[55] One of these limiting cycles, which exist about an unstable stationary state, is illustrated in Fig.7.

In conformity with the nature of the change in the degree of surface coverage by hydrogen and oxygen, it is possible to visualise the following mechanism of the generation of auto-oscillations. With increase in the amount of adsorbed oxygen on the surface of the nickel catalyst, the rate of reaction falls and the surface is covered by oxygen and hydrogen. Next, in consequence of the desorption of oxygen, there is a rapid decrease of its concentration on the catalyst surface. After

---

#See E.A.Ivanov, G.A.Chumakov, M.G.Slinko, D.D.Bruns, and D.Luss, Chem.Eng.Sci. (in the Press).

the attainment of the limiting value of θ_O, the quantity $e^{-\mu_1\theta_O}$ begins to increase rapidly as θ_O diminishes, the adsorbed hydrogen and oxygen react at a high rate, and the surface is almost completely freed from oxygen. Then the adsorption of oxygen begins again and leads to an increase of its concentration on the catalyst surface and the inhibition of the reaction. This process terminates the cycle. The above mechanism of the auto-oscillations of the rate of reaction is analogous to the mechanism of the thermokinetic auto-oscillations in an ideal mixing reactor with the difference that the reactants are supplied by chemisorption and the acceleration of the reaction is determined by the influence of the amount of adsorbed oxygen on the rate of formation of water.

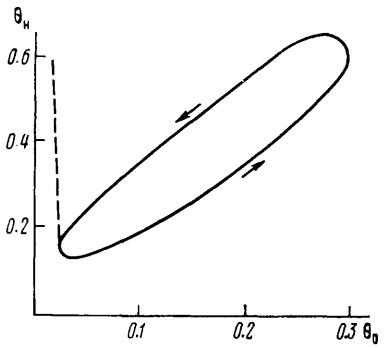


Figure 7. The limiting cycle of model (5) found for the following system parameters: $k_1 p_{O_2} = 15.6\ s^{-1}$; $k_{-1} = 1\ s^{-1}$; $k_2 p_{H_2} = 30\ s^{-1}$; $k_{-2} = 0$; $k_3 = 10^{-5}\ s^{-1}$; $\mu_1 = 40$.[55]

The auto-oscillations of the rate observed in the oxidation of hydrogen on platinum have also been described in terms of feedback of type (3).[53] However, in view of the different composition of the reaction mixture and the decrease of the stationary rate of reaction with increasing hydrogen pressure in the gas phase, the influence of the hydrogen concentration alone on the activation energy for the stage involving the interaction of the adsorbed substances was examined and α_1 was assumed to be zero. On the assumption that $\mu_2 = \alpha_2/RT$, the dependence of the rate constant for the third stage on the surface coverage by hydrogen can be written in a form analogous to Eqn.(4):

$$k_3 = k_{30}\, e^{-\mu_2\theta_H}. \qquad (12)$$

Taking into account Eqn.(12), Eqns.(2) can be written as follows:

$$\begin{aligned} \frac{d\theta_O}{dt} &= k_1 p_{O_2} (1 - \theta_O - \theta_H)^2 - k_{-1}\theta_O^2 - k_{30}\theta_O\theta_H^2\, e^{-\mu_2\theta_H} \\ \frac{d\theta_H}{dt} &= k_2 p_{H_2} (1 - \theta_O - \theta_H)^2 - k_{-2}\theta_H^2 - 2k_{30}\theta_O\theta_H^2\, e^{-\mu_2\theta_H} \end{aligned} \qquad (13)$$

The mechanism of the development of auto-oscillations in this system is analogous to that presented above for system (5).

Models (5) and (13) were compared with experimental data obtained for the interaction of hydrogen with oxygen on nickel and platinum catalysts respectively. These models reflect correctly the nature of the change in the amplitude and the critical conditions for the appearance and disappearance of auto-oscillations as the composition of the reaction mixture is varied. However, the models are of limited validity for the description of low-frequency oscillations. When the calculated and experimental rates averaged over the period of oscillations agreed, the maximum period of the auto-oscillations calculated on the basis of models (5) and (13) was ~1 s. Such frequencies were observed on a nickel foil and a platinum wire at high temperatures. At lower temperatures, low-frequency oscillations were noted, which cannot be described in terms of models (5) and (13). The maximum periods in models (5) and (13) are reached when k_{-1} and k_{-2} respectively are reduced. When these constants approach zero, the auto-oscillations in the rate of reaction vanish. This indicates the necessity for the existence of an additional removal of the substance influencing the catalytic activity of the metal from the surface of the catalyst.

Bearing in mind the low rates of desorption of oxygen from platinum[45] and nickel[46] catalysts, Zelenyak and Slin'ko[56] added to mechanism (1) a stage involving the Eley–Rideal impact mechanism, during which the adsorbed oxygen can be removed from the surface and can react with the gas-phase hydrogen:

$$[M - O] + H_2 \xrightarrow{k_4} [M] + H_2O. \qquad (14)$$

Allowance for this stage leads to the appearance of an additional term in the mathematical model (5), describing the removal of oxygen from the surface of nickel. The dynamic behaviour of the new system is unaltered if the rate constant for the fourth stage is independent of the degree of surface coverage by adsorbed substances. It is natural to suppose that the adsorbed oxygen decreases the rates of all the water formation stages in the oxidation of hydrogen on a nickel catalyst. Assuming that the activation energy for the fourth stage E_4 increases linearly with the degree of surface coverage by oxygen, i.e. $E_4 = E_{40} + \alpha_4\theta_O$, we obtain a mathematical model in the following form:

$$\begin{aligned} \frac{d\theta_O}{dt} &= k_1 p_{O_2} (1 - \theta_O - \theta_H)^2 - k_{-1}\theta_O^2 - k_{30}\theta_O\theta_H^2\, e^{-\mu_1\theta_O} - k_{40} p_{H_2}\theta_O\, e^{-\mu_4\theta_O}, \\ \frac{d\theta_H}{dt} &= k_2 p_{H_2} (1 - \theta_O - \theta_H)^2 - k_{-2}\theta_H^2 - 2k_{30}\theta_O\theta_H^2\, e^{-\mu_1\theta_O}. \end{aligned} \qquad (15)$$

With the aid of model (15), it is possible to obtain a much better agreement between the experimental and calculated data. Auto-oscillations at low frequencies for a high average rate during the period arise if the following relation between the constants holds:

$$k_1 p_{O_2},\ k_{40} \gg k_2 p_{H_2},\ k_{-2},\ k_{30}.$$

In this case the slow variation of the degree of surface coverage by hydrogen ensures a low oscillation frequency, while a high rate of reaction is attained as a result of the high rate of the impact stage.

A qualitative study of system (15) has been carried out by Belyaev, Chumakov, and Plikhta§. They showed that the introduction of an additional parameter, in relation to system (5), complicates the dynamic behaviour of the system. Fig.8 illustrates the types of phase plots which are possible in the given system. Evidently, depending on the values of the parameters, up to five stationary states and stable and unstable limiting cycles can arise in the system.

The dynamic behaviour of the hydrogen and carbon monoxide oxidation reactions is surprisingly similar. Attention was drawn to this by Langmuir as early as 1918 [47] and was confirmed by the experimental investigations of Kuchaev and Temkin[45,48], who observed that the kinetics of these two

§Quoted by T.I.Zelenyak and M.G.Slin'ko, Kinetika i Kataliz, **18**, 1235 (1977).

reactions have many features in common and can be described in terms of analogous mechanisms, including both impact and adsorption reaction pathways. The following mechanism has been proposed[48] for the oxidation of CO:

$$\begin{gathered} O_2 + 2\,[M] \overset{k_1}{\rightarrow} 2\,[M{-}O] \\ CO + [M] \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} [M{-}CO] \\ [M{-}O] + [M{-}CO] \overset{k_3}{\rightarrow} 2\,[M] + CO_2 \\ [M{-}O] + CO \overset{k_4}{\rightarrow} [M] + CO_2 \end{gathered} \qquad (16)$$

The kinetic model corresponding to mechanism (16) has a form analogous to that of system (2) and differs from it only by the different orders of the adsorption and desorption reactions of one of the components of the reaction mixture and also by the additional term describing the interaction of the adsorbed oxygen with gaseous carbon monoxide:

$$\begin{gathered} \frac{d\theta_O}{dt} = k_1 p_{O_2} (1 - \theta_O - \theta_{CO})^2 - k_{-1}\theta_O^2 - k_3\theta_O\theta_{CO} - k_4 p_{CO}\theta_O, \\ \frac{d\theta_{CO}}{dt} = k_2 p_{CO} (1 - \theta_O - \theta_{CO}) - k_{-2}\theta_{CO} - k_3\theta_O\theta_{CO} \end{gathered} \qquad (17)$$

The difference between the orders of adsorption and desorption reactions of the reactants is responsible for the possible appearance in system (17) of several stationary states, since condition (8) can break down. However, the Bendickson criterion remains negative over the entire range of parameters and auto-oscillations are therefore impossible. In order to explain the appearance of auto-oscillations, one must take into account, by analogy with the preceding systems, the experimental decrease of the rate of reaction with increasing CO pressure in the gas phase. One can then postulate the following dependence of the activation energies for the third and fourth stages on the degree of surface coverage of the catalyst by carbon monoxide:

$$\begin{aligned} E_3 &= E_{30} + \alpha_1\theta_{CO}, \\ E_4 &= E_{40} + \alpha_2\theta_{CO}. \end{aligned} \qquad (18)$$

Taking into account the influence of adsorbed carbon monoxide on the rate constants for the third and fourth stages, we obtain a kinetic model for the oxidation of carbon monoxide analogous to Eqns.(15):

$$\begin{gathered} \frac{d\theta_O}{dt} = k_1 p_{O_2} (1 - \theta_O - \theta_{CO})^2 - k_{-1}\theta_O^2 - k_{30}\theta_O\theta_{CO} e^{-\mu_1\theta_{CO}} - k_{40} p_{CO}\theta_O e^{-\mu_2\theta_{CO}}, \\ \frac{d\theta_{CO}}{dt} = k_2 p_{CO} (1 - \theta_O - \theta_{CO}) - k_{-2}\theta_{CO} - k_{30}\theta_O\theta_{CO} e^{-\mu_1\theta_{CO}}. \end{gathered} \qquad (19)$$

This system can be used to compare the calculated and experimental parameters of the oscillations in the oxidation of CO on platinum.

Mechanism (16) and feedback of type (3) have also been used[14] to construct a kinetic model of the auto-oscillations of the rate of oxidation of CO on platinum catalysts. The authors examined four types of models consisting of two differential equations and differing in the choice of dynamic variables. Mathematical analysis of the model including the oxygen and carbon monoxide pressures in the gas phase as dynamic variables showed that auto-oscillations in the rate of reaction are possible only for unrealistic values of the parameters of the model. Oscillatory conditions were observed in models where the pressure of carbon monoxide in the gas phase was chosen as one of the dynamic variables while the degrees of surface coverage either by oxygen or by carbon monoxide or by one of the forms of adsorbed carbon monoxide served as the second dynamic variable. For this choice of dynamic variables, the surface concentration of the second reactant was assumed to correspond to equilibrium with respect to its pressure in the gas phase. The authors[14] in no way justified the choice of the dynamic variables of the models. It remains obscure why only one of the surface concentrations is stationary with respect to the gas phase. The experimental CPD and the photocurrent during the auto-oscillations of the rate of reaction show that a more probable cause of the development of auto-oscillations in the rate of reaction is oscillations in the composition of the surface of the catalyst,

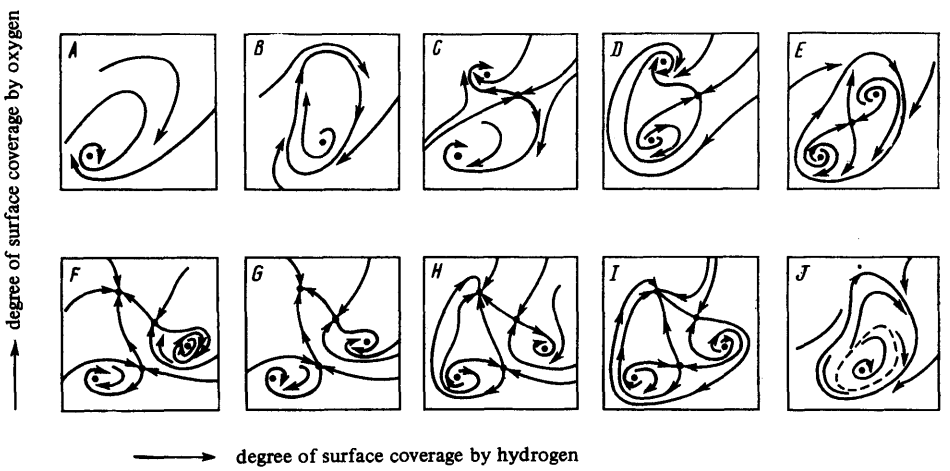


Figure 8. Phase plots for system (15) obtained for different values of the parameters of the model[56].

which can be non-stationary in relation to the composition of the gas phase.

The data obtained in the study of the auto-oscillations of the rates of heterogeneous catalytic reactions show that the periods of the auto-oscillations vary within wide limits—from 1 to 3600 s. The lower limit of this range is determined by the inertia and the upper limit by the stability of the instruments with the aid of which auto-oscillatory conditions are detected. The occurrence of auto-oscillations with long periods necessitates the assumption of the existence of phenomena which decrease the frequencies of the auto-oscillations. One of such causes may be the presence on the surface of an inactive form of the reactant, which constitutes a kind of buffer of the active form on the surface and can reduce the frequency of the auto-oscillations. It is known[49] that two forms of adsorbed hydrogen can exist on platinum catalysts. Presumably the adsorption of hydrogen on the surface of the platinum catalyst takes place with formation of an inactive form H_i. The latter can then be converted on the surface into the active form H_a, which interacts with the adsorbed oxygen. The reaction mechanism is formulated as follows:

$$\begin{gathered} O_2 + 2\,[M] \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2\,[M{-}O]\ , \\ H_2 + 2\,[M] \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} 2\,[M{-}H_i]\ , \\ [M{-}H_i] \cdot \underset{k_{-i}}{\overset{k_i}{\rightleftarrows}} [M{-}H_a]\ , \\ 2\,[M{-}H_a] + [M{-}O] \xrightarrow{k_3} 3\,[M] + H_2O\ . \end{gathered} \tag{20}$$

If the active hydrogen on the surface alters the rate constant for the third stage in accordance with the expression

$$k_3 = k_{30}\, e^{-\mu_3 \theta_{H_a}},$$

then the kinetic model can be formulated as follows in conformity with mechanism (20):

$$\begin{gathered} \frac{d\theta_O}{dt} = k_1 p_{O_2} (1 - \theta_O - \theta_{H_a} - \theta_{H_H})^2 - k_{-1}\theta_O^2 - k_{30}\theta_O\theta_{H_a}^2 e^{-\mu_3\theta_{H_a}}, \\ \frac{d\theta_{H_H}}{dt} = k_2 p_{H_2} (1 - \theta_O - \theta_{H_a} - \theta_{H_H})^2 - k_{-2}\theta_{H_H}^2 - k_H\theta_{H_H} + k_{-H}\theta_{H_a}, \\ \frac{d\theta_{H_a}}{dt} = k_H\theta_{H_H} - k_{-H}\theta_{H_a} - 2k_{30}\theta_O\theta_{H_a}^2 e^{-\mu_3\theta_{H_a}}. \end{gathered} \tag{21}$$

If k_i, $k_{-i} \gg k_1$, k_{-1}, k_2, k_{-2}, k_3, then the active and inactive forms of hydrogen are in equilibrium and there is a linear relation between their surface concentrations:

$$\theta_{H_i} = K_p \theta_{H_a}, \tag{22}$$

where $K_p = k_{-i}/k_i$.

Taking into account Eqn.(22), it is possible to formulate a system of differential equations [Eqns.(23)] describing the variation of the concentration of surface oxygen and the overall concentration of the hydrogen adsorbed in two forms:

$$\begin{gathered} \frac{d\theta_O}{dt} = k_1 p_{O_2} (1 - \theta_O - (1 + K_p)\,\theta_{H_a})^2 - k_{-1}\theta_O^2 - k_{30}\theta_O\theta_{H_a}^2 e^{-\mu_3\theta_{H_a}}, \\ (1 + K_p)\frac{d\theta_{H_a}}{dt} = k_2 p_{H_2} (1 - \theta_O - (1 + K_p)\,\theta_{H_a})^2 - k_{-2}K_p^2\theta_{H_a}^2 - \\ - 2k_{30}\theta_O\theta_{H_a}^2 e^{-\mu_3\theta_{H_a}}. \end{gathered} \tag{23}$$

In Eqns.(23) there is an additional term on the left-hand side of the differential equation, compared with system (13), representing the inertia $(1 + K_p)$. The appearance of this term increases the period of the oscillations for values of the parameters close to those for system (13). Thus, when the amount of the active form of hydrogen is twice that of the inactive form ($K_p = 0.5$), the period of the auto-oscillations increases by a factor of two.

A possible mechanism of the development of auto-oscillations with participation of the active and inactive forms of one of the reactants was also examined by Eigenberger[50]. Assuming the existence of two forms of oxygen adsorbed on platinum, the author proposed the following mechanism for the oxidation of carbon monoxide on platinum catalysts:

$$\begin{gathered} CO + [M] \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [M{-}CO]\ , \\ O_2 + 2\,[M] \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} 2\,[M{-}O_a]\ , \\ 2\,[M{-}O_a] + 2\,[M{-}CO] \xrightarrow{k_3} 2CO_2 + 4\,[M]\ , \\ O_2 + 2\,[M] \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} [M{-}O_{2i}]\ . \end{gathered} \tag{24}$$

Next he assumes that the amount of oxygen adsorbed in an active form is in equilibrium with respect to its pressure in the gas phase and is small owing to the high rate of desorption ($k_{-2} \gg k_2 p_{O_2}$). With these postulates, mechanism (24) assumes the following form:

$$\begin{gathered} CO + [M] \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [M{-}CO]\ , \\ 2\,[M{-}CO] + O_2 + 2\,[M] \xrightarrow{k_3} 2CO_2 + 4\,]M]\ , \\ O_2 + 2\,[M] \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} [M{-}O_{2i}]\ . \end{gathered} \tag{25}$$

The feedback in this sytem also occurs via the influence of the adsorbed substances on the rate of formation of carbon dioxide. However, it is assumed that this influence is not exerted by the adsorbed substances on the catalytic properties but occurs via the change in the number of active sections of the catalyst surface involved in the reaction. This form of feedback can occur subject to the author's assumption[50] that the concentration of the active form of oxygen is low owing to the high rate of its desorption from the surface of platinum. Despite the fact that this conflicts with experimental data showing low rates of desorption of oxygen from platinum, the author[50] was able to account for the region of development and the periods of the auto-oscillations in the rate of oxidation of CO on a platinum mesh observed by Hugo and Jakubith[9].

The buffer capacity for the adsorbed substance active in the reaction can be created not only on the catalyst surface as a result of substances inactive in the reaction but also in the surface layer of the catalyst due to the dissolved reactants. The high solubility of hydrogen in nickel[51] can lead to the saturation of the surface layer of the latter by hydrogen when the reaction takes place in an excess of this gas. If the rate of dissolution of hydrogen is assumed to be proportional to the rate of coverage of the catalyst by hydrogen and to the fraction of vacancies in the metal accessible to dissolved hydrogen while the rate of diffusion of hydrogen from the metal is assumed to be proportional to the amount of dissolved hydrogen and the fraction of surface free from adsorbed hydrogen, then the change in the fraction of hydrogen dissolved in nickel will be described by the following equation[55]:

$$\frac{dz_H}{dt} = K_5\theta_H (1 - z_H) - K_{-5} z_H (1 - \theta_H), \tag{26}$$

where $K_5 = k_5 NS/V$, $K_{-5} = k_{-5} NS/V$, z_H is the concentration of hydrogen dissolved in the surface layer of the catalyst and referred to the limiting concentration of the dissolved hydrogen, N the number of adsorbed atoms per cm^2 of the catalyst, S the catalyst area, and V the volume of the surface layer of the catalyst.

If $K_5 = K_{-5} = K \gg k_1$, k_{-1}, k_2, k_{-2}, k_3, then the fraction of hydrogen dissolved in the metal will be proportional to its surface concentration: $z_H = K\theta_H$.

If Eqn.(26) is added to mechanism (1), then system (5) can be formulated as follows:

$$\frac{d\theta_O}{dt} = k_1 p_{O_2}(1-\theta_O-\theta_H)^2 - k_{-1}\theta_O^2 - k_{30}\theta_O\theta_H^2 e^{-\mu_1\theta_O},$$
$$\frac{d\theta_H}{dt} = k_2 p_{H_2}(1-\theta_O-\theta_H)^2 - k_{-2}\theta_H^2 - 2k_{30}\theta_O\theta_H^2 e^{-\mu_1\theta_O} - \frac{dz_H}{dt}. \quad (27)$$

Since $dz_H/dt = Kd\theta_H/dt$, we obtain system (28), which differs from system (5) only by the inertia term. It appears in the equation describing the variation of the fraction of the surface covered by hydrogen:

$$\frac{d\theta_O}{dt} = k_1 p_{O_2}(1-\theta_O-\theta_H)^2 - k_{-1}\theta_O^2 - k_{30}\theta_O\theta_H^2 e^{-\mu_1\theta_O},$$
$$(1+K)\frac{d\theta_H}{dt} = k_2 p_{H_2}(1-\theta_O-\theta_H)^2 - k_{-2}\theta_H^2 - 2k_{30}\theta_O\theta_H^2 e^{-\mu_1\theta_O}. \quad (28)$$

With increase of K, there is an increase in the amount of dissolved hydrogen in equilibrium with adsorbed hydrogen, which increases the period of the auto-oscillations.

In the general case both components of the gas phase can dissolve in the surface layer of the metal and the overall mechanism of the interaction of hydrogen and oxygen includes the following stages in this case:

$$O_2 + 2[M] \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2[M{-}O],$$
$$H_2 + 2[M] \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} 2[M{-}H],$$
$$2[M{-}H] + [M{-}O] \xrightarrow{k_3} 3[M] + H_2O,$$
$$[M{-}O] + H_2 \xrightarrow{k_4} [M] + H_2O,$$
$$[M{-}H] + [M_V] \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} [M_V{-}H] + [M],$$
$$[M{-}O] + [M_V] \underset{k_{-6}}{\overset{k_6}{\rightleftarrows}} [M_V{-}O] + [M],$$

where $[M_V]$ is an atom in the surface layer of the metallic catalyst and $[M_V{-}H]$ and $[M_V{-}O]$ are the hydrogen and oxygen atoms dissolved in the surface layer.

Assuming that in a thin surface layer of the catalyst there is virtually complete mixing, one can formulate a generalised kinetic model as follows:

$$\frac{d\theta_O}{dt} = k_1 p_{O_2}(1-\theta_O-\theta_H)^n - k_{-1}\theta_O^p - k_4 p_{H_2}\theta_O - k_3\theta_O\theta_H^q - \beta_O\frac{dz_O}{dt},$$
$$\frac{d\theta_H}{dt} = k_2 p_{H_2}(1-\theta_O-\theta_H)^m - k_{-2}\theta_H^q - 2k_3\theta_O\theta_H^q - \beta_H\frac{dz_H}{dt},$$
$$\frac{dz_H}{dt} = k_5\theta_H(1-z_H) - k_{-5}z_H(1-\theta_H-\theta_O), \quad (29)$$
$$\frac{dz_O}{dt} = k_6\theta_O(1-z_O) - k_{-6}z_O(1-\theta_H-\theta_O),$$

where n, m, p, and q are the orders of the corresponding stages and β_O and β_H are the limiting amounts of oxygen and hydrogen dissolved in the surface layer of the catalyst and expressed in terms of the number of monolayers.

In the interpretation of the experimental data obtained in the study of the oxidation of hydrogen on platinum catalysts the following additional assumptions were made[57]: (1) the adsorption and desorption of hydrogen are second-order reactions, while the adsorption and desorption of oxygen are first-order reactions: $m=q=2$ and $n=p=1$; (2) the concentration of oxygen in the surface layer of the platinum catalyst changes little: $dz_0/dt \cong 0$; (3) the hydrogen dissolved in a thin surface layer of platinum increases linearly the activation energy for the water formation stages:

$$E_3 = E_{30} + \gamma_3 z_H,$$
$$E_4 = E_{40} + \gamma_4 z_H.$$

These assumptions lead to the following relations between the rate constants for the water formation stages and the amount of dissolved hydrogen:

$$k_3 = k_{30}e^{-\mu_1 z_H};\ k_4 = k_{40}e^{-\mu_2 z_H},$$

where $\mu_1 = \gamma_3/RT$ and $\mu_2 = \gamma_4/RT$. With these assumptions, the form of the kinetic model (29) is:

$$\frac{d\theta_O}{dt} = k_1 p_{O_2}(1-\theta_O-\theta_H) - k_{-1}\theta_O - k_{40}p_{H_2}\theta_O e^{-\mu_2 z_H} - k_{30}\theta_O\theta_H^2 e^{-\mu_1 z_H},$$
$$\frac{d\theta_H}{dt} = k_2 p_{H_2}(1-\theta_O-\theta_H)^2 - k_{-2}\theta_H^2 - 2k_{30}\theta_O\theta_H^2 e^{-\mu_1 z_H} - \beta_H\frac{dz_H}{dt}, \quad (30)$$
$$\frac{dz_H}{dt} = k_5\theta_H(1-z_H) - k_{-5}z_H(1-\theta_H-\theta_O).$$

Depending on the values of the parameters, system (30) makes it possible to describe both relaxation auto-oscillations and auto-oscillations which are nearly harmonic over a wide range of frequencies. The form of the auto-oscillations is determined by the relative values of the group of rate constants $k_1 p_{O_2}$, $k_2 p_{H_2}$, k_4, k_3, and k_{-2} for the processes occurring on the surface and the constants k_5 and k_{-5} characterising the involvement of the surface layer in the reaction. The period of the auto-oscillations depends on the rate of exchange between the surface and the bulk of the layer.

A novel mathematical model, also consisting of three differential equations, has been proposed[52] for the interpretation of the experimental auto-oscillations in the rate of oxidation of CO on platinum catalysts[12,13]. The authors[52] based their model on mechanism (16). In order to account for the development of auto-oscillations in the rate of reaction, they assumed a temperature difference between the first active layers of the catalyst and the external medium, whose temperature was assumed to be equal to that of the deep layers of the catalyst. It was also assumed that the rates of all the stages vary exponentially with the temperature of the surface layer of the catalyst. The mechanism of the development of auto-oscillations reduces in this case to the following: in the first instant the interaction of the adsorbed reactants proceeds at a low rate and the sites on the catalyst surface liberated by the reaction are immediately occupied by oxygen. The heat evolved in the reaction accelerates the surface interaction of carbon monoxide with oxygen and this autocatalytic process terminates only when the entire surface of the metal has been covered by oxygen. After this, the surface is rapidly cooled and the removal of oxygen from it begins as a result of its interaction with the carbon monoxide in the gas phase; this reaction takes place at a virtually constant temperature of the surface layer. As soon as the concentration of oxygen on the surface has been reduced and that of carbon monoxide increased, the surface interaction of these substances begins and leads to a new rise in the temperature of the surface layer and the cycle is repeated.

The above mechanism shows that the feedback arises in this case owing to the influence of the temperature of the surface layer on the rate of reaction. The mathematical model has a form analogous to that of model (30), but the third equation describes the change in the temperature of the surface layer of the catalyst and not the change in the concentration of hydrogen dissolved in the surface layer. Analysis of the mathematical model showed that the mechanism of the auto-oscillations in the rate described above is possible for long thermal relaxation times. Estimates of thermal relaxation times in the course of reactions on metals lead to much smaller values, so that the model described by the authors[52] is physically unsound.

V. CONCLUSION

The data presented above show that in recent years there has been a sharp increase of the number of studies and publications devoted to the auto-oscillations in the rates of heterogeneous catalytic reactions. This is because the discovery of this phenomenon is important for the development of the theory of the kinetics of heterogeneous catalytic reactions. The auto-oscillations in the rate observed in heterogeneous catalysis show that the catalytic properties of the surface vary under the influence of the catalytic process and that the composition of the surface can be non-stationary in relation to the composition of the gas phase. The auto-oscillations in the rate of reaction occur only under conditions remote from equilibrium. From this it follows that the mechanisms of heterogeneous catalytic reactions can be different in the vicinity of and far from equilibrium conditions. The reaction on different active sections of the catalyst surface remote from one another takes place synchronously.

The amplitude and period of the auto-oscillations in the rate of reaction are very sensitive to the structure of the catalytic system and to the values of its parameters. There is a possibility of quasi-harmonic, relaxation, complex, and random oscillatory conditions. The frequencies of the auto-oscillations vary within wide limits. The development of oscillations with low frequencies indicates the occurrence in the system of stages which are slower than that involving the formation of the final products.

The mathematical models of the auto-oscillations in the rates of heterogeneous catalytic reactions consist of systems of two or several non-linear differential equations. Their form and properties depend on the way which the results of the catalytic process influence its characteristics. This feedback can be due to various causes, namely: (a) the change in the reaction rate constant under the influence of the change in the concentrations of the reactants on the surface or in a thin surface layer of the catalyst; (b) competition by stages involving the adsorption of the reactants and a change in the number of active sites on the catalyst surface during the reaction; (c) superheating of a thin layer of the catalyst surface; (d) the development of homogeneous-heterogeneous stages in the catalytic process; (e) a complex sequence of three and more surface stages.

The present scope of experimental studies in the field of catalysis is limited owing to the lack of methods for the continuous observation of the composition and temperature of the surface and of the surface layer of the catalyst. At the present stage of investigations the choice of a particular type of feedback and a complete quantitative description of the auto-oscillations in the rates of heterogeneous catalytic reactions are therefore difficult. In order to develop a theory of the auto-oscillations, it is also necessary to establish a relation between the reaction at the molecular level and the observed rate and to elucidate the causes of the synchronisation of the oscillations on individual active sites of the surface. Thus one may hope that studies in the field of the auto-oscillations in the rate will permit a more complete investigation of the kinetics and will lead to the elucidation of the mechanisms of heterogeneous catalytic reactions.

During the preparation of the review for the press, studies on auto-oscillatory conditions have been combined into a new field of the kinetics of heterogeneous catalytic reactions. The first investigations of the auto-oscillations in the rates of heterogeneous catalytic reactions were part of the programme of an international congress devoted to the kinetics of physicochemical oscillations, which was held on 19th September 1979 in Aachen (German Federal Republic). During this period, there has been a significant increase of the number of heterogeneous catalytic systems in which the given phenomenon has been observed. These include the interaction of NO and CO on polycrystalline platinum[58], the oxidation of methanol on aluminosilicate catalysts containing palladium[59], the oxidation of ammonia on platinum–rhodium catalysts[60], and the oxidation of octane, hexane, and 1-propanol on platinum catalysts in the presence of organophosphorus compounds[61]. The oscillations in the rate of reaction of NO and CO are interesting because they arise at a pressure of only 5×10^{-4} mmHg, while the auto-oscillations in the rate in all other known systems have been observed only at atmospheric pressure.

Further investigation of the auto-oscillations in the rate of oxidation of CO on deposited and metallic platinum catalysts revealed a high sensitivity of the region where the oscillations occur and of their properties to the composition of the reaction mixture. It has been found that the addition of but-1-ene[62] and of organophosphorus compounds[61] to the initial reaction mixture induces the appearance of auto-oscillations in the rate of the reaction. It has been shown[63] that when electrolytic oxygen is used in the oxidation of carbon monoxide on deposited platinum catalysts, auto-oscillations arise in the rate of reaction whose properties are different from those of the oscillations in the rate of reaction involving oxygen obtained from air and containing a significantly larger amount of impurities. Modelling of the auto-oscillations in the rate of reaction in the given system has been continued[64,65]. The most complete interpretation of the experimental data published previously[9] has been achieved by Ali and Hugo[65]. The authors used model (17), having taken into account the activation energies for the third and fourth stages of mechanism (16) in the adsorption of both components of the reaction mixture. The model also takes into account the influence of the adsorbed oxygen on the activation energy for the CO desorption stage and the influence of both adsorbed components on the activation energy for the oxygen adsorption stage.

The study of the auto-oscillations in the rate of oxidation of hydrogen on platinum[66] and nickel[67] catalysts has also been continued. Particular attention has been devoted to the investigation of complex and irregular dynamic conditions, which have recently been referred to as random oscillations. Thorough experimental proof that the existence of random oscillations in the oxidation of hydrogen on a nickel foil has been published[67]. A mechanism has been proposed[68] for this reaction whose kinetic model can reflect the observed[67] random oscillations in the rate of reaction. The interest in complex and random oscillations can be explained by the fact that they can arise only in systems described by three and more differential equations. This imposes additional limitations on the possible reaction mechanism. Thus the reaction mechanism proposed by Schmiltz et al.[68] includes stages involving the alternate oxidation and reduction of the surface. It is suggested that the reduced surface is inactive, while the adsorption of the reactants and the reaction between them take place only on the oxidised surface. The mathematical model of the reaction also includes an equation describing the variation of the temperature of the catalyst surface. Random oscillations have been observed[66] in the rate of oxidation of H_2 on a platinum wire. The authors[66] believe that the random oscillations can be induced by the incomplete synchronisation of the rates of reaction on different catalyst surface sites.

A homogeneous-heterogeneous mechanism of the oxidation of cyclohexane on the NaX zeolite has been examined by Berman and Elinek[69]. They proposed a non-stationary kinetic model, which describes the variation of the gas-phase concentrations of the peroxy-compounds and peroxy-radicals

formed in the oxidation of cyclohexane. The model describes the earlier results qualitatively[22].

REFERENCES

1. A.A.Andronov, "Sobranie Trudov" (Collected Works), Izd.Akad.Nauk SSSR, Moscow, 1956.
2. A.A.Andronov, A.A.Vitt, and S.E.Khaikin, "Teoriya Kolebanii" (Theory of Oscillations), GIFML. Moscow, 1959.
3. Symposium, "Kolebatel'nye Protsessy v Biologicheskikh i Khimicheskikh Sistemakh" (Oscillatory Processes in Biological and Chemical Systems), Izd.Nauka, Moscow, 1967, Vol.1.
4. Symposium, "Kolebatel'nye Protsessy v Biologicheskikh i Khimicheskikh Sistemakh" (Oscillatory Processes in Biological and Chemical Systems), Pushchino-on-Oka, 1971, Vol.2.
5. J.J.Higgins, Ind.Eng.Chem., **59**, 19 (1967).
6. H.Degn, J.Chem.Educ., **49**, 302 (1972).
7. A.M.Zhabotinskii, "Kontsentratsionnye Kolebaniya" (Concentration Oscillations), Izd.Nauka, Moscow, 1974.
8. Faraday Sympos.Chem.Soc., **9** (1975).
9. P.Hugo and M.Jakubith, Chem.Ing.Techn., **44**, 383 (1972).
10. H.Beuch, P.Fieguth, and E.Wicke, Chem.Ing.Techn., **44**, 445 (1972).
11. E.McCarthy, J.Zahradnic, G.C.Kuczynski, and J.J.Carberry, J.Catal., **39**, 29 (1975).
12. J.P.Dauchot and J.Van Cakenberghe, Nature, Phys.Sci., **249**, 61 (1973).
13. J.P.Dauchot and J.Van Cakenberghe, Japan J.Appl. Phys., 1974, Suppl.2, 533.
14. M.Sheintuch and R.A.Schmitz, Catal.Rev.Sci.Eng., **15**, No.1, 107 (1977).
15. V.D.Belyaev, M.M.Slin'ko, M.G.Slin'ko, and V.I.Timoshenko, Kinetika i Kataliz, **14**, 10 (1973).
16. V.D.Belyaev, M.M.Slin'ko, M.G.Slin'ko, and V.I.Timoshenko, Dokl.Akad.Nauk SSSR, **214**, 1098 (1974).
17. V.D.Belyaev, M.G.Slin'ko, and V.I.Timoshenko, Kinetika i Kataliz, **16**, 555 (1975).
18. V.D.Belyaev, M.M.Slin'ko, and M.G.Slin'ko, "Proceedings of the International Conference on Catalysis, London, 1976", p.B-15.
19. H.Beusch, P.Fieguth, and E.Wicke, "Ist International Symposium on Chemical Reaction Engineering, Washington, 1970", 1972, p.615.
20. S.A.Zhukov and V.V.Barelko, Dokl.Akad.Nauk SSSR, **229**, 655 (1976).
21. I.L.Tsitovskaya, O.V.Al'tshuler, and O.V.Krylov, Dokl.Akad.Nauk SSSR, **212**, 1400 (1973).
22. O.V.Al'tshuller, A.D.Berman, I.L.Tsitovskaya, A.V.Elinek, A.A.Kadushin, A.A.Ukharskii, and O.V.Krylov, "Vsesoyuznaya Konferentsiya po Mekhanizmu Geterogennykh Kataliticheskikh Reaktsii" (All-Union Conference on the Mechanisms of Heterogeneous Catalytic Reactions), IKhF Akad, Nauk SSSR, Moscow, 1974, Preprint 77.
23. A.A.Kadushin, N.K.Kontsev, O.V.Krylov, V.A.Matyshak, and D.M.Shopov, "Vsesoyuznaya Konferentsiya po Mekhanizmu Geterogennykh Kataliticheskikh Reaktsii" (All-Union Conference on the Mechanisms of Heterogeneous Catalytic Reactions), IKhF Akad.Nauk SSSR, Moscow, 1974, Preprint 108.
24. M.G.Slin'ko, V.S.Beskov, and N.A.Dubyaga, Dokl. Akad.Nauk SSSR, **204**, 1174 (1972).
25. V.V.Barelko and Yu.E.Volodin, Dokl.Akad.Nauk SSSR, **211**, 1373 (1973).
26. J.Horiuti, Ann.N.Y.Acad.Sci., **213**, 5 (1973).
27. M.D.Korzukhin, Symposium, "Kolebatel'nye Protsessy v Biologicheskikh i Khimicheskikh Sistemakh" (Oscillatory Processes in Biological and Chemical Systems), Izd.Nauka, Moscow, 1967, Vol.1, p.231.
28. E.E.Sel'kov, in "Bionika" (Bionics), Izd.Nauka, Moscow, 1965, p.173.
29. J.W.May, Adv.Catal., 21, 151 (1970).
30. G.A.Somorjai, Catal.Rev., 7 (1) (1972).
31. G.Kneringer and F.P.Netzer, Surface Sci., 49, 125 (1975).
32. A.E.Morgan and G.A.Somorjai, Surface Sci., 12, 405 (1968).
33. H.P.Bonzel and R.Ku, Surface Sci., 33, 91 (1972).
34. P.H.Holloway and J.B.Hudson, Surface Sci., 43, 123 (1974).
35. J.E.Demuth and T.N.Rhodin, Surface Sci., 45, 249 (1974).
36. K.Christmann, O.Schober, G.Ertl, and M.Neumann, J.Chem.Phys., 60, 4528 (1974).
37. K.A.Dadayan, G.K.Boreskov, V.I.Savchenko, and N.I.Bulgakov, Kinetika i Kataliz, 18, 574 (1977).
38. J.W.May and L.H.Germer, "The Structure and Chemistry of Solid Surfaces" (Edited by G.A.Somorjai), Wiley, New York, 1969.
39. A.M.Kolchin and V.F.Malakhov, Symposium, "Doklady Soveshchaniya po Izotopnomu Obmenu na Tverdykh Katalizatorakh, Novosibirsk, 1973" (Reports of the Conference on Isotope Exchange on Solid Catalysts, Novosibirsk, 1973), Preprint 27.
40. M.I.Temkin, "I Sovetsko-Yaponskii Seminar po Katalizu, Novosibirsk, 1971" (The Ist Soviet–Japanese Seminar on Catalysis, Novosibirsk, 1971), Preprint 15.
41. Y.Nishiyama and H.Wise, J.Catal., 32, 50 (1974).
42. R.W.McCabe and L.D.Schmidt, Surface Sci., 60, 85 (1976).
43. D.D.Perlmutter, "Stability of Chemical Reactors" (Translated into Russian), Izd.Khimiya, Moscow, 1976.
44. W.H.Ray, A.Uppal, and A.B.Poore, Chem.Eng.Sci., 29, 967 (1974).
45. V.L.Kuchaev and M.I.Temkin, Kinetika i Kataliz, 13, 1024 (1972).
46. D.Brennan, D.O.Hayward, and B.M.Trapnell, Proc. Roy.Soc.A, 256, 81 (1960).
47. I.Langmuir, J.Amer.Chem.Soc., 40, 1394 (1918).
48. V.L.Kuchaev, "Proceedings of the VIth International Congress on Catalysis, London, 1976", Preprint A-25.
49. R.Lewis and R.Gomer, Surface Sci., 17, 333 (1969).
50. G.Eigenberger, "Proceedings of the IVth International Symposium on Chemical Reaction Engineering, Heidelberg, West Germany", Dechema, 1976, p.290.
51. W.M.Robertson, "VI Konferenz der Kernforschungsanlage, Julich, 1977", Vol.2, p.449.
52. R.Dagonnier and J.Nuyts, J.Chem.Phys., 65, 2061 (1976).
53. M.M.Slin'ko, Candidate's Thesis, University of Friendship among Nations, Moscow, 1977.
54. M.G.Slin'ko and A.K.Avetisov, Kinetika i Kataliz, 19, 17 (1978).
55. V.D.Belyaev, Candidate's Thesis, Institute of Catalysis, Siberian Division of the USSR Academy of Sciences, 1977.
56. T.I.Zelenyak and M.G.Slin'ko, Kinetika i Kataliz, 18, 1235 (1977).

57. G.A.Chumakov, M.M.Slin'ko, V.D.Belyaev, and M.G.Slin'ko, Dokl.Akad.Nauk SSSR, **234**, 399 (1977).
58. W.Adlhoch, H.G.Lintz, and T.Weisker, in "Kinetics of Physicochemical Oscillations", Preprints of the International Symposium on Kinetics of Physicochemical Oscillations, Aachen, 1979, Vol.1, p.231.
59. N.I.Jaeger, P.J.Plath, and E.van Raaij, in "Kinetics of Physicochemical Oscillations", Preprints of the International Symposium on Kinetics of Physicochemical Oscillations, Aachen, 1979, Vol.1, p.183.
60. J.Barcicki and A.Wojnowski, React.Kinet.Catal. Letters, **9**, 59 (1978).
61. T.Lamb, R.P.Scott, P.Watts, D.Holland, S.J.Gentry, and A.Jones, Chem.Comm., 882 (1977).
62. M.R.Cultip and C.N.Kenney, "Vth International Symposium on Chemical Reaction Engineering", ACS Symp.Ser., **65**, 475 (1978).
63. P.Vargherse, J.J.Carberry, and E.E.Wolf, J.Catalysis, **55**, 76 (1978).
64. M.Sheintuch and R.A.Schmitz, See Ref.62, p.487.
65. M.Ali and P.Hugo, See Ref.58, p.161.
66. J.E.Zuniga and D.Luss, J.Catalysis, **53**, 312 (1978).
67. R.A.Schmitz, G.T.Renola, and P.C.Garrigan, Annals N.Y.Acad.Sci., **316**, 638 (1979).
68. R.A.Schmitz, G.T.Renola, and A.P.Ziodas, See Ref.58, p.221.
69. A.D.Berman and A.V.Elinek, Dokl.Akad.Nauk SSSR, **248**, 643 (1979).

Karpov Physicochemical Institute,
Moscow

Topchiev Institute of Petrochemical
Synthesis, USSR Academy of Sciences,
Moscow

Translated from *Uspekhi Khimii*, **49**, 588 - 617 (1980) U.D.C. 541.135.8;541.49

Polarographic Study of Complex Formation Equilibria in Solutions

E.A.Mambetkaziev and S.I.Zhdanov

Methods for the calculation of the coordination numbers and stability constants of complexes formed in solution from polarographic data are examined and methods for the determination of the parameters governing the formation of a single complex and stepwise complex formation as well as the formation of mixed and polynuclear complexes and complexonates are described. It is shown how kinetic and catalytic waves, the waves of the ligand, and the waves due to irreversible processes can be used for this purpose. Attention is drawn to the necessity to take into account the adsorption of the components of a system involving complex formation.
The bibliography includes 64 references.

CONTENTS

I. Introduction 310
II. Reversible electrode processes 310
III. Irreversible electrode processes 321

I. INTRODUCTION

The use of polarography for the study of the compositions, equilibrium formation constants, and dissociation constants of complexes in solution is based on the simple principles first formulated in 1935 by Heyrovský and Ilkovič[1]. The electrode reduction or oxidation of any depolariser at a mercury electrode is reflected in the polarogram by the corresponding wave whose principal parameters are the half-wave potential $E_{1/2}$ and the limiting current i_d. Heyrovský and Ilkovič introduced the equation of the wave $E = f(i)$ for a reversible electrode process with participation of n electrons and showed that the potential $E_{1/2}$ is in this case close to the normal value (E^0):

$$E_{1/2} = E^0 - \frac{RT}{nF} \ln \left(\frac{D_o}{D_r}\right)^{1/2},$$

where D_o and D_r are the diffusion coefficients of the oxidised and reduced forms of the depolariser ($cm^2\ s^{-1}$). According to the Nernst equation,

$$E = E^0 - \frac{RT}{nF} \ln \frac{[O]}{[B]},$$

the electrode potential is determined by the ratio of the concentrations (more precisely activities) of the components of the oxidation-reduction system. Complex formation leads to a decrease of the concentration of a particular form of the depolariser, which influences the position of the polarographic wave: it shifts along the potential axis. The direction and magnitude of the shift of the wave depend on which component of the redox system forms a more stable complex, the composition of the complex, and its equilibrium formation constant. This fact is in fact used in polarography to determine the complex formation parameters in solution enumerated above.

Thus the polarographic method for the study of complex formation equilibria is in essence close to the potentiometric method. In both cases one uses the dependence of the potential on the concentrations of the components of the redox system. The difference consists in the fact that in potentiometry the ratio of the concentrations of the system components is varied by altering the composition of the solution, while in polarography it is varied by electrolysis at a mercury dropping indicator electrode, which is technically much simpler. The polarographic method is somewhat inferior to the potentiometric method as regards accuracy, but an enormous amount of experimental data on complex formation in solutions has been obtained by the former method[2]. This was promoted by the fact that polarography makes it possible to obtain information not only about the equilibrium properties of the complexes but also about the mechanisms and kinetics of electrode processes involving them, the kinetics of the dissociation of the complexes, and their electrochemical activity as a function of structures.

In the course of the study of equilibria in solutions by the polarographic method, instances of simple and stepwise complex formation, the formation of mixed-ligand and polynuclear complexes, the formation of complexes by metal ions with ligands involved in complex acid–base interactions (for example, with complexones), and the formation of molecular organic complexes and ion pairs have been examined. Methods of calculation from experimental data, including computer calculations, have been greatly improved and methods have been proposed for the investigation of electrochemically inactive complexes with the aid of indicator ions; it has become possible to use kinetic and catalytic waves as well as waves due to irreversible processes. One may conclude that, overall, the level of development of the polarographic method in this field is high.

This review describes the present state of the methods for the investigation of complex formation equilibria in solution with the aid of polarography. The original literature was surveyed inadequately in previous reviews[3-12] and many important studies have been published only in recent years.

II. REVERSIBLE ELECTRODE PROCESSES

Reversible electrode processes involving complexes are more favourable for the study of the compositions of the complexes and their equilibrium formation constants, because it is possible to derive definite useful relations even for very complex systems. It is therefore desirable to select as far as possible experimental conditions which lead to the attainment of reversibility in electrode process. Naturally, before using the relations derived for a reversible process, it is necessary to make sure that the process is indeed reversible. If the process is fully or partly irreversible, the shift of the wave in consequence of complex formation is added to the shift due to the retardation of one of the stages of the electrode process, i.e. to the overvoltage, and the calculation leads to unduly high equilibrium formation constants for the complexes.

In polarography there are a number of criteria which are normally employed to test the reversibility of the process.

1. The equation of the wave of a reversible process is

$$E = E_{1/4} - \frac{2,3RT}{nF} \lg \frac{i}{(i_d - i)} \cdot \quad (1)$$

A linear relation is obtained by plotting $\lg [i/(i_d - i)]$ against E, whose slope is $\partial E/\partial \lg [i/(i_d - i)] = 2.3RT/nF$. At 25 °C the latter is $2.3RT/nF \cong 0.06(V)/n$. According to Tomeš's criterion, which is readily obtained from Eqn.(1), we have

$$E_{3/4} - E_{1/4},\ V = -\frac{0.06}{n} \lg 9 = -\frac{0.058}{n}.$$

2. The values of $E_{1/2}$ for the waves corresponding to the forward and reverse processes in reversible systems are equal. Cathodic and the corresponding anodic waves with humps of equal height arise on the cyclic voltamperogram for such a system when a stationary electrode is used, the peak potentials differing by $0.058/n$ volts.

3. For reversible processes the diffusion of the depolariser species to the electrode is the slowest stage at all points in the wave. The instantaneous diffusion current at any point in the wave is described by the Ilkovič equation:

$$i,\ \mu A = 706nD^{1/2}m^{2/3}t^{1/6}(c - c_0),$$

where m (mg s^{-1}) is the rate of flow of mercury from the capillary, t(s) the time elapsed from the start of the growth of the drop, and c and c_0 (10^{-3} M) are the concentrations of the depolariser in the bulk of the solution and at the electrode respectively. According to the Ilkovič equation, $i = kt^{1/6}$, along the rising section of the wave, which can be tested experimentally with the aid of an oscillographic polarograph (for irreversible processes, this equation is valid only for the upper part of the wave).

4. A distinct symmetric peak, the potential at the vertex of which consists only of the value of $E_{1/2}$ for the wave on a classical polarogram, arises on an a.c. polarogram for a reversible system. The peak width at half its height is $0.088/n$ volts. In phase-selective a.c. polarography such peaks have the same shapes and heights: $[(i_p)_R = (i_p)_C]$ are obtained on the curves relating the potentials to the active (i_R) and reactive (i_C) components of the alternating current.

To test the reversibility of this process, it is of course not necessary to employ all the criteria enumerated, which is laborious; however, the reliability of the conclusions is naturally higher the greater the number of criteria used.

In a system with complex formation a series of species are present simultaneously at equilibrium: free metal ions, complex species of various compositions, and the free ligand. In principle, not only free metal ions are discharged at the electrode, which is usually assumed for simplicity in the derivation of the quations, but also the complex species. However, if the process is reversible, and its overall rate is determined solely by diffusion, then experiment does not yield information about which particular species is reduced or oxidised at the electrode; the disappearance of an electrochemically active species at the electrode leads to a change in the concentrations of species of all types at the electrode owing to rapid equilibration.

On the basis of the accumulated experimental data, it is in some cases possible to predict the reversibility of the process involving complexes[5,9]. If a labile metal complex is reduced with preliminary dissociation and the free metal ions are discharged at the electrode, then the process as a whole will be reversible, provided that the metal ions are reduced reversibly[9]. The Tl^+/Tl, Hg^{2+}/Hg, Cu^+/Cu, Cu^{2+}/Cu, Cd^{2+}/Cd, and Pb^{2+}/Pb systems are reversible. Under certain conditions, the Sn^{2+}/Sn, Bi^{3+}/Bi, Sb^{3+}/Sb, and In^{3+}/In systems are also reversible. The labile complexes of these metals are likewise reduced reversibly. We may note that the metals enumerated form amalgams[5]

Sometimes free hydrated metal ions are reduced irreversibly, while in a system with complex formation the process becomes reversible. For example, the hydrated In^{3+} and Ni^{2+} ions are reduced irreversibly, while many of their complexes are reduced reversibly. In such cases one can apparently postulate that complex species and not free metal ions are reduced directly at the electrode.

If the complex is not reduced to the metallic state and the process involves merely a change in the valence of the central complex-forming ion, then it proceeds as a rule reversibly with participation of a single electron[5]. The Fe^{3+}/Fe^{2+}, Cu^{2+}/Cu^+, V^{3+}/V^{2+}, Ti^{4+}/Ti^{3+}, U(VI)/U(V), U^{4+}/U^{3+}, Eu^{3+}/Eu^{2+} and more rarely Cr^{3+}/Cr^{2+}, Mn^{3+}/Mn^{2+}, Co^{3+}/Co^{2+}, Ru^{3+}/Ru^{2+}, Nb(V)/Nb(IV), and Np^{4+}/Np^{3+} are reversible.

Reversibility is particularly characteristic of the reduction of inert complexes, whose oxidised and reduced forms have the same compositions. Thus the hexacyanoferrate(III)/hexacyanoferrate(II), ferrocenium cation/ferrocene, $Cr(CN)_6^{3-}/Cr(CN)_6^{4-}$, etc. systems are reversible. On the other hand, if the oxidised and reduced forms have different structures, then the system is in most cases irreversible. The simple empirical rules enumerated above are useful for the approximate assessment of the reversibility of the system investigated.

Solutions to which a large excess of an indifferent electrolyte has been added are used in polarography. A fairly high electrical conductivity of this solution is attained in this way and the ohmic potential losses can be neglected. At the same time one excludes the migration component of the current, whose presence would constitute an additional complication. Finally, the electrolyte is added also to maintain a constant ionic strength in the solution, ensuring thereby the constancy of the activity coefficients, which are usually difficult to meaure. This is why concentration equilibrium formation constants of the complexes and not their thermodynamic values are found by the polarographic method. The thermodynamic constant can also be estimated by extrapolating the relation between the concentration constant and ionic strength to zero value of the latter.

1. Systems with a Single Complex

The equations of the waves for this case were derived by von Stackelberg and von Freyhold in 1940 [13] and by Lingane in 1941.[14]

(a) Reduction of the complex with formation of an amalgam. In the derivation of the equations of the reduction wave of the complex by the Lingane method[14], one uses the equation for the equilibrium formation or dissociation constant of the complex, the Nernst equation, and the Ilkovič equation, whereby one converts the concentrations into the currents.

The reduction of the complex with formation of an amalgam

$$MX^{(n-pb)+} + ne + Hg \rightleftarrows M(Hg) + pX^{b-}$$

can be conveniently regarded as the sum of two partial reactions:

$$M^{n+} + pX^{b-} \rightleftarrows MX_p^{(n-pb)+}$$

and

$$M^{n+} + ne + Hg \rightleftarrows M(Hg)$$

(here X^{b-} is the ligand). If these reactions are fast and the process as a whole is reversible, then the potential of the indicator electrode will be described by the Nernst equation

for an amalgam electrode, which includes the concentrations at the surface of the electrode of the amalgam formed $[M(Hg)]_0$ and free metal ions $[M]_0$, their activity coefficients $f_{M(Hg)}$ and f_M, and the activity of mercury in the surface layer of the electrode a_{Hg}. Since a very dilute amalgam is formed on the mercury electrode, the activity of the mercury in the amalgam differs little from that of pure mercury and can be regarded as a constant.

The concentration of metal ions in terms of the complex formation equilibrium constant can be substituted in the Nernst equation. The concentration of the complex in solution and of the metal in the amalgam near the interface are found with the aid of the Ilkovič equations for the diffusion of the complex in the solution and of the metal in the amalgam. Since the ligand is liberated in the reduction of the complex, the concentration of the former at the surface of the electrode does not remain constant as the potential of the latter varies along the wave:

$$[X]_0=[X]+pi/\varkappa_X, \qquad (2)$$

where $\varkappa_X = 605nD_X^{1/2}m^{2/3}\tau^{1/6}$, D_X is the diffusion coefficient of the ligand, and τ is the drop time.

Allowance for the change in the ligand concentration at the electrode greatly complicates the equation of the wave. The ligand concentration in the bulk of the solution is therefore made considerably greater than that of the metal ions, whereupon the term $pi/\varkappa_X$ in Eqn.(2) can be neglected and one can assume that $[X]_0 = [X]$.

Ultimately we obtain

$$E = E_{1/2} - \frac{2.3RT}{nF}\lg\frac{i}{i_d - i} \qquad (3)$$

and

$$(E_{1/2})_c = E^0 - \frac{2.3RT}{nF}\lg\frac{K_p f_{M(Hg)}}{f_{MX_p}} - \frac{2.3RT}{2nF}\lg\frac{D_c}{D_a} - p\frac{2.3RT}{nF}\lg[X]f_X. \qquad (4)$$

In the derivation of Eqns.(3) and (4) account was taken of the diffusion to the electrode of complex species alone. If the diffusion of free ions M^{n+} is also taken into account, then instead of Eqn.(4) we obtain[5]:

$$(E_{1/2})_c = E^0 - \frac{2.3RT}{nF}\lg\frac{K_p f_{M(Hg)}}{f_{MX_p}} - \frac{2.3RT}{2nF}\lg\frac{D_c}{D_a} - \frac{2.3RT}{nF}\lg(1+K_p[X]^p f_X^p).$$

For stable complexes, the diffusion of M^{n+} ions to the electrode can be neglected.

Inspection of Eqn.(3) shows that the equation of the wave for the reversible reduction of the complex in no way differs from the equation of the wave for any reversible process. Consequently all the polarographic criteria of reversibility are applicable to the reduction of the complex.

Eqn.(4) does not include the concentration of the complex, so that $E_{1/2}$ is independent of the concentration of the depolariser, as should be the case for the wave corresponding to a reversible process.

It can be readily shown that the following equation is valid for the wave due to the discharge of simple ions:

$$(E_{1/2})_s = E^0 - \frac{2.3RT}{nF}\lg\frac{f_{M(Hg)}}{f_M} - \frac{2.3RT}{2nF}\lg\frac{D_M}{D_a}. \qquad (5)$$

From Eqns.(4) and (5), we obtain the difference between the half-wave potentials of the complex and the simple ion:

$$(E_{1/2})_c - (E_{1/2})_s = \frac{2.3RT}{nF}\lg\frac{f_{MX_p}}{K_p f_{M^{n+}}} + \frac{2.3RT}{2nF}\lg\frac{D_M}{D_c} - p\frac{2.3RT}{nF}\lg[X]f_X.$$

If the experiment is carried out under the conditions of a constant ionic strength, then the contribution of the activity coefficients is usually disregarded. The contribution of the term including the ratio of the diffusion coefficients is also rarely taken into account, although the latter can be readily determined experimentally as the ratio of the limiting currents. The final form of the equation for the shift of $E_{1/2}$ on complex formation is as follows:

$$(E_{1/2})_c - (E_{1/2})_s = \frac{2.3RT}{nF}\lg\frac{(i_d)_M}{(i_d)_c} - \frac{2.3RT}{nF}\lg K_p - p\frac{2.3RT}{nF}\lg[X]. \qquad (6)$$

According to Eqn.(6), the dependence of $\Delta E_{1/2}$ on $\lg[X]$ is represented by a straight line with a slope $2.3pRT/nF$; the coordination number of the complex p can be found from the slope. The straight line makes an intercept $(2.3RT/nF)\lg(1/K_p)(i_d)_M/i_d)_c$ on the ordinate axis, i.e. at $[X]=1$; hence it is easy to find the equilibrium formation constant for the complex K_p.

Lingane[14] used Eqn.(6) in the study of the hydroxo-complex of lead and established that, in the concentration range of alkali 0.01–1 *N*, the coordination number $p = 3$. The electrode process

$$HPbO_2^- + 2e + H_2O + Hg \rightleftarrows Pb(Hg)_f + 3OH^-$$

corresponds to the lead wave.

(b) The reduction of a complex involving the transition from one oxidation state of the complex-forming metal to another. We shall now consider the case of a reversible electrode process as a result of which the complex is not reduced to the metal but gives rise to a valence state of the complex-forming metal differing from the initial state:

$$MX_p^{(n-pb)+} + (n-m)e = MX_q^{(m-qb)+} + (p-q)X^{b-}.$$

Suppose that only one of two complexes, for example $MX_p^{(n-pb)+}$, is present in the bulk of the solution. Both complexes are labile and are involved in a mobile equilibrium with the metal ions in the ligand:

$$M^{n+} + pX^{b-} \underset{}{\overset{K_p}{\rightleftarrows}} MX_p^{(n-pb)+}, \qquad (I)$$

$$M^{m+} + qX^{b-} \underset{}{\overset{K_q}{\rightleftarrows}} MX_q^{(m-qb)+}. \qquad (II)$$

The ligand is taken in excess, so that $[X]_0 = [X]$.

Using the Nernst equation, the equations for the equilibrium constants of reactions (I) and (II), and the Ilkovič equations for the diffusion of the complexes $MX_p^{(n-pb)+}$ and $MX_q^{(m-qb)+}$, we obtain

$$E = E^0 - \frac{RT}{(n-m)F}\ln\frac{K_p}{K_q} - \frac{RT}{(n-m)F}\ln\frac{i}{i_d - i} - \frac{RT}{(n-m)F}\lg\frac{\varkappa_p}{\varkappa_q} - \frac{(p-q)}{(n-m)}\frac{RT}{F}\ln[X], \qquad (7)$$

$$(E_{1/2})_c = E^0 - \frac{RT}{(n-m)F}\ln\frac{K_p}{K_q} - \frac{RT}{(n-m)F}\ln\frac{\varkappa_p}{\varkappa_q} - \frac{(p-q)}{(n-m)}\frac{RT}{F}\ln[X] \qquad (8)$$

and

$$(E_{1/2})_c - (E_{1/2})_s = \frac{2.3RT}{(n-m)F}\lg\frac{\varkappa_{M^{n+}}+\varkappa_q}{\varkappa_{M^{m+}}+\varkappa_p} - \frac{2.3RT}{(n-m)F}\lg\frac{K_p}{K_q} - 2.3\frac{(p-q)}{(n-m)}\frac{RT}{F}\lg[X]. \qquad (9)$$

If both complexes are present in solution, then the term involving the currents in Eqn.(7) assumes the following form:

$$\frac{RT}{(n-m)F}\ln\frac{i-(i_d)_q}{(i_d)_p - i}$$

where $(i_d)_p$ is the limiting current of the complex $MX_p^{(n-pb)+}$ and $(i_d)_q$ is the limiting current of the complex $MX_q^{(m-qb)+}$; Eqns.(8) and (9) retain their previous form. A single

anodic–cathodic wave arises on the polarogram, its anodic component corresponding to the oxidation of the complex $MX_q^{(m-qb)+}$ and the cathodic component corresponding to the reduction of the complex $MX_p^{(n-pb)+}$.

Eqns.(8) and (9) show that, by studying the dependence of $E_{1/2}$ on lg [X], it is possible to find in this instance only the difference between the coordination numbers and the ratio of the stability constants of the two complexes in the system. In particular, if the composition of the complex does not change on reduction, i.e. $p-q=0$, then the potential $E_{1/2}$ will be independent of the ligand concentration; at the same time it will not be equal to $E_{1/2}$ for the reduction of the simple ion M^{n+}. On the other hand, following the addition of the first portion of the ligand in excess with respect to the M^{n+} ions, the reduction wave of the latter shifts in the cathodic or anodic direction depending on which complex is more stable, but a further change in ligand concentration does not entail a shift.

If the composition and the formation constant of one of the complexes are known, then it is possible to determine by Eqns.(8) and (9) the corresponding parameters for the other complex. As an illustration, we shall consider a system consisting of the oxalate complexes of bivalent and tervalent iron[13,14]:

$$Fe(C_2O_4)_3^{3-} + e \rightleftarrows Fe(C_2O_4)_q^{(3-2q)+} + (3-q)\,C_2O_4^{2-}.$$

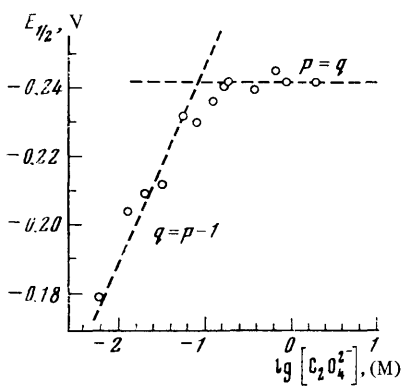


Figure 1. Dependence of the half-wave potential for the reduction of the complex $Fe(C_2O_4)_3^{3-}$ on the logarithm of the concentration of oxalate ions. Reference electrode—saturated calomel half-cell[14].

This system was investigated at 25 °C and an Fe^{3+} concentration of $(1–2)\times10^{-3}$ M. The $K_2C_2O_4$ concentration was varied[14] in the range 6.1×10^{-3}–1.76 M. The solutions also contained 0.3–0.6 M KCl. The dependence of $E_{1/2}$ of the reduction wave of the iron(III) oxalate complex on the logarithm of the oxalate concentration is illustrated in Fig.1. The plot consists of two sections. At an oxalate concentration in excess of ~0.15 M the half-wave potential $E_{1/2}$ is independent of $[C_2O_4^{2-}]$; consequently $p-q=0$ and the iron(II) and iron iron(III) complexes have the same compositions:

$$Fe(C_2O_4)_3^{3-} + e \rightleftarrows Fe(C_2O_4)_3^{4-}.$$

For $[C_2O_4^{2-}] < 0.15$ M, $E_{1/2}$ does depend on $[C_2O_4^{2-}]$ and $\partial E_{1/2}/\partial \lg [C_2O_4^{2-}] = 58$ mV, which corresponds to $p-q=1$ for $n-m=1$. Consequently, under these conditions, the reduction of the complex $Fe(C_2O_4)_3^{3-}$ leads to the formation of the complex $Fe(C_2O_4)_2^{2-}$:

$$Fe(C_2O_4)_3^{3-} + e \rightleftarrows Fe(C_2O_4)_2^{2-} + C_2O_4^{2-}.$$

The independence of $E_{1/2}$ of the ligand concentration for partial reduction of the complex is characteristic of the polarographic behaviour of metal complexonates which as a rule have the simplest composition, 1:1.

If the complex $MX_q^{(m-qb)+}$ is reduced with formation of an amalgam of the complex-forming metal at more negative potentials,

$$MX_q^{(m-qb)+} + m\,e + Hg \rightleftarrows M(Hg) + q\,X^{b-}$$

and a separate second wave arises on the polarogram, then both the composition and the stability constants of the two complexes can be determined by analysing the properties of the two waves. The properties of the first wave are fully consistent with Eqns.(7)–(9); those of the second wave are described by Eqns.(3), (4), and (6), but a number of corrections must be applied to them. Firstly, at the potentials of the second wave the current is determined by the rate of diffusion of the complex $MX_p^{(n-pb)+}$ and not $MX_q^{(m-qb)+}$ although its concentration does in fact fall almost to zero at the potentials of the first wave. Secondly, m electrons are involved in the process. Thirdly, at the potentials of the first and second waves the characteristics of the capillary differ owing to the influence of the potential on the drop time. Taking into account the above corrections, the following equations were obtained[13]

$$E'' = E''_{1/2} - \frac{2.3RT}{mF}\lg\frac{i''}{i''_d - i''},$$

$$(E''_{1/2})_c = E_2^0 - \frac{2.3RT}{mF}\lg K_q - \frac{2.3RT}{mF}\lg\frac{(n-m)}{m}\frac{\varkappa_q}{\varkappa_a} - q\frac{2.3RT}{mF}\lg[X],$$

and

$$(E''_{1/2})_c - (E''_{1/2})_s = \frac{2.3RT}{mF}\lg\frac{m}{(n-m)}\frac{\varkappa_{M^{m+}}}{\varkappa_q} - \frac{2.3RT}{mF}\lg K_q - q\frac{2.3RT}{mF}\lg[X].$$

In these equations E'' and $E''_{1/2}$ are respectively the potential of any point in the second wave and its half-wave potential, E_2^0 the normal potential for the process

$$M^m + me + Hg \rightleftarrows M(Hg);$$

i'' and i''_d are the current and the limiting current of the second wave reckoned from the limiting current of the first wave, K_q is the stability constant of the complex $MX_q^{(m-qb)+}$, $\varkappa_q$ the constant of the Ilkovič equation for the complex, $\varkappa_a$ the corresponding constant for the amalgam of M at the limiting current potential of the second wave, and $\varkappa_{M^{m+}}$ the corresponding parameter for the ion M^{m+} also at the limiting current potential of the second wave.

The reduction of certain copper complexes, particularly ammine complexes, serves as a striking example of a stepwise reduction process. Free copper(II) ions are reduced in one stage with formation of an amalgam, so that the normal potential for the process

$$Cu^+ + e + Hg \rightleftarrows Cu(Hg)$$

is more positive than that (and hence also $E_{1/2}$) for the process

$$Cu^{2+} + e \rightleftarrows Cu^+.$$

Ammine complexes of bivalent and univalent copper are formed in ammonia-containing solutions but the copper(I) complexes are more stable. The copper waves move apart; for this reason, at a fairly high ammonia concentration two waves arise on the polarogram of bivalent copper and can be used to investigate the composition and stabilities of the complexes of copper in both valence states. This system has been investigated by von Stackelberg and von Freyhold[13]; the experimental and calculated data obtained are illustrated in Fig.2. Evidently the stepwise reduction of the copper(II) ammine complex is observed at an ammonia concentration of 0.001 M and above. Fig.2 shows that the slopes of the plots of $E_{1/2}$ against lg $[NH_3]$ correspond to the complexes having this composition. In the reduction of the copper(II) complex this relation (curve *1*) has an anomalous form: along the initial section the increase of the ammonia concentration causes a shift of the wave in the positive direction. This is because at a very low ammonia concentration mainly complexes of Cu^{2+} with one or two ammonia molecules are formed, while copper(I) forms mostly a complex with two ammonia molecules under the same conditions. The ratio $K_p/K_q \ll 0$ and $\lg(K_p/K_q) < 0$, but this term has the minus sign in Eqn.(9). Furthermore, $p-q$ is either −1 or 0. As a result of the influence of these two parameters, the initial shift of the wave in the positive direction is observed. In the presence of ammonia the process

$$Cu^{2+} + 2e + Hg \rightleftarrows Cu\,(Hg)$$

does not occur (curve *2*).

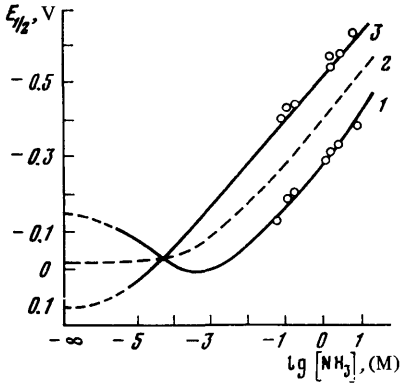


Figure 2. The influence of the concentration of ammonia on the half-wave potentials for different processes: 1) Cu^{2+}/Cu^{+} $[Cu(NH_3)_4^{2+}/Cu(NH_3)_2^{+}]$; 2) $Cu^{2+}/Cu(Hg)$; 3) Cu^{+}/Cu $[Cu(NH_3)_2^{+}/Cu(Hg)]$. Lines—calculations; circles—experimental data. Reference electrode—saturated calomel half-cell[13].

In the derivation of the equations of the reduction wave of the complex it was assumed that the ligand is present in solution in a fairly large excess. On the other hand, it is desirable to vary the concentration of the ligand within the widest possible limits. It is therefore necessary to know what excess is adequate. The change in the ligand concentration at the electrode as a result of the reduction of the complex is responsible for the undesirable shift of the wave. The excess of the ligand N, for which the error of the measurement of $E_{1/2}$ does not exceed $\Delta E_{1/2}$ for the reason discussed above, can be calculated by the equation (Heyrovský and Kuta[15], p.137)

$$N = \frac{p^2}{2} \cdot \frac{RT}{nF} \cdot \left(\frac{D_c}{D_X}\right)^{1/2} \cdot \frac{2}{\Delta E_{1/2}}.$$

Here $RT/F = 25$ mV at 25 °C. Thus, when $E_{1/2}$ is measured to within 2 mV, the excess of the ligand should be at least by a factor of 100 if $p = 4$ and $n = 1$ and a factor of 12 if $p = 2$, subject to the condition that $(D_C/D_X)^{1/2} = 1$. It follows from these calculations that a smaller excess of the ligand is required the smaller the value of p and the larger the value of n.

(c) Mercury complexes. The reduction waves of mercury complexes or the oxidation waves of metallic mercury involving the formation of a complex have an unusual form and properties. The explanation is that one of the components of the oxidation-reduction system is metallic mercury, whose activity is always constant. For this reason, the initial Nernst equation has a simpler form:

$$E = E^0 + \frac{RT}{2F} \ln [Hg^{2+}]_0.$$

Simple relations are also obtained where there is no excess of the ligand in solution.

The reasoning followed in the derivation of the equation of the wave is of the usual kind: the concentration of mercury ions is found from the equation for the stability constant of the complex and is substituted in the Nernst equation The concentrations are converted into the currented with the aid of the Ilkovič equation. It is therefore desirable to quote and discuss only the final equation in this instance (Heyrovský and Kuta, Ref.15, p.151).

The reduction of the mercury complexes will be considered in relation to the electrode process

$$Hg^{2+} + 2CN^- \overset{K}{\rightleftarrows} Hg(CN)_2,$$
$$Hg^{2+} + 2e \rightleftarrows Hg.$$

The equation of the wave is

$$E = E^0_{Hg^{2+}} - \frac{RT}{2F} \ln \frac{i^2}{(i_d - i)} \frac{\varkappa_c}{(\varkappa_X)^2} K, \qquad (10)$$

$$(E_{1/2})_c = E^0_{Hg^{2+}} - \frac{RT}{2F} \ln \frac{i_d}{2} \frac{\varkappa_c}{(\varkappa_X)^2} K. \qquad (11)$$

Eqns.(10) and (11) show that the wave of the mercury complex can be expressed in a linear form by plotting E against lg $[i^2(i_d - i)]$, the straight line intersecting the potential axis not at $E_{1/2}$ but at the potential

$$E^* = E^0_{Hg^{2+}} - \frac{2.3RT}{2F} \lg \frac{\varkappa_c}{(\varkappa_X)^2} - \frac{2.3RT}{2F} \lg K,$$

which depends on the characteristics of the capillary and the stability constant of the complex. The half-wave potential is a function of the concentration of the complex.

In the general case we have for the reduction of the complex HgX_p

$$E = E^0_{Hg^{2+}} - \frac{RT}{2F} \ln \frac{i^p}{(i_d - i)} \frac{\varkappa_c}{(\varkappa_X)^p} K_p$$

and

$$E_{1/2} = E^0_{Hg^{2+}} - \frac{RT}{2F} \ln \left(\frac{i_d}{2}\right)^{p-1} \frac{\varkappa_c}{(\varkappa_X)^p} K_p.$$

In the example under consideration CN^- is the anion of a weak acid, $K_a = [CN^-][H^+]/[HCN] = 7.2 \times 10^{-10}$. Taking this factor into account, we obtain somewhat different equations of the wave:

$$E = E^0_{Hg^{2+}} - \frac{RT}{2F} \ln \frac{i^2}{(i_d - i)} \frac{\varkappa_c}{(\varkappa_X)^2} K - \frac{RT}{F} \ln \frac{K_a}{K_a + [H^+]} .$$

When $[H^+] \gg K_a$ (i.e. at pH < 8) and a constant concentration of the complex $Hg(CN)_2$, we obtain

$$E_{1/2} = E^0_{Hg^{2+}} + \frac{RT}{F} \ln [H^+] + \text{const.}$$

Consequently at $[H^+] \gg K_a$ the half-wave potential $E_{1/2}$ is a function of the pH. On the other hand, if $[H^+] \ll K_a$ (i.e. at pH > 10), then $E_{1/2}$ is independent of the pH.

The principles governing the allowance for the acid–base equilibrium involving the ligand in simple complex formation equilibria without taking into account the participation of the protonated ligand in the complex formation reaction have been demonstrated in relation to the reduction of the complex $Hg(CN)_2$. More complicated cases will be considered below.

The equilibria in the formation of mercury complexes can be investigated also on the basis of the influence of the ligands on the anodic dissolution of mercury. Suppose that metallic mercury undergoes anodic dissolution in the presence of a small amount of CN^- ions;

$$Hg \rightleftarrows Hg^{2+} + 2e,$$
$$Hg^{2+} + 2CN^- \overset{K}{\rightleftarrows} Hg(CN)_2.$$

The CN^- ions bind the Hg^{2+} ions formed in a complex and the concentration of mercury ions at the electrode falls. As a result, an anodic wave arises on the polarogram, its height being determined by the diffusion of CN^- ions to the electrode and its position being related mainly to the stability constant of the mercury complex formed: the more stable the complex the more cathodic are the potentials at which the wave is located.

The equation of the anodic wave is

$$E = E^0_{Hg^{2+}} + \frac{RT}{2F} \ln \frac{i}{(i_d - i)^2} \frac{(\varkappa_X)^2}{\varkappa_c K} , \quad (12)$$

$$(E_{1/2})_c = E^0_{Hg^{2+}} + \frac{RT}{2F} \ln \frac{(\varkappa_X)^2}{\varkappa_c \cdot 0{,}5 i_d K} , \quad (13)$$

or

$$(E_{1/2})_c = E^0_{Hg^{2+}} + \frac{RT}{2F} \ln \left(\frac{D_X}{D_c}\right)^{1/2} \frac{2}{K[CN^-]} ,$$

since $i_d = \varkappa_X [CN^-]$. Comparison of Eqns.(10) and (11), on the one hand, and Eqns.(12) and (13), on the other, shows that the anodic wave for the formation of the mercury complex and the cathodic wave for its reduction have similar properties. This is understandable: the waves correspond to the forward and reverse processes of a single system.

The anodic waves of mercury are convenient for the investigation of mercury complexes. They have been used to study the equilibria in the formation of mercury complexes with the anions CN^-, SO_3^{2-}, $S_2O_3^{2-}$, SCN^- as well as complexones and ethylenediamine. In the presence of an excess of the ligand in solution, we obtain for the reduction wave of the mercury complex[15]

$$E = E^0 + \frac{RT}{2F} \ln (i_d - i) - \frac{RT}{2F} \ln \varkappa_c - \frac{RT}{2F} \ln K_p - p \frac{RT}{2F} \ln [X], \quad (14)$$

$$E_{1/2} = E^0 + \frac{RT}{2F} \ln \frac{i_d}{2} - \frac{RT}{2F} \ln \varkappa_c - \frac{RT}{2F} \ln K_p - p \frac{RT}{2F} \ln [X] \quad (15)$$

or

$$E_{1/2} = E^0 + \frac{RT}{2F} \ln \frac{[HgX_p]}{2} - \frac{RT}{2F} \ln K_p - p \frac{RT}{2F} \ln [X]. \quad (16)$$

Evidently the wave in this case is even more asymmetric, beginning from a sharp break at the potential

$$E_{i=0} = E^0 + \frac{RT}{2F} \ln [HgX_p] - \frac{RT}{2F} \ln K_p - p \frac{RT}{2F} \ln [X]. \quad (17)$$

The wave represents, as it were, the upper half of the normal reduction wave of a complex involving the formation of an amalgam. The half-wave potential is a function of the concentration of the complex, but is independent of the characteristics of the capillary; the equation can be expressed in a linear form by plotting E against $\lg (i_d - i)$.

If the complex is reduced with formation of a metal insoluble in mercury, then the wave has exactly the same shape and Eqns.(14)–(17) are valid for it.

(d) The displacement method[16]. If the solution contains only one ligand X and the two metal ions M and N, then the equilibrium mixture should contain the free ions M and N and the complexes MX and NX:

$$MX + N \rightleftarrows NX + M, \qquad K_{III} = [NX][M]/[MX][N] = K_{NX}/K_{MX} . \quad (III)$$

The additional unknowns in this equation are eliminated with the aid of the material balance equations

$$c_M = [M] + [MX],$$
$$c_N = [N] + [NX],$$
$$c_X = [MX] + [NX].$$

The relation is particularly simple if the experiment is carried out in such a way that $c_M = c_N = c_X = c$. Then

$$K_{III} = [M]^2/(c - [M])^2 = K_{NX}/K_{MX}.$$

[M] is determined polarographically and the ratio of the stability constants of the complexes NX and MX is calculated. If one of the constants is known, the other can be obtained from the ratio.

The experiment is carried out as follows[16]. A solution containing the complex MX, which is reduced with formation of a single wave on the polarogram, is treated with a salt containing the cation N. After the establishment of the new equilibrium, the reduction wave of the complex MX is preceded by the wave of the displaced free ions M. One of the conditions for the application of the displacement method is the slowness of the attainment of equilibrium (III). Only then is the reduction wave of the ions M of a purely diffusional type and its height characterises the equilibrium concentration of these ions. It is also necessary that the cation N and the complex NX are electrochemically more active than the ions M.

This procedure has been widely used[16] in the polarographic study of the formation of metal complexonates.

2. Stepwise Complex Formation

If several complexes are formed in solution, the dependence of the half-wave potential for the reduction of the complex-forming metal on the logarithm of the activity of the ligand will no longer be linear. In this case the plot of $E_{1/2}$ against lg [X] consists either of several linear sections (in accordance with the number of complexes formed, whose formation constants differ fairly appreciably) or of a smooth curve which is convex with respect to the abscissa axis, (with increase of the activity of the ligand, complexes with a larger coordination number are formed and the slope of the plot increases). The smooth curve is obtained when the stability constants of the complexes do not differ very markedly and the regions of

their existence overlap. In the former case the equations derived in the preceding section are applicable to the individual linear sections and it is possible to determine with their aid both the coordination number p and the formation constant K for each complex. The second case requires a more complicated analysis.

(a) Method based on the logarithmic Yatsimirskii plot[17–20]. We shall assume that at any ligand concentration not more than two complexes are formed in solution and these are in equilibrium:

$$MX_p + X \rightleftarrows MX_{p+1},$$
$$\beta_{p+1} = [MX_{p+1}]_0/[MX_p]_0[X].$$

(β_{p+1} is the successive formation constant of the complex MX_{p+1}). The ligand is again present in solution in a fairly large excess.

An expression for $[MX_{p+1}]_0$ and then for $[M]_0$ can be obtained from the equation for β_{p+1}. Having substituted $[M]_0$ in the Nernst equation and having replaced the concentrations by the currents with the aid of the Ilkovič equation, we arrive at the following equations for the wave, $E_{1/2}$, and $\Delta E_{1/2}$:

$$E = E^0 - \frac{RT}{nF}\ln\frac{i}{(i_d - i)} - \frac{RT}{nF}\ln\frac{\varkappa_c}{\varkappa_a} - \frac{RT}{nF}\ln[X]^p(1 + \beta_{p+1}[X]),$$

$$E_{1/2} = E^0 - \frac{RT}{nF}\ln\frac{\varkappa_c}{\varkappa_a} - \frac{RT}{nF}\ln K_p - \frac{RT}{nF}\ln[X]^p(1 + \beta_{p+1}[X]),$$

$$(E_{1/2})_s - (E_{1/2})_c = \Delta E_{1/2} = \frac{RT}{nF}\ln[X]^p(1 + \beta_{p+1}[X]) + \frac{RT}{nF}\ln K_p + \frac{RT}{nF}\ln\frac{\varkappa_c}{\varkappa_M}. \quad (18)$$

According to Eqn.(18), the function $\Delta E_{1/2} = f\{\ln[X]\}$ is represented by a curve whose slope at any point is determined by the derivative

$$\frac{\partial \Delta E_{1/2}}{\partial \ln[X]} = \frac{RT}{nF}\left(p + \frac{[X]}{\beta_{p+1}^{-1} + [X]}\right).$$

When $[X] \gg \beta_{p+1}^{-1}$, we have $\partial \Delta E_{1/2}/\partial \ln[X] = RT(p+1)/nF$ and Eqn.(18) is converted into Eqn.(6); the complex MX_{p+1} predominates in the solution. When $[X] \ll \beta_{p+1}^{-1}$, we have $\partial \Delta E_{1/2}/\partial \ln[X] = RTp/nF$ and Eqn.(18) is again transformed into Eqn.(6); the complex MX_p predominates in the solution.

When the concentrations of the two complexes are equal, i.e. $[X] = \beta_{p+1}^{-1}$, we have

$$\Delta E_{1/2} = \frac{RT}{nF}\ln[X]^p + \frac{RT}{nF}\ln K_p - \frac{RT}{nF}\ln\frac{\varkappa_M}{\varkappa_c} + \frac{RT}{nF}\ln 2, \quad (19)$$

$$\frac{\partial \Delta E_{1/2}}{\partial \lg[X]} = \frac{2.3RT}{nF}\left(p + \frac{1}{2}\right). \quad (20)$$

In conformity with these derivations, the experimental data are represented by a plot of $\Delta E_{1/2}$ against $\lg[X]$ and a series of tangents are drawn; their slopes are defined by Eqn.(20) in which integral values of p are substituted (1, 2, 3, etc.). The tangential points correspond to the equality of the concentrations of the complexes MX_p and MX_{p+1}, while the ligand concentrations at these points are numerically equal to β^{-1}. Knowing p and the corresponding values of $[X]$, it is possible to calculate the constants K_p by Eqn.(19). Yatsimirskii called this method the logarithmic plot method.

If a tangent is drawn having put $p = 0$, then the tangential point will correspond to the equality of the concentrations of the free ions M^{n+} and the complex MX, while the concentration of the ligand at this point is equal to the instability constant of the complex MX.[21]

Adamovich and Novakovskii[22] and also Tur'yan[23] considered the conditions under which the logarithmic plot method is applicable. According to these workers, the method can be used to determine the parameters p, K, and β even for non-existent complexes in those cases where for some reason ligands do not add to the metal ion solely one by one. Adamovich and Novakovskii therefore recommend that the method be used only for complexes whose existence has been demonstrated independently. However, real complex formation is reflected in the form of the relation between $E_{1/2}$ and $\lg[X]$ and for a non-existent complex the Yatsimirskii method should in principle yield the corresponding successive formation constants.

Tur'yan[23] pointed out that the logarithmic plot method is an approximation, so that the hypothesis that two adjacent complexes predominate when their concentrations are equal does not correspond exactly to reality. Sometimes it is altogether invalid and the situation depends on the ratio of the formation constants of the complexes. For this reason, the stability constants of the complexes determined by the logarithmic plot method are approximate. Nevertheless the method merits attention in view of its simplicity.

The method of tangents[9] is similar to the logarithmic plot method. In this procedure tangents are also drawn to the $\Delta E_{1/2} = f\{\lg[X]\}$ curve, but with the slope defined by Eqn.(6), i.e. $\partial \Delta E_{1/2}/\partial \lg[X] = 2.3RTp/nF$ with integral values of p. The tangential points correspond to the ligand concentrations at which a single complex MX_p predominates in the solution. The method of tangents is also approximate and practice has shown[9] that it leads to less accurate stability constants than the logarithmic plot method. The explanation is that the condition governing the predominance of two adjacent complexes usually holds better than the condition governing the predominance of a single complex.

(b) The graphical method of De Ford and Hume[24]. If n complexes are formed in solution, then each causes a shift of $E_{1/2}$ in accordance with Eqns.(6). The overall shift of $E_{1/2}$ can therefore be determined by adding together the shifts of $E_{1/2}$ corresponding to all the complexes:

$$(E_{1/2})_s - (E_{1/2})_c = \frac{RT}{nF}\lg\sum_{p=0}^{p=n} K_p[X]^p + \frac{RT}{nF}\ln\frac{\varkappa_c}{\varkappa_M},$$

$$\sum_{p=0}^{p=n} K_p[X]^p = F_0([X]) = \text{anti lg}\left\{\frac{nF}{2.3RT}[(E_{1/2})_s - (E_{1/2})_R] + \lg\frac{(i_d)_M}{(i_d)_c}\right\}, \quad (21)$$

$$F_0([X]) = 1 + K_1[X] + K_2[X]^2 + \ldots + K_n[X]^n. \quad (22)$$

The right-hand side of Eqn.(21) contains quantities which are determined experimentally. If $F_0\{[X]\}$ is plotted against $[X]$ then, according to Eqn.(22), one obtains a curve whose extrapolation to $[X] = 0$ yields unity, i.e. the formation constant of the zeroth complex.

In order to find K_1, we introduce the function $F_1\{[X]\}$:

$$E_1([X]) = \frac{F_0([X]) - 1}{[X]} = K_1 + K_2[X] + \ldots + K_n[X]^{n-1} \quad (23)$$

The plot of this function is also curved and its extrapolation to $[X] = 0$ yields K_1.

The plot of the function

$$F_2([X]) = \frac{F_1([X]) - K_1}{[X]} = K_2 + K_3[X] + \ldots + K_n[X]^{n-2} \quad (24)$$

and its extrapolation to $[X] = 0$ yield K_2, etc. The plot of the penultimate function against $[X]$ consists of an inclined straight line and that for the last function is represented by a straight line parallel to the abscissa axis.

It follows from Eqns.(22)–(24) that the slope of the plot of the function is initially equal to the next stability constant of the complex:

$$\left(\frac{\partial F_0([X])}{\partial [X]}\right)_{[X]\to 0} = K_1;\ \left(\frac{\partial F_1([X])}{\partial [X]}\right)_{[X]\to 0} = K_2, \text{etc.}$$

Graphical analysis of the Leden functions $F\{[X]\}$ by the method of De Ford and Hume makes it possible to determine how many and what complexes are formed in the solution and to determine their formation constants.

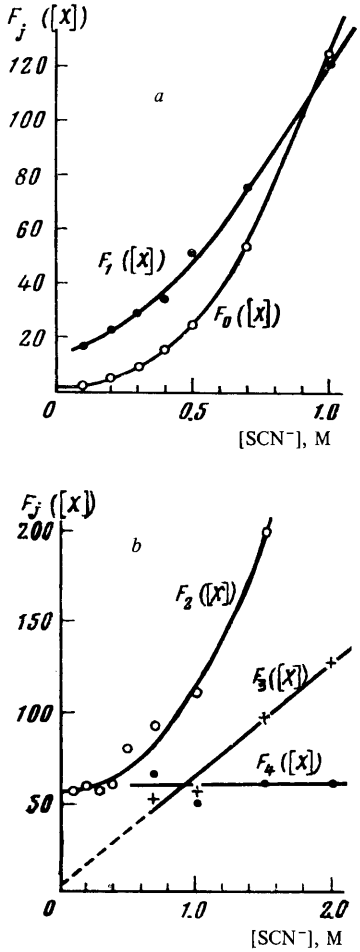


Figure 3. The De Ford and Hume analysis of the functions $F_j\{[X]\}$ for the Cd^{2+}/SCN^- system at an ionic strength $I = 2$ (established by the addition of KNO_3).[25]

Fig.3 illustrates plots of the functions $F\{[X]\}$ for the Cd^{2+}/SCN^- system at a constant ionic strength of 2. Evidently four complexes are formed in this system: $CdSCN^+$, $Cd(SCN)_2$, $Cd(SCN)_3^-$, and $Cd(SCN)_4^{2-}$, with the stability constants $K_1 = 11 \pm 0.5$, $K_2 = 56 \pm 2$, $K_3 = 6 \pm 5$, and $K_4 = 60 \pm 10$. This example demonstrates the fruitfulness of the method of graphical analysis, but at the same time it reveals its weak aspect, namely the increase of the error with increasing complexity of the complex. The existence of the complex $Cd(SCN)_3^-$ is doubtful. It is noteworthy that the reliability of the conclusions arrived at is greater the more stable the complex.

Hume et al.[25] determined $E_{1/2}$ to within 1 mV. A significant improvement of the accuracy of the measurements can be achieved by improving the experimental technique. Piljac et al.[26] prepared the solutions directly in the cell and introduced the ligand-containing solution with the aid of an accurate microburette. The potential was applied to the cell by means of a polarograph and the potential of the mercury dropping electrode relative to the reference electrode was measured by a precision pH-meter. The current was measured at the instant of separation of the drop with the aid of an undamped mirror galvanometer. All the measurements were made by hand and not automatically. The reproducibility of the measurement of the potential in these experiments was to within 0.2 mV.

More accurate stability constants are obtained by calculation and not by the graphical analysis of the Leden function. The problem reduces to the solution of a system of linear equations of type (22), the number of equations equal to the number of measurements of $F_0\{[X]\}$ exceeding the number of unknowns, i.e. the formation constants of the complexes:

$$1 + K_1[X]_1 + K_2[X]_1^2 + \ldots + K_n[X]_1^n - F_0([X])_1 = 0, \quad (25)$$

$$1 + K_1[X]_2 + K_2[X]_2^2 + \ldots + K_n[X]_2^n - F_0([X])_2 = 0, \quad (26)$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

$$1 + K_1[X]_m + K_2[X]_m^2 + \ldots + K_n[X]_m^n - F_0([X])_m = 0 \quad (27)$$

$(m > n)$. The calculations are performed mainly by the method of least squares[27–29], whereby the number of equations is reduced to the number of unknowns. The system of equations obtained is then solved by matrix algebra.

If the experiment has been formulated in such a way that

$$[X]_2 - [X]_1 = [X]_3 - [X]_2 = [X]_4 - [X]_3 = \ldots = [X]_m - [X]_{m-1},$$

i.e. $\Delta[X] = \text{const.}$, then calculations by the method of least squares are less laborious[28,29].

When the method of least squares is used, one must make an assumption about the number of complexes formed in solution. If the assumption is wrong, some of the calculated formation constants of the complexes are negative, which lacks physical significance. Calculations are therefore repeated for another postulated number of complexes and this is continued until all the constants obtained are positive. It is therefore desirable to combine calculations by the method of least squares with a graphical method whereby one determines initially the number of complexes and the approximate values of the constants.

Calculations using iterative or successive approximation methods, particularly the relaxation method, are much less laborious[30]. In the last method Eqns.(25)–(27) are solved by trying different values of the constants K_1–K_n until the left-hand sides of all the equations differ from zero by fairly small amounts. Computers are used successfully in the calculation of the stability constants for stepwise complex formation processes[26,31].

3. Mixed Complexes

If only one mixed complex is formed in solution,

$$M^{n+} + pX + qY \rightleftarrows MX_pY_q,$$

we obtain from the shift of the half-wave potential[32] $E_{1/2}$

$$(E_{1/2})_c - (E_{1/2})_s = \frac{RT}{nF}\ln\frac{\varkappa_M}{\varkappa_c} - \frac{RT}{nF}\ln K_{pq} - p\frac{RT}{nF}\ln[X] - q\frac{RT}{nF}\ln[Y].$$

The coordination numbers p and q can be determined by measuring experimentally the dependence of $\Delta E_{1/2}$ on lg [X] for [Y] = const., and on lg [Y] for [X] = const.:

$$\left(\frac{\partial \Delta E_{1/2}}{\partial \lg [X]}\right)_{[Y]=\text{const}} = -p\frac{2.3RT}{nF},$$

$$\left(\frac{\partial \Delta E_{1/2}}{\partial \lg [Y]}\right)_{[X]=\text{const}} = -q\frac{2.3RT}{nF}.$$

In the general case, involving the stepwise formation of simple and mixed complexes, Leden functions can also be used to analyse the data[33,34]:

$$F_{00}([X][Y]) = \sum_{p=0}^{p=m}\sum_{q=0}^{q=n} K_{pq}[X]^p[Y]^q.$$

The functions can be analysed by the graphical method of De Ford and Hume. For this purpose, one finds the dependence of $E_{1/2}$ on the concentration of one ligand corresponding to the constant concentration of the other and conversely, and it is necessary to consider series of constant concentrations of each ligand in order to investigate the system fully.

4. Metal Complexonates

A characteristic feature of complexones is their polydentate nature, so that more than one ligand only comparatively rarely interacts with a single metal ion. On the other hand, the complexones are polybasic acids which are characterised by the formation of protonated complexes, the number of protons attached to them increasing with increasing acidity of the medium.

In order to determine the stability constants of normal and protonated complexes of complexones, Gorelov[35] suggested a procedure based on the analysis of the dependence of $E_{1/2}$ on pH at constant metal and complexone concentrations.

When 1 : 1 complexes are formed, the following equilibria obtain in solution:

$$M + H_pX \overset{K_p}{\rightleftarrows} MH_pX.$$

Using the expressions for the equilibrium constants, one can obtain:

$$[M] = \frac{\sum_{p=0}^{p=n}[MH_pX]}{[X]\sum_{p=0}^{p=n} K_p[H]^p/k_nk_{n-1}\cdots k_{n-p+1}},$$

where K_p is the formation constant of the complex, MH_pX and

$$k_n = \frac{[H][X]}{[HX]},$$

$$k_{n-1} = \frac{[H][HX]}{[H_2X]} = \frac{[H]^2[X]}{k_n[H_2X]},$$

$$k_{n-2} = \frac{[H][H_2X]}{[H_3X]} = \frac{[H]^3[X]}{k_nk_{n-1}[H_3X]},$$

etc. are the successive dissociation constants of the complexone. The sum $\sum_{p=0}^{p=n} K_p[H]^p/k_nk_{n-1}\cdots k_{n-p+1}$ will be denoted by $F_0\{[H]\}$:

$$F_0([H]) = K_0 + K_1\frac{[H]}{k_n} + K_2\frac{[H]^2}{k_nk_{n-1}} + \ldots + K_n\frac{[H]^n}{k_nk_{n-1}\cdots k_1}.$$

Having substituted the expression for [M] in the Nernst equation and having carried out the usual transformations (the complexonate is reduced with formation of an amalgam), we obtain

$$F_0([H]) = \text{anti lg}\left\{\frac{nF}{2.3RT}\Delta E_{1/2} + \lg\frac{\varkappa_M}{\varkappa_c} - \lg(c_X - c_M) + \lg\alpha\right\}, \quad (28)$$

where c_X and c_M are the analytical concentrations of the complexone and the metal ions, while

$$\alpha = 1 + \frac{[H]}{k_n} + \frac{[H]^2}{k_nk_{n-1}} + \ldots + \frac{[H]^n}{k_n\cdots k_1}. \quad (29)$$

Eqns. (28) and (29) make it possible to determine $F_0\{[H]\}$ at a given hydrogen ion concentration. The formation constants of the complexes are found graphically: $F_0\{[H]\}$ is plotted against [H] and K_0 is found by extrapolating the plot to [H] = 0.

The new function

$$F_1([H]) = \frac{\{F_0([H]) - K_0\}k_n}{[H]} = K_1 + K_2\frac{[H]}{k_{n-1}} + K_3\frac{[H]^2}{k_{n-1}k_{n-2}} + \ldots.$$

is then calculated. The extrapolation of the plot of $F_1\{[H]\}$ to [H] = 0 yields K_1. By calculating the successive functions, it is possible to find the formation constants of all the protonated complexes.

If the species H_pX forms a 1 : 2 complex, i.e.

$$M + 2H_pX \overset{K_p}{\rightleftarrows} M(H_pX)_2,$$

then analogous reasoning[36] shows that one must calculate the functions $F_j\{[H]^2\}$:

$$F_0([H]^2) = K_0 + K_1\frac{[H]^2}{k_n^2} + K_2\frac{[H]^4}{k_n^2k_{n-1}^2} + \ldots + K_n\frac{[H]^{2n}}{k_n^2\cdots k_1^2}.$$

The final expression for $F_0\{[H]^2\}$ is

$$F_0([H]^2) = \text{antilg}\left[\frac{nF}{2.3RT}\Delta E_{1/2} + \lg\frac{\varkappa_M}{\varkappa_c} - 2\lg(c_X - 0.5c_M) + 2\lg\alpha\right].$$

When 2 : 1 complexes are formed,

$$2M + H_pX \overset{K_p}{\rightleftarrows} M_2H_pX$$

one analyses the same function $F_0\{[H]\}$ as in the formation of 1 : 1 complex but the final expression for $F_0\{[H]\}$ assumes a somewhat different form[36]:

$$F_0([H]) = \text{antilg}\left[0.903 + \frac{2nF}{RT}\Delta E_{1/2} + \lg\frac{D_M}{D_c} - 2\lg c_M - \lg(c_X - 2c_M) + \lg\alpha\right].$$

The composition of the complex is again found from the dependence of $E_{1/2}$ on the logarithm of the analytical concentration of the ligand.

Using the method described, Gorelov[35] investigated the formation of thallium complexes of ethylenediaminetetraacetic and ethylenediamine-*N*,*N*'-disuccinic acids. Only normal and monoprotonated complexes are formed in these systems. More complex phenomena are observed[36] in the Cd^{2+}–hydroxyethylidenediphosphonic acid (HEDPA) system. 1 : 1 complexes are formed in this system at concentrations in the range 10^{-3}–10^{-2} M HEDPA and 1 : 2 complexes are formed at higher concentrations. Fig. 4 presents the functions $F_j\{[H]\}$ for the 1 : 1 complex. Evidently Cd^{2+} ions form not only the normal complex but also four protonated complexes with HEDPA (HEDPA is a pentabasic acid). Furthermore, Fig. 4 shows that each specific complex must have its own extrapolation region of the function $F_j\{[H]\}$ closely adjoining the pH range corresponding to the existence of the given ligand. If the metal ion has a high affinity for hydroxide ions, then the region of high pH values becomes inaccessible to measurements. In this case the constants of certain protonated

complexes can nevertheless be determined by analysing the incomplete function $F_j\{[H]\}$.

5. Polynuclear Complexes

The formation of polynuclear complexes, for example M_mX_p, can be investigated polarographically:

$$m\,M + p\,X \overset{K_{mp}}{\rightleftarrows} M_mX_p,$$

$$\Delta E_{1/2} = -\frac{2.3RT}{mnF}\lg\frac{mK_{mp}}{2^{n-1}} - \left(1-\frac{1}{m}\right)\frac{2.3RT}{nF}\lg[M] - \frac{p}{m}\frac{2.3RT}{nF}\lg[X],$$

$$\frac{\partial\Delta E_{1/2}}{\partial\lg[M]} = -\frac{2.3RT}{nF}\left(1-\frac{1}{m}\right)$$

These relations were obtained by Souchay and Faucherre[32], who identified with their aid polymeric copper complexes of tartaric acid in alkaline media. The stepwise formation of polymeric complexes can be also examined in principle.

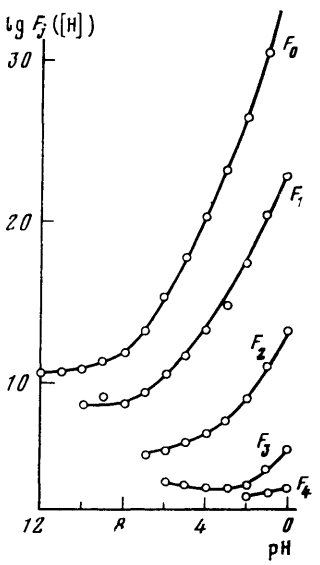


Figure 4. Dependence of the functions $\lg F_j\{[H]\}$ on the pH for the Cd^{2+}–hydroxyethylidenediphosphonic acid system at a complexone concentration of 0.004 M. Cd^{2+} concentration 1×10^{-4} M.[36]

6. Kinetic Waves

Hitherto we have considered cases where the complex species and the metal ions are involved in a rapid equilibrium. However, systems are encountered in which one of the dissociation stages is slow and a kinetic wave arises on the polarogram. The limiting current of the kinetic wave i_c is smaller than the limiting current of the usual diffusion wave i_d. Koryta[37] solved this problem under the condition where free metal ions are reduced reversibly with formation of an amalgam and the ligand is present in excess. The equation for the difference between the half-wave potentials $E_{1/2}$ is as follows:

$$(E_{1/2})_c - (E_{1/2})_s = \frac{RT}{nF}\ln\frac{i_d}{i_c} - \frac{RT}{nF}\ln\sum_{p=0}^{p=n}K_p[X]^p. \qquad (30)$$

In this equation $(E_{1/2})_c$ is the half-wave potential of the kinetic wave. Eqn.(30) is common to diffusion and kinetic waves for the reduction of complexes with formation of an amalgam in stepwise complex formation. It differs from the equation of De Ford and Hume only by the correction term $\ln(i_d/i_c)$, which corrects $E_{1/2}$ for the kinetic wave:

$$(E_{1/2})_d = (E_{1/2})_c - \frac{RT}{nF}\ln\frac{i_d}{i_c}.$$

When $i_c = i_d$, Eqn.(30) is transformed into the equation of De Ford and Hume.

7. Catalytic Waves

Yatsimirskii and Budarin[38–40] showed that the complex formation reaction can be identified and investigated from the decrease of the catalytic activity of metals in polarography. For example, molybdenum in acid solutions catalyses the reduction of hydrogen peroxide, but the introduction of phosphoric acid lowers the limiting current of the catalytic wave.

The catalytic activity of molybdenum is explained by the fact that the product of its interaction with hydrogen peroxide is reduced more readily than free hydrogen peroxide:

$$\begin{aligned} &H_2MoO_4 + H_2O_2 \rightleftarrows H_2MoO_5 + H_2O,\\ &H_2MoO_5 + 2\,H^+ + 2\,e \rightarrow H_2MoO_4 + H_2O. \end{aligned} \qquad (IV)$$

In the presence of phosphoric acid, the complex interacts with hydrogen peroxide:

$$H_2MoO_4 + H_3PO_4 \rightleftarrows MoO_2HPO_4 + 2\,H_2O, \qquad (V)$$

$$\begin{aligned} &MoO_2HPO_4 + H_2O_2 \rightleftarrows H_2O_2MoO_2HPO_4,\\ &H_2O_2MoO_2HPO_4 + 2\,e + 2\,H^+ \rightarrow MoO_2HPO_4 + 2\,H_2O, \end{aligned} \qquad (VI)$$

reaction (VI) being slower than reaction (IV). With increase of phosphoric acid concentration, the limiting current of the catalytic wave therefore diminishes, but not to zero, reaching a limiting value. Hence it follows that the complex $MnO_2.HPO_4$ also exhibits a catalytic activity, albeit smaller than that of free molybdic acid.

In the presence of a large excess of H_2O_2 and in the absence of H_3PO_4, we have

$$(i_c)_1 = A_1 c_{H_2O_2}[Mo].$$

In the presence of a sufficiently large excess of H_3PO_4 (for example 0.113 M at a hydrogen ion concentration of 0.444 M and an H_2MoO_4 concentration of 5.95×10^{-6} M), when the reduction of H_2O_2 is catalysed solely by the complex MoO_2. $.HPO_4$ (designated by convention as MoP), we have

$$(i_c)_2 = A_2 c_{H_2O_2}[MoP].$$

If the amount of phosphoric acid is insufficient to bind the entire molybdenum in a complex, then

$$i_c = c_{H_2O_2}(A_1[Mo] + A_2[MoP]).$$

Furthermore,

$$[MoP] = \alpha_1 c_{Mo},$$

$$[Mo] = (1-\alpha_1)c_{Mo}$$

where [Mo] and [MoP] are the equilibrium concentrations, c_{Mo} is the analytical concentration of H_2MoO_4, and α_1 is the fraction of complex formed:

$$i_c = c_{H_2O_2}c_{Mo}[\alpha_1 A_2 + (1-\alpha_1)A_1].$$

Hence

$$\alpha_1 = [(i_c)_1 - i_c]/[(i_c)_1 - (i_c)_2].$$

Having determined α_1, it is possible to calculate the equilibrium constant for reaction (V):

$$K = \alpha_1/(1-\alpha_1)(c_{H_3PO_4} - \alpha_1 c_{Mo}).$$

At still higher phosphoric acid concentration the catalytic wave again begins to fall and ultimately vanishes completely. This means that a more complex compound is produced:

$$MoO_2HPO_4 + H_3PO_4 \rightleftarrows H_4MoO_2(PO_4)_2,$$

which no longer exhibits a catalytic activity. By repeating the above reasoning, we obtain

$$\alpha_2 = [(i_c)_2 - i_c]/(i_c)_2.$$

In the general case, in the presence of stepwise complex formation, there should be a relation between the catalytic current and the ligand concentration[40]:

$$i_c = \frac{(i_c)_0 + (i_c)_1 K_1[X] + (i_c)_2 K_2[X]^2 + \ldots}{1 + K_1[X] + K_2[X]^2 + \ldots}, \quad (31)$$

where $(i_c)_0$ is the catalytic current and $[X] = 0$, $(i_c)_1$ and $(i_c)_2$, ... are the catalytic activities of the complexes MX_1, MX_2, ... The stability constants of the complexes and their catalytic activities can be determined from the relation between i_c and [X]. For this purpose, Eqn.(31) is transformed into an equation of the type

$$i_c = (i_c)_1 + \varphi_1/K_1 + [(i_c)_2 - i_c]\beta_2[X] + [(i_c)_3 - i_c]\beta_2\beta_3[X]^2 + \ldots$$

$$i_c = (i_c)_2 + \varphi_2/\beta_2 + [(i_c)_3 - i_c]\beta_3[X] + \ldots,$$

where β are successive stability constants:

$$\varphi_1 = [(i_c)_0 - i_c]/[X],$$

$$\varphi_2 = [(i_c)_0 - i_c]/K_1[X]^2 + [(i_c)_1 - i_c]/[X].$$

The quantities $(i_c)_1$ and K_1 can be determined graphically from the relation between i_c and ϕ_1 by extrapolation to $[X] \to 0$ and $(i_c)_2$ and β_2 can be determined from the relation between i_c and ϕ_2. $(i_c)_3$ and β_3 can be calculated analogously, etc. The quantities $(i_c)_1$, $(i_c)_2$, β_1, β_2, ... can also be found by another procedure. For this purpose, Eqn.(31) is transformed by substituting $y = [X]^{-1}$:

$$i_c = \frac{(i_c)_n K_n + (i_c)_{n-1} K_{n-1} y + (i_c)_{n-2} K_{n-2} y^2 + \ldots + (i_c)_0 y^n}{K_n + K_{n-1} y + K_{n-2} y^2 + \ldots + y^n}. \quad (32)$$

By extrapolating the relation between i_c and y to $y \to 0\{[X] \to \infty\}$, we find $(i_c)_n$.

Eqn.(32) can be put in the form

$$i_c = (i_c)_{n-1} + \psi_1\beta_n + [(i_c)_{n-2} - i_c]\frac{y}{\beta_{n-1}} + \ldots,$$

$$i_c = (i_c)_{n-2} + \psi_2\beta_{n-1}[(i_c)_{n-3} - i_c]\frac{y}{\beta_{n-2}} + \ldots,$$

where $\psi_1 = [(i_c)_n - i_c]/y$ and $\psi_2 = [(i_c)_{n-1} - i_c]/y - [i_c - (i_c)_n] \cdot \beta_n/y^2$. $(i_c)_{n-1}$ and β_n are determined graphically from the relation between i_c and ψ_1 and $(i_c)_{n-2}$ and β_{n-1} are found from the relation between i_c and ψ_2. All the quantities $(i_c)_i$ and β_i can be obtained similarly.

8. Determination of the Characteristics of the Complex from the Shift of the Ligand Wave

If the ligand, particularly an organic compound, is reduced more readily than the central metal ion, then inferences about complex formation can be drawn from the shift of the ligand wave. An equation has been derived[41] for the shift of the ligand wave subject to the condition that the ligand is reduced reversibly, that the complexes are dissociated rapidly, that metal ions are present in large excess, and that the ligand reduction product does not form complexes with the metal ions:

$$F_0([M]) = \text{antilg}\left(\frac{nF}{2.3RT}\Delta E_{1/2} - \lg\frac{(i_d)_c}{(i_d)_s}\right),$$

$$F_0([M]) = 1 + K_1[M] + K_{1/2}[M]^{1/2} + K_{1/3}[M]^{1/3} + \ldots.$$

In these equations $(i_d)_s$ and $(i_d)_c$ are the limiting currents of the ligand reduction waves in the absence of a metal ion and in its presence respectively and K_1, $K_{1/2}$, $K_{1/3}$, ... are the equilibrium constants of the complex formation reaction

$$X + pM \overset{K_p}{\rightleftarrows} M_pX.$$

($p = 1$, 1/2, 1/3, ...). The formation constants of the complexes are found by the graphical analysis of the relation between $\Delta E_{1/2}$ and [X] or by computational methods. This case is of limited applicability because only the 1:1 complex is formed as a rule in the presence of an excess of metal ions.

9. Organic Molecular Charge Transfer Complexes and Ionic Associated Species

The formation of organic molecular complexes and ionic associated species has been studied successfully by the polarographic method[42-45]. These phenomena are more distinctive in solvents with a low dielectric constant. Furthermore, the solvent must be aprotic in order that the reduction of the organic compound proceeds reversibly. The formation of molecular complexes was therefore studied in chloroform and methylene chloride.

Aromatic compounds are reduced reversibly in an aprotic medium:

$$A + e \rightleftarrows A^{\cdot-}.$$

The initial molecule A is a much stronger electron acceptor than the radical-anion $A^{\cdot-}$. After the addition of an electron donor, a complex is therefore formed with A and not with $A^{\cdot-}$ and the overall mechanism of the electrode process is as follows:

$$DA \overset{K}{\rightleftarrows} D + A \overset{e}{\rightleftarrows} D + A^{\cdot-}.$$

Complex formation shifts the wave of A in the cathodic direction and the composition and stability constant of the complex can be determined from the dependence of $E_{1/2}$ on the concentration of D either by calculation or graphically. The shift of the wave of the acceptor A can be due in principle not only to complex formation but also to a change in the potential of the liquid compound as well as a change in solvation. However, since experiment has shown that $E_{1/2}$ of the second wave of A does not change following the introduction of D, these effects must be insignificant. Studies have shown[44] that, in methylene chloride in the presence of 0.5 M $(C_4H_9)_4NClO_4$ as the supporting electrolyte, 2,3-dichloro-5,6-dicyanoquinone forms two complexes, 1:1 and 1:2, with hexamethylbenzene; 7,7',8,8'-tetracyanoquinodimethane also forms two complexes with pyrene. Only one complex is formed in each of the systems tetracyanoethylene/hexamethylbenzene, 7,7',8,8'-tetracyanoquinodimethane/hexamethylbenzene, chloranil/hexamethylbenzene, chloranil/pyrene, 1,2,4,5-tetracyanobenzene/hexamethylbenzene, and 1,2,4,5-tetracyanobenzene/pyrene. The stability constants as a rule differ significantly from the spectroscopic values. It has been noted in the literature that the spectroscopic determination of the equilibrium formation constants of charge-transfer

complexes is difficult, since the situation is complicated by the energy levels of the molecules of complex formation. In polarography this complication does not exist, since the acceptor molecule is reduced in a free state. It is therefore postulated that the stability constants of charge-transfer complexes found by the polarographic method are closer to the true values than the constant determined spectroscopically.

In aprotic solvents the radical-anions $A^{\cdot-}$, generated on reduction of the organic compound, interact with the counterions of the indifferent electrolyte, forming ionic associated species. As a result, the reduction wave shifts towards less negative potentials. Experiment shows[44] that the cations with a smaller crystallographic radius and with a larger charge are more effective. In dimethylformamide tetraalkylammonium cations do not interact with the radical-anions of quinones, while the anthraquinone radical-anion interacts with the lithium cation to form a 1:1 associated species having $K = 39$ litre mol^{-1}. Dianions interact with cations more strongly. For example, the anthraquinone dianion forms an associated species with three lithium ions. Very large effects are observed when polyvalent cations are introduced into the solution. Thus the addition of neodymium at a concentration of 0.002 M shifts the first wave of the quinone at a concentration of 0.003 M by 550 mV and the second wave by 950 mV (in acetonitrile). These equilibria have also been studied successfully by the polarographic method[44].

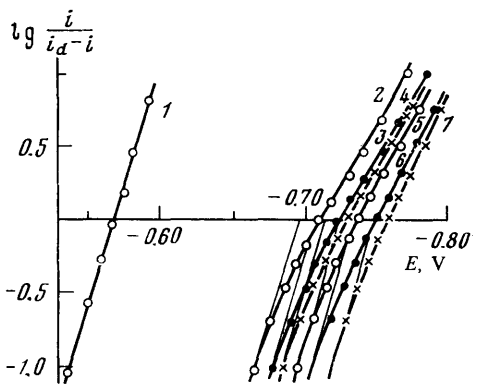


Figure 5. Logarithmic analysis of the waves of the Cd^{2+} ion and of its 2,2'-bipyridyl complex in aqueous solutions; molar concentration of 2,2'-bipyridyl: 1) 0; 2) 0.005; 3) 0.0063; 4) 0.00795; 5) 0.01; 6) 0.0126; 7) 0.02. Cd^{2+} concentration 1×10^{-4} M.[46]

10. The Influence of Adsorption

Organic ligands and complexes are adsorbed on mercury from aqueous solutions. It is therefore to be expected that the reduction waves of the complexes will in certain cases be complicated by the autoinhibition of the electrode process. Insufficient attention has been devoted to this problem in the literature. Autoinhibition is responsible for the additional shift of the wave of the complex in the cathodic direction and, if it is disregarded, the calculation leads to an unduly high stability constant of the complex. Autoinhibition is fully or partly eliminated by the addition of an organic solvent, since organic substances are adsorbed on mercury much less strongly from organic and mixed solvents. However, one should bear in mind that the addition of non-aqueous solvents influences the complex formation equilibrium.

If the autoinhibition phenomenon is not too pronounced, then in certain cases it is nevertheless possible to find the true stability constants. For example, the reduction wave of the trisbipyridylcadmium complex is only partly deformed and its lower part retains its original shape. The semilogarithmic plot of the wave is curved, but its lower part has a slope which approaches asymptotically the theoretical value $2.3RT/2F \cong 0.03$ V (Fig.5). This makes it possible to determine, by drawing tangents to the lower sections of the $\lg [i/(i_d - i)] - E$ plot, the values of $E_{1/2}$ unaltered by autoinhibition and to calculate the true stability constant[46]. A.c. measurements showed that 2,2'-bipyridyl exhibits a higher surface activity than its cadmium complexes. On this basis, it was concluded that the autoinhibition is due to the adsorption of free 2,2'-bipyridyl and the 2,2'-bipyridyl liberated on reduction of the complex[47].

Bond and Hefter observed[48] that the stability constants of the lead iodide and bromide complexes found by the polarographic method are significantly greater than the values obtained by other procedures. The authors suggested that, owing to the adsorption of the anions on mercury, the phenomenon of "additional complex formation" in the electrical double layer, where the ligand concentration is higher than in the bulk of the solution, is observed in this case. However, the experimental justification of this conclusion is open to objection. Thus it follows from a number of studies[49,50,51] that lead complexes and not free halide ions exhibit a higher surface activity in the Pb^{2+}/Br^- and Pb^{2+}/I^- systems. The additional complex formation effect could not therefore occur. It is more likely that the discrepancy between the stability constants observed by Bond and Hefter is in fact due to autoinhibition (the adsorption of the complex). It has been shown[52] that the phenomenon of "additional complex formation" postulated by Bond and Hefter is ruled out by its incompatibility with the thermodynamics of reversible processes.

III. IRREVERSIBLE ELECTRODE PROCESSES

In those cases where the criteria of reversibility enumerated in section II show that the reduction of the complex is irreversible overall, the use of the equations derived for reversible processes becomes impossible: the position of the wave is influenced not only by the equilibrium properties of the complexes but also by the kinetics of electrode processes. Kinetic analysis of irreversible waves yields very interesting information about the nature of the species which are reduced directly at the electrode[53-58]. This leads to the possibility of studying the relation between the reactivity of complexes and their structure.

Several approaches, permitting the study also of the equilibrium properties of complexes which are reduced irreversibly at the dropping mercury electrode, have been developed.

1. Determination of the Characteristics of the Complex from the Shift of the Half-Wave Potential

The principles of the study of the equilibria in the formation of complexes under conditions where the reduction is fully irreversible have been examined in detail[59]. Equations

have been derived for the current at any point in the polarographic wave and for the half-wave potential under the following conditions: (1) only mononuclear complexes are formed in solution; (2) the complex formation is rapid; (3) each complex can be reduced at the electrode independently with formation of an amalgam; (4) there is no specific adsorption in the experimental range of potentials.

The initial equation is that of the fully irreversible wave:

$$\frac{i_{\text{irrev}}}{i_d - i_{\text{irrev}}} = \frac{0.886 k^0 \tau^{1/3}}{D^{1/3}} \exp\left[-\frac{\alpha n F}{RT}(E - E^0)\right]. \qquad (33)$$

where k^0 is the rate constant at the normal potential E^0, τ the drop time, and i_{irrev} the current at the potential E of the irreversible wave.

The rate of the process $\nu = kc$ is equal to the sum of the rates of reduction of each complex:

$$kc = k_0[\text{M}] + k_1[\text{MX}] + k_2[\text{MX}_2] + \ \ldots\ + k_n[\text{MX}_n],$$

whence, taking into account the complex formation equilibria, we have

$$k = \frac{k_0 + k_1 K_1 [\text{X}] + k_2 K_2 [\text{X}]^2 + \ \ldots\ + k_n K_n [\text{X}]^n}{1 + K_1 [\text{X}] + K_2 [\text{X}]^2 + \ \ldots\ + K_n [\text{X}]^n}.$$

Since

$$k_p = k_p^0 \exp\left[-\frac{\alpha_p n F}{RT}(E - E^0)\right],$$

it follows that

$$k = \frac{\sum_{p=0}^{p=n} k_p^0 K_p [\text{X}]^p \exp\left[-\frac{\alpha_p n F}{RT}(E - E^0)\right]}{\sum_{p=0}^{p=n} K_p [\text{X}]^p}.$$

On substituting the expression for k in the initial Eqn.(33), we obtain

$$\frac{i_{\text{irrev}}}{i_d - i_{\text{irrev}}} = 0.886 \left(\frac{\tau}{D_c}\right)^{1/3} \frac{\sum_{p=0}^{p=n} k_p^0 K_p [\text{X}]^p \exp\left[-\frac{\alpha_p n F}{RT}(E - E^0)\right]}{\sum_{p=0}^{p=n} K_p [\text{X}]^p}, \qquad (34)$$

where D_c is the average diffusion coefficient of the complex.

The partial derivatives A, B, and C can be used conveniently for the analysis of experimental data:

$$A = \left(\frac{\partial}{\partial E} \ln \frac{i_{\text{irrev}}}{i_d - i_{\text{irrev}}}\right)_{[\text{X}]=\text{const}} = -\frac{\alpha n F}{RT},$$

where α is the average transfer coefficient. If the number of electrons is known (and this is frequently the case), α can be found from the derivative A. This quantity is useful for the elucidation of the mechanism of the electrode process: if it is independent of E and [X], then, on changing the ligand concentration and the potential along the wave, the mechanism remains unaltered, i.e. the same species is reduced, and the calculations are simplified. On the other hand, if α does depend on E, the implication is that two reactions with different α take place at the electrode.

The derivative B is of the form

$$B = \left(\partial \frac{i_{\text{irrev}}}{i_d - i_{\text{irrev}}} \Big/ \partial \ln [\text{X}]\right)_{E=\text{const}} = p_{\text{el}} - p,$$

where p_{el} is the average coordination number of the complexes being reduced and p is the average coordination number of the complexes formed in solution. If the difference $p - p_{\text{el}}$ for the maximum [X] is equal to the maximum coordination number for the given cation, then free cations are reduced at the electrode. At any rate, if p can be found independently, it is possible to discover from the derivative B which complex is reduced at the electrode.

The derivative C is

$$C = -\left(\frac{\partial E}{\partial \ln [\text{X}]}\right)_{i_{\text{irrev}}=\text{const}} = p - p_{\text{el}}.$$

If the difference $p - p_{\text{el}}$ over a range of values of [X] remains constant, then presumably only one complex predominates in solution and only one complex is reduced.

The overall equation of the wave for the fully irreversible reduction of the complexes is extremely involved. However, in reality frequently simpler cases are encountered where only one of the species involved in the equilibrium is reduced at the electrode.

If it has been established by studying A, B, and C that free cations are reduced at the electrode, then Eqn.(34) simplifies:

$$\frac{i_{\text{irrev}}}{i_d - i_{\text{irrev}}} = 0.886 \left(\frac{\tau}{D_c}\right)^{1/3} k_0^0 \frac{\exp\left[-\frac{\alpha n F}{RT}(E - E^0)\right]}{\sum_{p=0}^{p=n} K_p [\text{X}]^p}.$$

Hence

$$(E_{1/3})_c = E^0 + \frac{RT}{\alpha n F} \ln\left(0.886 \left(\frac{\tau}{D_c}\right)^{1/3} k_0^0\right) - \frac{RT}{\alpha n F} \ln \sum_{p=0}^{p=n} K_p [\text{X}]^p,$$

$$(E_{1/3})_s - (E_{1/3})_c = \Delta E_{1/3} = \frac{RT}{\alpha n F} \ln \sum_{p=0}^{p=n} K_p [\text{X}]^p - \frac{RT}{\alpha n F} \ln \frac{(i_d)_s}{(i_d)_c}.$$

This expression is similar to the equation for $\Delta E_{1/2}$ in the case of the reversible reduction of complexes and can be analysed in exactly the same way, i.e. by the graphical De Ford and Hume analysis, by computational methods, or by the method based on the Yatsimirskii logarithmic plot.

On the other hand, if the analysis of the derivatives A, B, and C shows that one of the complexes MX_i and not free cations, is reduced, then Eqn.(34) becomes

$$\frac{i_{\text{irrev}}}{i_d - i_{\text{irrev}}} = 0.886 \left(\frac{\tau}{D_c}\right)^{1/3} k_i^0 \frac{\exp\left[-\frac{\alpha_i n F}{RT}(E - E^0)\right]}{\sum_{0}^{n} K_j K_i^{-1} [\text{X}]^{(j-i)}}. \qquad (35)$$

The sum in Eqn.(35) is of the following form:

$$\sum_{0}^{n} \frac{K_j}{K_i} [\text{X}]^{(j-i)} = \frac{1}{\beta_1 \beta_2 \ \ldots\ \beta_i [\text{X}]} + \frac{1}{\beta_2 \beta_3 \ \ldots\ \beta_i [\text{X}]^{(i-1)}} + \ \ldots\ +$$

$$+ \frac{1}{\beta_i [\text{X}]} + 1 + \beta_{i+1} [\text{X}] + \beta_{i+1}\beta_{i+2} [\text{X}]^2 + \ \ldots\ + \beta_{i+1}\beta_{i+2} \ \ldots\ \beta_{n-1} [\text{X}]^{(n-i)},$$

where β_i are the successive stability constants of the complexes. The sum can be significantly simplified by making the reasonable assumption that the concentrations of complexes simpler than the complex MX_i being reduced at the electrode are negligible. Then

$$\frac{i_{\text{irrev}}}{i_d - i_{\text{irrev}}} = 0.886 \left(\frac{\tau}{D_c}\right)^{1/3} k_i^0 \frac{\exp\left[-\frac{\alpha n F}{RT}(E - E^0)\right]}{\sum_{i}^{n} [\text{X}]^{(j-i)} \prod_{i+1}^{j} \beta_m},$$

$$(E_{1/3})_c = E_i^0 + \frac{RT}{\alpha n F} \ln\left(0.886 \left(\frac{\tau}{D_c}\right)^{1/3} k_i^0\right) - \frac{RT}{\alpha n F} \ln \sum_{i}^{n} [\text{X}]^{(j-i)} \prod_{i+1}^{n} \beta_m$$

and

$$\Delta E_{1/3} = \frac{RT}{\alpha n F} \ln \sum_{i}^{n} [\text{X}]^{(j-i)} \prod_{i+1}^{j} \beta_m - \frac{RT}{\alpha n F} \ln \frac{(i_d)_i}{(i_d)_c}. \qquad (36)$$

Eqn.(36) can be solved particularly simply if the difference between the maximum coordination number and the coordination number of the complex being reduced $(n - i)$ does not exceed 2 {in this case the dependence of $\Delta E_{1/2}$ on ln [X] is linear}. When a mixture of complexes with $(n - i) > 2$ is present in solution, the logarithmic plot method can be used.

2. The Study of Complex Formation on the Basis of Limiting Diffusion Currents

The limiting diffusion current is the second source of information about complex formation in classical polarography. In fact, complex formation leads to a significant change in the size of the species; one must then bear in mind not only the dimensions of the central ions and the ligands but also those of the solvation shell around the complex species. This alters the diffusion coefficient of the species. The dependence of the limiting current on the ligand concentration is frequently of the expected type and can be used to determine the stability constants of the complexes[60,61]. Thus, when only one complex MX_1 is formed in solution, the average diffusion coefficient D is

$$D = (D_M + D_{MX}K_{MX}[X])/(1 + K_{MX}[X]).$$

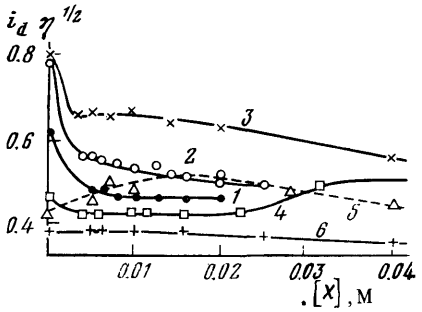


Figure 6. Dependence of the Cd^{2+} limiting current corrected for the viscosity of the medium ($i_d\eta^{1/2}$) on the 2,2'-bipyridyl concentration; ethanol content (vol.%): 1) 0; 2) 20; 3) 40; 4) 60; 5) 80; 6) ~100.[46]

The average diffusion coefficient is determined from the limiting current at the given ligand concentration, the diffusion coefficient of the free metal ions D_M can be found from the limiting current in the absence of the ligand, and the diffusion coefficient of the complex D_{MX} can be found from the limiting current in the presence of a large excess of the ligand, whereupon virtually only one complex is present in solution. The transition from the case involving the formation of only one complex to the more general case of stepwise complex formation does not give rise to fundamental difficulties.

The use of limiting diffusion currents for the calculation of equilibrium constants has an advantage over methods based on the measurement of half-wave potentials, which consists in the fact that it is applicable to all processes regardless of their reversibility. Instances of the successful application of this method in the study of the equilibria in the formation of ionic associated species have been described in a review[12].

However, when calculations based on limiting diffusion currents are used, caution must be exercised because there are frequent instances of anomalous relations between the diffusion coefficients and the ligand concentration. For example, an unusual type of influence of the ligand concentration has been observed in the Cd^{2+}–2,2'-bipyridyl system in a mixed aqueous alcoholic solvent (Fig.6) and the employment of the given method becomes difficult[46].

3. The Indicator Method

An indicator method has been proposed[62] for the determination of the stability constants, which is suitable when the complex is reduced irreversibly or is altogether electrochemically inactive. Its essential feature is as follows. One selects an indicator ion whose complexes with the given ligand are reduced reversibly and at less negative potentials than the complex investigated. The dependence of $E_{1/2}$ for the indicator ion on the ligand concentration is plotted on the basis of experimental or calculated (if the stability constants are known) data, and then the test cation is introduced into the solution and the change in $E_{1/2}$ for the indicator ion, occurring as a result of the formation of a complex by the test ion with the given ligand, is measured. The concentration of the free ligand is found from the plot of $E_{1/2} = f\{[X]\}$ for the indicator ion. Knowing the equilibrium concentration of the ligand [X] and the analytical concentrations of the ligand (c_X) and the test metal (c_M), it is possible to calculate the formation function for the given metal at the half-wave potential:

$$\bar{n} = \left(c_X - [X] - \frac{1}{2} n_i c_i\right) / c_M,$$

where $\bar{n}_i$ is the formation function of the indicator ion and c_i the analytical concentration of the latter. The stability constants can be determined from the formation functions of the test ion by the Bjerrum or Fronaeus methods[20]. The indicator ion method has been frequently tested[61,63,64].

---o0o---

Thus, a survey of the literature shows that a wide variety of problems, associated with the equilibria in the formation of complexes and ionic associated species in solution, can be studied by the method of classical polarography virtually without limitations arising from the complexity of the equilibria and the reversibility of the electrode processes. One must note that many relations derived for classical polarography are applicable (without modifications or with certain non-fundamental changes) also when other varieties of polarography are used (oscillographic and a.c. polarography, chronopotentiometry, etc.)[12].

REFERENCES

1. J.Heyrovský and D.Ilkovič, Coll.Czech.Chem.Comm., 7, 198 (1935).
2. L.G.Sillén and A.E.Martell, "Stability Constants of Metal-Ion Complexes", Spec.Publ.of Chemical Society, London, 1964, No.17.
3. K.B.Yatsimirskii, Uspekhi Khim., 22, 410 (1953).
4. P.Papoff and M.Caliumi, Gazzetta, 84, 1006 (1954).
5. J.Koryta, Chem.Techn.Berlin, 7, 464 (1955).

6. H.M.N.Irving, "Advances in Polarography (Proc.II Intern.Cong., Cambridge, 1959)", Pergamon Press, 1960, Vol.1, p.42.
7. H.L.Schlafer, in "Kompexbildung in Losung. Methode zur Bestimmung der Zusammensetzung und der Stabilitätskonstanten gelöster Komlexverbindungen", Springer Verlag, Berlin–Göttingen–Heidelberg, 1961, p.179.
8. J.Koryta, "Progress in Polarography", Intersci.Publ., New York–London, 1962, Vol.1, p.291.
9. J.Hala, Chem.Listy, 59, 365 (1965).
10. D.R.Crow and J.V.Westwood, Quart.Rev., 19, 57 (1965).
11. D.R.Crow, "Polarography of Metal Complexes", Acad. Press, London, 1969.
12. R.Tamamushi and G.D.Sato, "Progress in Polarogr-graphy", Intersci.Publ., New York–London–Sydney–Toronto, 1972, Vol.3, p.1.
13. M.von Stackelberg and H.von Freyhold, Z.Elektrochem., 46, 120 (1940).
14. J.J.Lingane, Chem.Rev., 29, 1 (1941).
15. J.Heyrovský and J.Kuta, "Principles of Polarography" (Translated into Russian), Izd.Mir, Moscow, 1965.
16. G.Schwarzenbach, R.Gut, and G.Anderegg, Helv. Chim.Acta, 37, 937 (1954).
17. K.B.Yatsimirskii, "Sbornik Statei po Obshchei Khimii" (Collected Reports on General Chemistry), 1953, Vol.1, p.193.
18. K.B.Yatsimirskii, Uspekhi Khim., 22, 410 (1953).
19. K.B.Yatsimirskii, Zhur.Neorg.Khim., 1, 412 (1956).
20. K.B.Yatsimirskii and V.P.Vasil'ev, "Konstanty Nestoikosti Kompleksnykh Soedinenii" (Instability Constants of Complex Compounds), Izd.Akad.Nauk SSSR, Moscow, 1959.
21. Ya.I.Tur'yan and G.F.Serova, Zhur.Neorg.Khim., 2, 336 (1957).
22. L.P.Adamovich and M.S.Novakovskii, Zhur.Obshch. Khim., 25, 1308 (1955).
23. Ya.I.Tur'yan, Zhur.Obshch.Khim., 26, 2084 (1956).
24. D.De Ford and D.N.Hume, J.Amer.Chem.Soc., 73, 5321 (1951).
25. D.N.Hume, D.De Ford, and G.C.B.Cave, J.Amer. Chem.Soc., 73, 5323 (1951).
26. I.Piljac, B.Grabaric, and I.Filipovic, J.Electroanalyt. Chem., 42, 433 (1973).
27. Yu.S.Lyalikov, Izv.Mold.Fil.Akad.Nauk SSSR, No.12 (78) 13 (1960).
28. P.Kivalo and J.Rastas, Suomen.Kem., 30B, 128 (1957).
29. J.Rastas and P.Kivalo, Suomen Kem., 30B, 143 (1957).
30. K.O.Watkins and M.M.Jones, J.Inorg.Nuclear Chem., 16, 187 (1961).
31. K.Momoki, H.Sato, and H.Ogawa, Analyt.Chem., 39, 1072 (1967).
32. P.Souchay and J.Faucherre, Bull.Soc.chim.France, 529 (1947).
33. W.B.Schaap and D.L.McMasters, J.Amer.Chem.Soc., 83, 4699 (1961).
34. H.Matsuda, Rep.Gov.Chem.Ind.Inst., Tokyo, 61, 315 (1966).
35. I.P.Gorelov, Zhur.Anal.Khim., 29, 1057 (1974).
36. B.D.Mul'kina, S.I.Zhdanov, and E.A.Mambetkaziev, Zhur.Obshch.Khim., 48, 29 (1978).
37. J.Koryta, Coll.Czech.Chem.Comm., 24, 2903 (1959).
38. K.B.Yatsimirskii and L.I.Budarin, Coll.Czech.Chem. Comm., 26, 215 (1961).
39. K.B.Yatsimirskii and L.I.Budarin, Zhur.Neorg.Khim., 6, 1850 (1961) [Russ.J.Inorg.Chem., No.8 (1961).
40. K.B.Yatsimirskii and L.I.Budarin, Zhur.Neorg.Khim., 7, 1824 (1962) [Russ.J.Inorg.Chem., No.8 (1962)].
41. E.Casassar and L.Eek, J.Chem.Phys.et Phys.-Chim. Biol., 64, 971 (1967).
42. M.E.Peover, Proc.Chem.Soc., 167 (1963).
43. M.E.Peover, Trans.Faraday Soc., 60, 417 (1964).
44. M.E.Peover and J.D.Davies, "Polarography 1964 (Proc. III Internat.Congr.Southampton)", (Edited by G.J.Hills), McMillan, London–Melbourne, 1966, Vol.2, p.1003.
45. R.D.Holm, W.R.Carper, and J.A.Blander, J.Phys. Chem., 71, 3960 (1967).
46. A.Shaldybaeva, S.I.Zhdanov, E.A.Mambetkaziev, and B.B.Damaskin, Elektrokhimiya, 11, 15 (1975).
47. E.A.Mambetkaziev, A.Shaldybaeva, and S.I.Zhdanov, Elektrokhimiya, 13, 1371 (1977).
48. A.M.Bond and G.Hefter, J.Electroanalyt.Chem., 31, 477 (1971).
49. V.S.Srinivasan and A.K.Sundaram, Austral.J.Chem., 15, 729 (1962).
50. V.S.Srinivasan and A.K.Sundaram, Austral.J.Chem., 15, 734 (1962).
51. F.S.Anson and D.J.Barclay, Analyt.Chem., 40, 1791 (1968).
52. M.Sluyters-Rehbach and J.H.Sluyters, J.Electroanalyt. Chem., 39, 339 (1972).
53. H.Gerischer, Z.phys.Chem., 202, 292 (1953).
54. H.Gerischer, Z.Elektrochem., 57, 604 (1953).
55. A.G.Stromberg and A.I.Kartushinskaya, Zhur.Fiz. Khim., 35, 1058 (1961) [Russ.J.Phys.Chem., No.5 (1961)].
56. A.G.Stromberg and A.I.Kartushinskaya, Zhur.Fiz. Khim., 35, 518 (1961) [Russ.J.Phys.Chem., No.3 (1961)].
57. A.G.Stromberg, Zhur.Fiz.Khim., 38, 2999 (1964) [Russ.J.Phys.Chem., No.12 (1964)].
58. A.G.Stromberg and M.K.Ivantsova, Dokl.Akad.Nauk SSSR, 100, 303 (1964).
59. J.Bernat and M.Baranowska-Zralko, Electrochim.Acta, 17, 1867 (1972).
60. V.Kačena and L.Matoušek, Coll.Czech.Chem.Comm., 18, 294 (1953).
61. Z.Zabransky, Coll.Czech.Chem.Comm., 24, 3075 (1959).
62. A.Ringbom and L.Eriksson, Acta Chem.Scand., 7, 1105 (1953).
63. N.C.Li, T.L.Shu, C.T.Fujii, and J.M.White, J.Amer. Chem.Soc., 77, 859 (1955).
64. P.Kivalo and R.Luoto, Suomen Kem., 30B, 163 (1957).

Kazakh State University,
Alma-Ata

All-Union Institute of Pure Chemical
Reagents and Specially Pure Chemicals

Translated from *Uspekhi Khimii*, **49**, 618-636 (1980) U.D.C. 532.732

The Volumes of Mixing of Liquids and Their Importance for the Modern Theory of Solutions

A.A.Tager and L.V.Adamova

The results of studies on volumes of mixing in liquid-liquid systems and in polymer solutions are surveyed and the causes of the volume change and its influence on the thermodynamic parameters of dissolution are examined.
The bibliography includes 131 references

CONTENTS

I. General ideas concerning the influence on thermodynamic parameters of the volume change on mixing 325
II. Volumes of mixing and the free volume 326
III. The volume change on mixing liquids 326
IV. The volumes of mixing in the dissolution of polymers 330
V. The influence of temperature on the volumes of mixing and consolute temperatures 330
VI. Theories of solutions and volumes of mixing 332

I. GENERAL IDEAS CONCERNING THE INFLUENCE ON THERMODYNAMIC PARAMETERS OF THE VOLUME CHANGE ON MIXING

The first studies on the volumes of mixing of liquids were carried out by Mendeleev[1,2] whose doctoral thesis was devoted to proving the fundamental postulates of his theory of solutions, particularly his ideas concerning the volume change on mixing the components. Subsequently many related data were obtained, which, however, did not receive due attention, since the volumes of mixing are small and it was believed possible to neglect them. All the theories of solutions (Hildebrand's theory of regular solutions, Guggenheim's theory of strictly regular solutions, etc.) were therefore based on the assumption that the volume is constant on dissolution. Theoretical internal energies of mixing (ΔU) were set equal to the enthalpy of mixing (ΔH). For example, the widely familiar Scatchard–Hildebrand equation was obtained on this basis[3]:

$$\Delta U=\Delta H=V(\delta_1-\delta_2)^2\varphi_1\varphi_2, \qquad (1)$$

where V is the volume of the solution, ϕ_1 and ϕ_2 are the volume fractions of the components of the solution, and δ_1 and δ_2 are the solubility parameters of the components equal to the square roots of the densities of their cohesion energies (DCE): $\delta=(\Delta E/V)^{1/2}$.

According to Eqns(1), dissolution can only be an endothermic process ($\Delta H>0$) and, when their values of δ are equal, the components should mix with a zero heat change. In reality neither the first nor the second postulate are valid. One of the causes of this is the volume change on mixing; the magnitude and sign of which have a significant influence on the thermodyanmic parameters. This can be readily shown using the equation of state[4]

$$\left(\frac{\partial U}{\partial V}\right)_T=-p+T\left(\frac{\partial p}{\partial T}\right)_V. \qquad (2)$$

On substituting Eqn.(2) in the expression

$$(\Delta H^m)_p=(\Delta U)_p+p(\Delta V^m)_p, \qquad (3)$$

we obtain

$$(\Delta H^m)_p=(\Delta U^m)_V+T\left(\frac{\partial p}{\partial T}\right)_V\cdot(\Delta V^m)_p. \qquad (4)$$

The derivative $(\partial U/\partial V)_T\equiv p$ is the internal pressure in the liquid or a real gas, which depends on the extent of the intermolecular interaction. The pressure p_i amounts to ~3500 atm for not unduly polar organic liquids, 12000 atm for water, and ~40000 atm for mercury[5]. The derivative $(\partial p/\partial T)_V\equiv\gamma$ is the temperature coefficient of pressure, related to the isothermal compressibility β_T and the coefficient of thermal expansion α_p by the expression

$$\gamma=\alpha_p/\beta_T. \qquad (5)$$

For liquids, γ varies from 10 to 14 atm K^{-1}. Consequently, even if the volume change on dissolution $(\Delta V^m)_p$ is indeed very small, the second term in Eqns.(4) is $(\Delta V^m)_p\times 3000$ (atm cm^3) (at room temperature) and makes a considerable contribution to $(\Delta H^m)_p$. $(\Delta U^m)_V$, which is calculated theoretically or determined experimentally at constant volume, can therefore differ significantly from the value of $(\Delta H^m)_p$ determined at constant pressure. For example, $(\Delta V^m)_p=0.65$ cm^3, $(\Delta H^m)_p=182$ cal, and $(\Delta U^m)_V=131$ cal for the benzene–cyclohexane system containing 0.5 mole of each component[6].

The entropies of mixing measured at constant volume and pressure also differ[4]. They are linked by the relation

$$T(\Delta S^m)_p=T(\Delta S^m)_V+T\left(\frac{\partial p}{\partial T}\right)_V(\Delta V^m)_p. \qquad (6)$$

Negative enthalpies or heats of mixing are frequently due to the negative sign of $(\Delta V^m)_p$, i.e. the decrease of volume on dissolution.

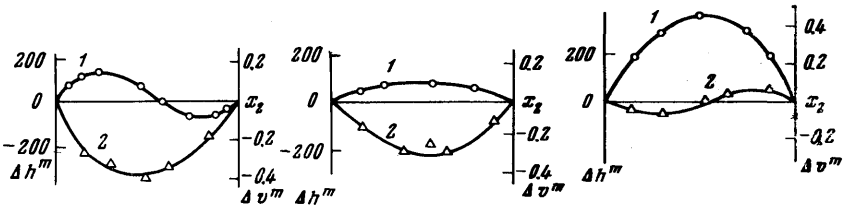


Figure 1. Dependence of the enthalpies Δh^m (curves *1*) and average volumes Δv^m (curves *2*) of mixing on the mole fraction of the second component x_2 for different systems: *a*) acetone–isopropyl alcohol; *b*) isopropyl alcohol–propionitrile; *c*) ethanol–acetonitrile[19].

The volume change observed on mixing liquids is the cause of the lower consolute temperature (LCT) of a special type, discovered by Rowlinson[7,8] for solutions of components with a similar chemical structure but differing in molecular size. Systems such as dodecane–ethane and n-hexadecane–n-hexane split into separate layers on heating to temperatures greatly exceeding the boiling point of the more volatile component. This type of LCT is characteristic of polymer solutions, since in this case the difference between the molecular sizes of the components is particularly marked[8]. The mechanism of layer formation in polymeric systems will be examined below.

Thus the volume change on dissolution or mixing plays an extremely great role. This is understandable, because negligible changes in distances between molecules can be the cause of enormous changes in the interaction energy, which is inversely proportional to the sixth power of the distance. In recent years there has therefore been a sharp growth of interest in measurements of the volume changes on mixing low-molecular-weigth liquids and on dissolution of polymers.

II. VOLUMES OF MIXING AND THE FREE VOLUME

The volume change on mixing substances is a consequence of the change in the free volume, since the intrinsic volume of the molecules hardly changes. The free volume is understood as the volume unoccupied by the intrinsic volume of the molecules of the given substance. We believe that it can be defined most correctly, as suggested by Hildebrand[9] and by Bondi[10], as the difference between the volume of one mole of the substance measured at a given temperature (V_T) and the intrinsic volume of the molecules contained in one mole (V_W):

$$V_E = V_T - V_w. \qquad (7)$$

The volume V_W is calculated as the sum of the volumes of the constituent atoms of the molecule and atomic groups taking into account the overlap of the shells of the atoms involved in the chemical bond. A scheme for such a calculation has been described[11] and the same communication contains tabulated volume increments, i.e. the volumes of different atomic groups. Hildebrand[9] calls the free volume calculated by Eqn.(7) the "empty volume" or the volume of vacancies V_E. Frenkel[12] proposed another method of calculating the free volume—as the difference between the volume of a body at a given temperature V_T and its volume V_0 at 0 K (on the assumption of maximum close packing):

$$V_f = V_T - V_0. \qquad (8)$$

The volume V_f calculated by Eqn.(8), which according to Hildebrand represents the "volume of expansion", differs from the values of V_E calculated by Eqn.(7).

According to modern ideas, the change in free volume on mixing liquids or on dissolution of solids can be due to three causes: (1) the difference in the cohesion energy between the molecules of the components; (2) the difference between the molecular sizes; (3) the differences between the molecular shapes. The latter two factors are referred to as geometrical. Attention to their role was first drawn by Mendeleev, who wrote that processes similar to the mixing of grains or spheres of different dimensions can occur on dissolution: "the smaller grains or spheres are accommodated in the gaps between the large spheres in a certain manner and the decrease in volume can then be readily demonstrated"[2].

The overall volume change observed on dissolution is represented by the sum of two components[13,14]:

$$\Delta V^m_{tot} = \Delta V^m_{inter} + \Delta V^m_{geom}$$

(ΔV^m_{inter} is the volume change due to the first cause).

III. THE VOLUME CHANGE ON MIXING LIQUIDS

The available data on the volumes of mixing for 800 liquid–liquid systems have been arranged systematically[15]. The Table compiled by the authors shows that only 20 systems are formed without a volume change (i.e. $\Delta v^m = 0$)†. These are systems whose components have both similar chemical structures and similar molecular sizes and shapes (the toluene–xylene, o-xylene–p-xylene, etc. systems). For the vast majority of two-component systems, $\Delta v^m \neq 0$. The volume changes can differ by three orders of magnitude (from 0.002 $cm^3\ mol^{-1}$ for the benzene–carbon tetrachloride system to 2.23 $cm^3\ mol^{-1}$ for a solution of triethylamine in methanol) and can have different signs.

It was assumed initially that the volume change on dissolution is caused only by the difference between the cohesion energies of the components. Thus, if the cohesion energy between unlike molecules $2\varepsilon_{12}$ is greater than between like molecules ($\varepsilon_{11} + \varepsilon_{22}$), unlike molecules should be attracted more strongly to one another, which should lead to a decrease of the volume (i.e. $\Delta v^m < 0$). Conversely, if the cohesion energy between like molecules is greater than

† Average thermodynamic parameters are normally employed when solutions are considered: the average molar enthalpy of mixing $\Delta h^m = \Delta H^m/(n_1 + n_2)$ and the average molar volume of mixing $\Delta v^m = \Delta V^m/(n_1 + n_2)$, where n_1 and n_2 are the numbers of moles of the components in the solution.

between unlike molecules, the molecules should be at greater distances in solution than in the pure substances, which should entail an expansion on dissolution ($\Delta v^m > 0$). At the same time, there may be a change in the internal energy of the system:

$$-\Delta u^m \simeq K[-\varepsilon_{11}-\varepsilon_{22}+2\varepsilon_{12}];$$
$$\text{if } |2\varepsilon_{12}| > |\varepsilon_{11}+\varepsilon_{22}|, \text{ then } \Delta u^m < 0;$$
$$\text{if } |2\varepsilon_{12}| < |\varepsilon_{11}+\varepsilon_{22}|, \text{ then } \Delta u^m > 0 .$$

Consequently, the signs of Δu^m and Δv^m should be identical.

Since $\Delta h^m = \Delta u^m + P\Delta v^m$, it was assumed that the signs of the heats and volumes of mixing should be identical, i.e. that contraction corresponds to exothermic mixing and expansion corresponds to endothermic mixing[2,16-18].

It has been shown[19] that this is not the case. There are data (Fig.1) demonstrating that the difference between the cohesion energies of the components is not the only cause of the volume change on dissolution; it is determined also by geometrical factors. The role of the latter was demonstrated in relation to a number of systems. Thus Marsh[20-22] used octamethylcyclotetrasiloxane as a model substance with large spherical molecules and benzene and carbon tetrachloride as substances with small molecules. Endothermic mixing and contraction, which in this case is a result solely of greater close packing, were observed for these systems.

The role of the geometrical factor in a "pure" form is manifested clearly in systems where the molecules have identical chemical structures but different dimensions, for example, in solutions of normal alkanes. The mixing of alkanes at room temperature is accompanied by the absorption of heat, which is greater the greater the difference between the molecular sizes of the mixed components[23,24]. On the basis of this experimental fact, Brønsted[25] formulated the principle of congruence, expressed by the equation

$$\Delta h^m = B(n_1-n_2)^2 x_1 x_2, \qquad (9)$$

where x_1 and x_2 are the mole fractions of the components in the solution, n_1 and n_2 are the numbers of carbon atoms in the molecules of n-alkanes, and B is a constant.

Table 1. The average energies (Δu^m, cal mol^{-1}), volumes (Δv^m, cm^3 mol^{-1}), and enthalpies (Δh^m, cal mol^{-1}) of mixing for mixtures of cyclic hydrocarbons[33].

System	Δu^m	Δv^m	Δh^m
Cycloheptane–cyclooctane	1.7	−0.03	−0.7
Cyclopentane–cyclohexane	3.1	0.042	6.2
Cyclohexane–cycloheptane	4.3	−0.034	1.7
Cyclopentane–cycloheptane	6.9	−0.102	−0.4
Cyclohexane–cyclooctane	12.0	−0.128	1.7
Cyclopentane–cyclooctane	13.2	−0.30	−10.1

If only cohesion energies were concerned, then expansion might be expected on mixing n-alkanes. In reality, the mixing of n-alkanes is accompanied by contraction, which is greater the greater the difference between the molecular sizes of the mixed components[26-30], as illustrated in Fig.2. Consequently, for mixtures of alkanes, $\Delta h^m > 0$ and $\Delta v^m < 0$. The ratio of these quantities is such that the internal energy of mixing, calculated from the equation $\Delta h^m = \Delta u^m + P\Delta v^m$, is always positive, i.e. the internal energy of the systems increases on mixing alkanes[24]. The positive value of Δu^m in such systems is due to the fact that the main type of interaction between the components is dispersion interaction, which is additive with respect to the length of chain molecules. The cohesion energy increses in the homologous series of n-alkanes, while the energy of contact between unlike molecules $2\varepsilon_{12}$ is smaller than for like molecules ($\varepsilon_{11} + \varepsilon_{22}$). The contraction in such systems is caused solely by geometrical factors; however, at room temperature, it is not large enough to alter the sign of the heat of solution, i.e. the Δu^m and Δh^m are positive.

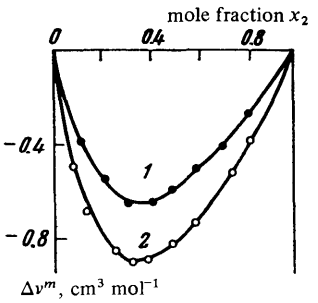


Figure 2. The average volumes of mixing Δv^m in different systems: 1) n-hexane–n-hexadecane; 2) n-pentane–n-hexadecane[26].

Positive internal energies of mixing and negative volumes of mixing are observed also on mixing cyclic hydrocarbons[33,34] (Table 1). Consequently, in this case the contraction is also due to geometrical causes. Thus, when two adjacent homologues are mixed, Δu^m is comparatively small, but increases with increase of the difference between the numbers of carbon atoms in the hydrocarbon molecule; under these conditions, there is as a rule an increase in the extent of contraction. The cyclopentane–cyclohexane system, whose formation involves expansion, constitutes an exception. However, the ratio of the absolute values of Δu^m and Δv^m is such that the signs of the Δh^m for these systems are different and it is very difficult to discover any kind of regularity.

The role of the geometrical factor is manifested also on mixing liquids between the molecules of which a dipole–dipole interaction takes place in addition to the dispersion interaction. This was demonstrated very clearly by Meares[35] in a study of the volumes and heats of mixing of two isomeric diesters: butylene diacetate (BDA) and diethyl succinate, the molecules of which are in essence dimers of ethyl acetate. The methylene group CH_2 and the oxygen atom have the same numbers of electrons in the outer orbital. The dispersion interaction in each contact between the molecules of these two diesters is therefore the same. They exhibit the same dipole–dipole interactions and their molecules have the same dimensions. The diesters therefore mix athermally and without a volume change. The heat of mixing of each with ethyl acetate is also zero, but there is a contraction due to the difference between the sizes of the mixed molecules.

All these findings show that, when systems having similar chemical structures but differing in molecular size are mixed, contraction is observed ($\Delta v^m < 0$), while $\Delta h^m \geqslant 0$. Thus the mixing of acetone with acetylacetone and acetonylacetone is accompaned by the absorption of heat and contraction[36] (Fig.3). In all these cases the contraction is due to purely geometrical factors.

When substances differing in chemical structure are mixed, the signs of the enthalpies and volumes of mixing are as a rule the same. Thus the mixing of alkanes with aliphatic ethers is accompanied by the absorption of heat and expansion, the values of which increase with increasing length of the hydrocarbon molecule or group[37]. The absorption of heat and expansion are also observed when carbon tetrachloride is mixed with chloroform and chlorobenzene and when n-hexane is mixed with acetone[23,38,39]. In all the systems enumerated, one of the components is more polar than the other and the energy expended on the rupture of bonds between the dipoles exceeds the energy gain due to the greater cohesion energy between unlike molecules. As a result, the internal energy of the system increases and the process is at the same time accompanied by expansion ($\Delta h^m > 0$ and $\Delta v^m > 0$).

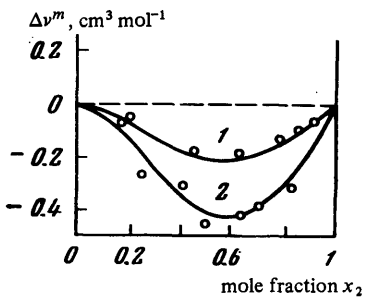


Figure 3. The average volumes of mixing Δv^m in different systems: 1) acetone–acetylacetone; 2) acetone–acetonylacetone[36].

More complex relations are observed for systems where there is a possibility of the formation of solvated complexes via hydrogen bonding or the interaction of π electrons. Systems in which hydrogen bonds can be formed can be divided into four groups in accordance with the classification of Belousov and Morachevskii[23], which is the same as the classification of Pimentel and McClellan[40].

1. Systems in which only one component tends to form hydrogen bonds (mixtures of alcohols, acids, and amines with straight-chain hydrocarbons and CCl_4). Endothermic heat changes are characteristic of such systems, because the decisive process in the formation of the solution is the rupture of hydrogen bonds between the molecules of the polar component. However, the volumes of mixing can have different signs. Thus the dissolution of straight-chain alcohols in straight-chain hydrocarbons is accompanied by expansion caused by the smaller cohesion energy between unlike molecules compared with like molecules. This is seen particularly clearly when an alcohol and a hydrocarbon having molecules of the same size are mixed. In this case the role of the geometrical factor is reduced to a minimum and the effect is determined solely by the difference between the cohesion energies, so that $\Delta h^m > 0$ and $\Delta v^m > 0$.[41,42]

If unlike molecules differ not only in chemical structure but also in shape, the geometrical factor again becomes decisive: contraction accompanies the mixing of alcohols and amines with carbon tetrachloride despite the fact that $\Delta h^m > 0$.[43–46]

2. Systems in which one of the components contains only proton-donating and the other only proton-accepting groups, i.e. hydrogen bonds can arise only between unlike molecules. These are solutions of ketones, aldehydes, and tertiary amines in chloroform and similar compounds. They are always formed exothermically ($\Delta h^m < 0$) and as a rule with contraction[15,23,47]. However, there are also exceptions. Thus the exothermic mixing of chloroform with methyl acetate is accompanied by expansion. In this case the geometrical factor again plays a dominant role: the chloroform molecule apparently cannot form a sufficiently close-packed structure with methyl acetate molecules ($\Delta V^m_{geom} > 0$, $\Delta V^m_{inter} < 0$, $\Delta V^m_{tot} > 0$).

3. Systems where one component contains simultaneously proton-donating and proton-accepting groups (acids, alcohols, water, and secondary amines) while the other contains only groups of one of these types (acetone, chloroform, etc.). In such systems the dissociation of the hydrogen bonds between like molecules can be partly or completely compensated by the formation of new hydrogen bonds between molecules of different kinds. The signs of the heat changes can therefore be different and can vary with the composition of the solution. The volume changes are also complex. For example, the mixing of straight-chain alcohols with acetone is accompanied by the absorption of heat due to the disruption of the alcohol structure, but this is accompanied by contraction and not expansion. Consequently $|\Delta V^m_{geom}| > |\Delta V^m_{inter}|$. When alcohols are mixed with chloroform, Δh^m changes sign as the solution composition is varied and over a large range of compositions exothermic mixing accompanied by expansion is observed[48].

4. Systems in which both components contain both proton-donating and proton-accepting groups. These are mixtures of alcohols with one another and mixtures of alcohols with acids and amines. When such substances are mixed, the size of the alkyl group plays the main role. The larger the group, the greater the dispersion interaction energy and properties characteristic of alkanes are manifested. Alcohols therefore mix with one another with absorption of heat, like n-alkanes. However, in contrast to mixtures of n-alkanes, expansion takes place in this instance, i.e. the interaction effect predominates over the geometrical factor ($\Delta V^m_{inter} > 0$ and $|\Delta V^m_{inter}| > |\Delta V^m_{geom}|$). The expansion is greater the greater the difference between the molecular sizes of the alcohols[49].

Aqueous solutions are of special interest. Water molecules are known to be capable of forming a three-dimensional network of hydrogen bonds, as a result of which water has a fairly distinct tetrahedral structure[50] with large cavities which can be penetrated by the molecules of other components. The dissolution of most substances in water is therefore accompanied by contraction[15]. This applies to aqueous solutions of alcohols, acetone, and even hydrocarbons. The mixing of water with methanol and ethanol is accompanied by the evolution of much heat and a marked contraction[51,52]. Evidently, in this case both $\Delta V^m_{inter} < 0$ and $\Delta V^m_{geom} < 0$. With increase in the size of the alkyl group, the exothermic effect and the degree of contraction diminish: 1-butanol is partially miscible with water and the mixing process is accompanied by the absorption of heat but there is again contraction, as in the mixing of water with alcohols having longer molecules[15]. The dominant role of the geometrical factor is manifested once more.

In all the previous examples the evolution of heat (decrease of enthalpy) was caused either by the greater interaction energy between unlike molecules or by the greater degree of contraction. A different situation arises when n-alkanes interact with water. They dissolve in water in very small

amounts and the process is accompanied by the evolution of heat and contraction, which is caused by the formation of very small crystalline clusters of water around hydrocarbon molecules[53,54] (so called hydrophobic bonds) and not by a strong interaction between unlike molecules.

In conclusion we shall consider solutions whose components are aromatic substances capable of strong donor–acceptor interactions involving the π electrons of the benzene ring. Aromatic compounds are self associated liquids and the energy expended on the disruption of these associated species on dissolution in straight-chain hydrocarbons is not compensated. The mixing of aromatic hydrocarbons with aliphatic and alicyclic hydrocarbons and with one another is usually accompanied by expansion and the absorption of heat[55–58]. This is observed even in a system such as benzene–toluene[58], which is frequently classified as ideal. However, $\Delta v^m = 0.35$ cm^3 mole^{-1} and $\Delta h^m = 15$ cal mol^{-1} for this system. A typical plot of the concentration dependence of Δh^m and Δv^m for mixutres of aromatic hydrocarbons is illustrated in Fig.4. However, the mixing with benzene of aromatic hydrocarbons which are elongated is accompanied by contraction. For example, there is a zero heat change in the mixing of benzene and bibenzyl and the process involves contraction[15,23]; the geometrical factor again plays the main role.

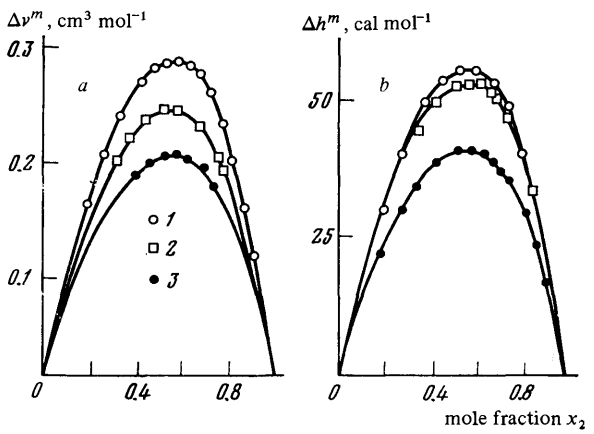


Figure 4. The average volumes Δv^m (*a*) and enthalpies Δh^m (*b*) of mixing for benzene–isomeric xylenes systems[55]: 1) *m*-xylene; 2) *o*-xylene; 3) *p*-xylene.

When benzene dissolves in carbon tetrachloride, the enthalpy and volume of mixing are positive and increase with temperature: $\partial \Delta h^m/\partial T > 0$ and $\partial \Delta v^m/\partial T > 0$ (Fig.5), which is attributed[59] to the formation of a compound at 239 K due to the interaction of the π electrons of the benzene ring and the vacant *d* levels of the chlorine atoms in the CCl_4 molecule, this compound dissociating on increase of temperature.

When aromatic hydrocarbons are mixed with substances whose molecules contain polar groups, complexes may be formed due to the interaction of the π electrons of the aromatic rings with the proton-donating groups. For this reason, these complexes are also not very stable at normal temperatures and the interaction between unlike molecules is weaker than between like molecules. The mixing of benzene with ethyl acetate is therefore accompanied by the absorption of heat and expansion, although these effects are much smaller than for solutions of ethyl acetate in n-alkanes[37]. The positive enthalpies of mixing are reduced still more in the benzene–ethyl benzoate system owing to the interaction between the aromatic rings of the components, the mixing process being accompanied by contraction.

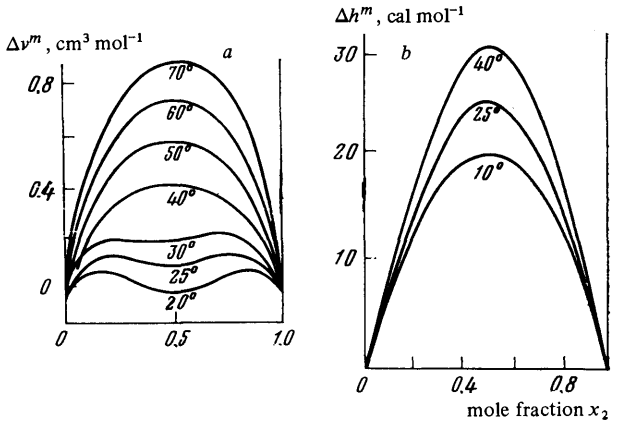


Figure 5. The ratios of the volumes of the solutions V^m to the sums of the volumes of the components V^0 (*a*)[59] and the average enthalpies of mixing Δh^m (*b*)[60] for the benzene–carbon tetrachloride system at different temperatures.

The presence of methyl substituents in the ring, which enhances the electron-donating capacity of the aromatic compound and gives rise to a dipole moment, is responsible for the possibility of additional interactions in solution. The mixing of ethyl benzoate with toluene is therefore less endothermic and involves a greater degree of contraction than the mixing with benzene[37].

The volumes and heats of mixing of aromatic hydrocarbons with aromatic amines have been measured in a series of studies[61–66]. For the majority of the compounds investigated, the signs of the excess volumes and heats are positive. According to the authors, this means that the energy expended on the dissociation of the hydrogen bonds N–H...N in the amines and the π–π bonds in the aromatic hydrocarbons themselves exceeds the energy of formation of new contacts of the N–π type.

If the bond dissociation energy in the pure components is compensated by the energy of formation of π-bonds between different aromatic compounds, then athermal mixing is observed. An example is provided by the benzene–pyridine system, which, however, is formed with contraction.

The molecules of aromatic compounds, which have electron-donating (proton-accepting) properties, are capable of forming hydrogen bonds with alcohols, but these are much weaker than the hydrogen bonds between the alcohol molecules. The mixing of benzene with alcohol therefore involves the absorption of heat and expansion[23,67].

All the facts enumerated above show that the volume changes in the mixing of the vast majority of liquids are non-additive and that geometrical factors play a major role in this process.

IV. THE VOLUMES OF MIXING IN THE DISSOLUTION OF POLYMERS

The first studies on the volumes of mixing of polymeric solutions, published in 1958,[68] showed that the dissolution of polyisobutylene (PIB) in n-heptane and of polystyrene (PS) in ethylbenzene is accompanied by contraction. Subsequently the volumes of mixing were measured also for other polymeric solutions[69-71]. Table 2 gives the signs of the volumes and enthalpies of mixing for certain polymeric solutions. In the first place there is a striking failure of solutions of high-molecular-weight hydrocarbons in lower alkanes to obey the Brønsted congruence rule [Eqn.(9)], according to which a very large endothermic effect should be observed for $n_1 \gg n_2$.[25] In reality the dissolution of polymers is frequently accompanied by the evolution of heat, which was first demonstrated by Delmas et al.[72]; at the same time, $\Delta u^m > 0$.[69] This shows undoubtedly that the negative values of Δh^m are caused by the negative values of Δv^m, which arise in this instance solely because of the difference between the molecular sizes of the mixed component.

Table 2. The consolute* temperature and the average enthalpies (Δh^m) and volumes (Δv^m) of mixing for polymer–solvent systems.

Polymer	Solvent	UCT, °C	LCT, °C	Δh^m	Δv^m
Polyisobutylene (PIB)	Isooctane	—	162[92]	<0[72]	<0[71]
PIB	Benzene	23[92]	160[92]	>0[104]	>0[71]
Polystyrene (PS)	Ethylbenzene	—	295[96]	<0[105]	<0[71]
PS	Cyclohexane	32[95]	206.5[95]	<0[104,106]	<0[71]
Poly(vinyl acetate) (PVA)	Ethyl acetate	—	204[96]	<0[86]	<0[71]
PVA	Methanol	−3[96]	209[103]	>0[106]	<0[71]
Polyoxypropylenediol (POPD)	Hexane	44[102]		>0[82]	=0[82]
POPD	Water	—	45[82]	<0[82]	<0[82]

* UCT and LCT are respectively the upper and lower consolute temperatures.

The free volume of the polymer is always smaller than that of its low-molecular-weight analogue, since intermolecular bonds 3–4 Å long are replaced by chemical bonds on polymerisation. When a polymer is mixed with a low-molecular-weight liquid and a solution is formed, the polymer expands (the free volume of the solvent is supplied to it), while the solvent contracts. However, these effects are not balanced. If the second effect predominates, the dissolution involves contraction, while if the first effect predominates expansion takes place.

For identical structures of the polymer and solvent molecules, when the cohesion energies are identical for like and unlike molecules, the geometrical factor plays the main role and the process involves contraction[69-71,73,74], which is the cause of the exothermicity. If the units of the polymer molecules differ in their chemical structure from those of the solvent molecules, the difference between the cohesion energies begins to play a role. The weaker interaction between unlike molecules than between like molecules leads to positive changes in the internal energy, volume, and enthalpy. The same polymer therefore dissolves with contraction in some solvents and with expansion in others. This can be seen from the data presented in Fig.6, which were obtained by Bianchi and Guniberty[69].

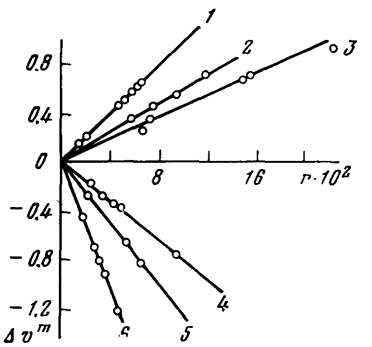


Figure 6. Variation of the volumes of polyisobutylene solutions[69]; solvent: 1) benzene; 2) toluene; 3) chlorobenzene; 4) cyclohexane; 5) methyl-cyclohexane; 6) n-heptane.

Natural rubber dissolves in benzene with expansion like low-molecular-weight hydrocarbons. Contraction is usually observed on dissolution of loosely packed polymers, for example PS[71,75-77], and also on dissolution of polyesters in water and carbon tetrachloride[68-83]. For example, polyoxyethylene and polyoxypropylene-diols dissolve in water with contraction[82], which may be due to the incorporation of their molecules into the water structure. The contraction observed when they dissolve in carbon tetrachloride is evidently associated with the formation of a more close-packed molecular arrangement in consequence of the difference between their dimensions[80,83].

Thus, like low-molecular-weight substances, polymers dissolve either with contraction or expansion.

V. THE INFLUENCE OF TEMPERATURE ON THE VOLUMES OF MIXING AND CONSOLUTE TEMPERATURES

The volume of mixing depends on temperature and Δv^m can become both more negative and more positive as the temperature increases. Thus the negative values of Δv^m for solutions of liquid alkanes increase with increasing temperature. This has been clearly shown by Davenport et al.[84] and is illustrated in Fig.7. A similar behaviour is observed in the n-hexane–n-hexadecane system. In these systems the main type of interaction is the dispersion interaction which is independent of temperature[85]. Consequently, Δu^m should not vary with temperature and an increase of the negative values of Δv^m alters the enthalpy of mixing. Thus at room temperature n-hexane mixes with n-hexadecane

with absorption of heat, the extent of which diminishes as the temperature rises[86,87]; Δh^m changes sign at 64 °C and at higher temperatures the dissolution becomes exothermic.

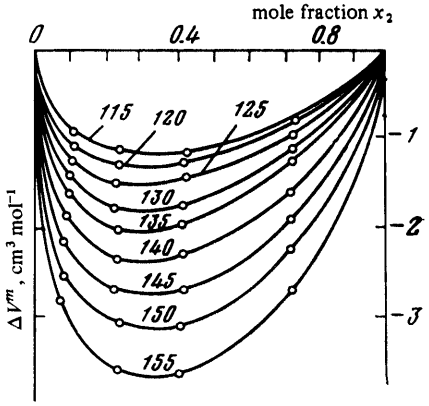


Figure 7. The average volumes of mixing of the methane–isopentane system (the numerals opposite the curves indicate the temperature in K)[84].

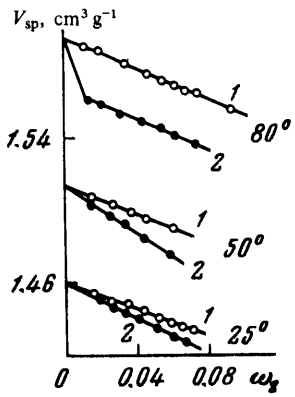


Figure 8. Dependence of the specific volumes of the polyisobutylene–isooctane system on the weight fraction of the polymer in solutions ω_2: 1) additive specific volumes of the solutions V^{sp}_{ad}; 2) experimental specific volumes of the solutions V^{sp}_{exp}.

The increase of the contraction at higher temperatures is caused by the difference between the coefficients of thermal volume expansion for the components, which depends on the difference between their free volumes. The free volume of the component having the higher molecular weight is smaller than that of the low-molecular-weight component, so that the thermal coefficient of the second component is greater than that of the first. However, in solution the low-molecular-weight component cannot expand on heating, as in the free state; with increase of temperature, it is therefore in a state close to that of a condensed gas, which leads to the association of its molecule and ultimately to the separation of the single-phase solution into two phases, i.e. to the appearance of a lower consolute temperature, which is in the temperature range above the boiling point of the more volatile component. The existence of the LCT of this type has been observed for solutions of hydrocarbons (n-hexane–n-hexadecane); this type of LCT is characteristic of solutions of all polymers, since the coefficient of volume expansion of the latter is smaller by an order of magnitude than that of low-molecular-weight liquids. For many polymeric solutions, the degree of contraction increases with increasing temperature (Fig. 8) and the thermodynamic criteria of the LCT, in particular $\Delta h^m < 0$, are valid.

LCT of this type in the range 160–300 °C have been observed for many polymer–solvent systems[90–100].

For solutions of low-molecular-weight substances containing polar components, the degree of contraction diminishes with increase of temperature; this behaviour has been observed, in particular, for mixtures of alcohols with phenols, aniline, and formaldehyde[44]. This is usually attributed to the dissociation of the hydrogen bond between unlike molecules.

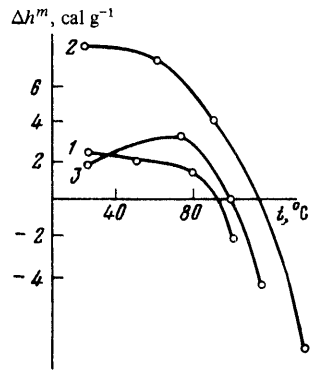


Figure 9. Temperature variation of the average enthalpies of mixing Δh^m in different systems: 1) polyisobutylene–benzene; 2) poly(vinyl acetate)–methanol; 3) polystyrene–cyclohexane (the weight fraction of the polymer in solution is $\omega_2 = 0.8$).

Prigogine and Defay[101] analysed the relation between the sign of the volume of mixing and the type of consolute temperature. They concluded that four cases can be observed for solutions of low-molecular-weight compounds:

1. UCT#: $\Delta h^m > 0$; $\Delta S^m > 0$; *a*) $\Delta v^m > 0$; *b*) $\Delta v^m < 0$.
2. LCT: $\Delta h^m < 0$; $\Delta S^m < 0$; *a*) $\Delta v^m > 0$; *b*) $\Delta v^m < 0$.

Systems of types 1*a* and 2*b* are encountered most frequently and there are also a certain number of systems of types 1*b*; examples of systems of types 2*a* are not known. The data presented in Table 2 show that, among polymer–solvent systems, exothermic systems with LCT involving contraction and systems with UCT, formed with absorption of heat and expansion, are typical; there are also systems with UCT, for which $\Delta h^m > 0$ and $\Delta v^m < 0$.

UCT = upper consolute temperature (Editor of Translation).

If the system has both a UCT and an LCT, then Δh^m must change sign as the temperature is varied (Fig.9).

VI. THEORIES OF SOLUTIONS AND VOLUMES OF MIXING

Despite the enormous amount of experimental data indicating the absence of additivity of the volume of the solution, most of the theories of solutions are based on the assumption that the volume remains unchanged on mixing. This is one of the causes of the discrepancies between theoretical results and experiment. The volume change exerts an influence in those cases where the remaining thermodynamic parameters of the dissolution process are measured at constant pressure (the commonest case). This question is discussed in the third edition of the book by Hildebrand et al.[109]. It is well known that the Scatchard–Hildebrand equation is valid only for the simplest systems of the type CCl_4–$SiCl_4$.[110] The equation does not hold even for mixtures of hydrocarbons, let alone more complex systems. It is therefore evidently necessary to take into account the volume change.

This was first done by Prigogine[111–113], who applied the principle of corresponding states to liquids with chain molecules. Prigogine's theory in its initial form was very complex and was not used for a long time, until Hijmans[114] and Patterson and coworkers[115] expressed it in a simpler form, which is described in a number of articles and books[85,116]. In Prigogine's theory a chain molecule is regarded as a sequence of r rigid quasi-spherical segments, whose behaviour differs from that of the free segments owing to the presence of chemical bonds between them. This leads to significant characteristic features of such systems, namely:

1. The surface of each segment is only partly free for intermolecular interactions, the remainder being blocked by neighbouring segments of the same molecule linked by valence forces to the given segment. The number of outer contacts between the molecules is therefore smaller than for free spherical segments.

2. The presence of chemical bonds between the segments limits their mobility, so that the number of degrees of freedom of each segment linked by valence forces (c) is smaller than the number of degrees of freedom of the free segment.

The theory deals only with external or configurational properties of liquids, i.e. properties which depend on the external degrees of freedom (translational and rotational movement) as well as hindered internal rotation in the molecule, which the authors[115] represent as a superposition of torsional vibrations on the transitions between different states of the rotational isomers. The idea of the outer contacts of the segments is expressed by the Lennard-Jones potential

$$\varphi(R)=4\varepsilon^*[(\sigma^*/R)^{12}-(\sigma^*/R)^6], \qquad (10)$$

where ε^* is the energy of the contact between the segments at 0 °C, σ^* the distance over which this contact is achieved (the diameter of the sphere of action), and R the distance between the molecules.

The normalising parameters are the so-called molecular units: for the internal energy–the quantity $u_0=Nq\varepsilon^*z$, which represents the energy of the contacts of all N molecules (z is the coordination number); for the volume—the quantity $v_0=Nr\sigma^{*3}$; for the entropy—the quantity $s_0=3NcR$ (R is the Boltzmann constant), etc. The above quantities can be expressed as follows:

Reduced free energy	$\tilde{U}=U/Nqz\varepsilon^*$;
Reduced volume	$\tilde{V}=V/Nr\sigma^{*3}$;
Reduced entropy	$\tilde{S}=S/3NcR$;
Reduced temperature	$\tilde{T}=T/T_0=3cRT/qz\varepsilon^*$.

The reduced temperature is defined as the ratio of the kinetic energy of the substance to its cohesion energy $z\varepsilon^*$. It depends on the parameter c/q, which Prigogine calls the structure factor, since this ratio is linked directly to the free volume, which is the most important characteristic of the structure of matter.

On passing to solutions, it is assumed that all the normalising parameters are additive. Thus

$$\langle v_0\rangle=x_1v_{01}+x_2v_{02} \qquad (11)$$

$$\langle u_0\rangle=x_1u_{01}+x_2u_{02} \qquad (12)$$

where x_1 and x_2 are the mole fractions of the components, v_{01}, v_{02}, u_{01}, and u_{02} are the corresponding reduced parameters, and $\langle v_0\rangle$ and $\langle u_0\rangle$ are the reduced parameters for the solution. With these assumptions, the reduced temperature of the solution $\langle\tilde{T}\rangle$ can be expressed by the equation

$$\langle\tilde{T}\rangle=\varphi_1\tilde{T}_1+\varphi_2\tilde{T}_2, \qquad (13)$$

where $\tilde{T}_1$ and $\tilde{T}_2$ are the reduced temperatures of the components and ϕ_1 and ϕ_2 are their volume fractions.

The volume of mixing is calculated from the equation

$$\Delta v^m=\langle v_0\rangle\{\tilde{V}-[\varphi_1\tilde{V}_1+\varphi_2\tilde{V}_2]\}, \qquad (14)$$

where $\tilde{V}$, $\tilde{V}_1$, and $\tilde{V}_2$ are the reduced volumes of the solution and the components respectively. Calculations by Eqn.(14) have shown that the mixing of substances consisting of molecules having similar chemical structures but differing in the dimensions of their chains should be accompanied by contraction.

For the homologous series of alkanes (from methane to polyethylene), polystyrene (from the dimer to infinite molecular weight), poly(ethylene oxides), polydimethylsiloxanes, and fluorinated alkanes, it has been shown[117–120] that the experimental data for the temperature variation of the volumes of mixing fit on a single curve. Consequently the principle of corresponding states can be applied also to polymeric liquids and even to polymeric glasses. It follows from the calculation carried out for solutions of certain polymers that they are formed with contraction[116].

Thus Prigogine's theory demonstrated the possibility, in principle, of calculating the volume of mixing as well as other thermodynamic functions. However, these calculations are difficult, owing to the difficulty of a quantitative choice of the parameters q, c, ε^*, and σ^*.

The theory of solutions developed by Flory and coworkers[121–124], which is based on all the postulates of Prigogine's theory but in which the reduced parameters have a clear physical significance and can be obtained from Tables, constituted a considerable step forward. The main reduced parameter in the so-called new Flory theory or the Flory–Prigogine theory is the intrinsic volume of the segment v^*, which is the sum of the volumes of all its constituent atoms, or the intrinsic volume of the molecules $V^*=rv^*$ (r is the number of segments in the molecule); it differs from the actual volume of the molecule by the free volume.

According to Hildebrand[9], the volume of one mole of a substance can be represented by the sum of the intrinsic volume of its molcules V_W and the free volume or the volume of the vacancies V_E (see above). If the overall volume occupied by N chain molecules is divided by the number of segments in this volume (Nr), then the local volume corresponding to a segment is obtained:

$$v=V/Nr. \qquad (15)$$

The reduced volume is

$$\tilde{v}=v/v^*=V/V^*=M/dV^*, \quad (16)$$

where V is the volume of one mole of the substance, M its molecular weight, and d the density.

Using the Tonks distribution function[125] for a two-dimensional system of N rigid species and having applied it to a one-dimensional system made up of a single chain of rigid segments, the authors[114,115] obtained the equation of state for a liquid with non-spherical chain molecules:

$$\frac{\tilde{p}\tilde{V}}{\tilde{T}}=\frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3}-1}-\frac{1}{\tilde{v}\tilde{T}}; \quad (17)$$

at $p=0$ (this is close to the atmospheric pressure $p=1$) Eqn.(17) assumes a simpler form:

$$\tilde{T}=\frac{\tilde{v}^{1/3}-1}{\tilde{v}^{4/3}}. \quad (18)$$

Differentiation of Eqn.(18) with respect to temperature leads to an expression involving the derivative $\partial V/\partial T$, which is related to the volume by the coefficient of thermal expansion α; as a result, we obtain the equation

$$\tilde{v}^{1/3}-1=\frac{\alpha T}{3(1+\alpha T)}. \quad (19)$$

When α for the substance and the experimental temperature are known, Eqn.(19) makes it possible to calculate the reduced volume $\tilde{v}$. Next, the intrinsic volume of the segment is calculated by Eqn.(16) and the reduced temperature is calculated by Eqn.(18).

The talks formulated by the authors[114,115] reduces to the calculation of the thermodynamic properties of solutions from those of the components. Two parameters are then introduced to express the concentration of the solution: the fraction of the segments ϕ_i and the fraction of sites θ_i. The parameters ϕ_2 and θ_2 of the second component are calculated by the equations

$$\varphi_2=m_2v^*_{sp2}/(m_1v^*_{sp1}+m_2v^*_{sp2}), \quad (20)$$

$$\theta_2=1-\theta_1=(S_2/S_1)\varphi_2/[\varphi_1+(S_2/S_1)\varphi_2], \quad (21)$$

where m_2 and m_1 are the masses of components, $v^*{}_{sp}{}^1$ and $v^*{}_{sp}{}^2$ are the reduction parameters for the specific volume, and S_2/S_1 is the ratio of the sufrace areas of the molecules being mixed, which is calculated from model representations. For example, an alkane molecule is modelled by a cylinder with an average radius 2.49 Å and a length $l^*=1.19n+1.32$, where n is the number of carbon atoms. These dimensions are consistent with the crystallographic radii and the intrinsic volumes V^* of n-alkane molecules.

The reduced volume of the solution is calculated by the equation

$$\frac{\tilde{v}^{1/3}-1}{\tilde{v}^{4/3}}=\tilde{T}=(\varphi_1p^*_1T^*_1+\varphi_2p^*_2T^*_2)/(\varphi_1p^*_1+\varphi_2p^*_2-\varphi_1\theta_2X_{12}), \quad (22)$$

where X_{12} is the energy parameter of the interaction of the components and the additive volume of the solution is found from the equation

$$\tilde{v}_0=\varphi_1\tilde{v}_1+\varphi_2\tilde{v}_2. \quad (23)$$

The reduced volume of mixing is calculated as the difference between the reduced volume of the solution $\tilde{v}$ and the reduced additive value:

$$\Delta\tilde{v}^m=\tilde{v}-\tilde{v}_0. \quad (24)$$

Flory and coworkers[121–123] proposed equations, which make it possible to calculate the partial enthalpies and entropies of mixing ($\overline{\Delta H_1}$ and $\overline{\Delta S_1}$) and the difference between the chemical potentials of the components $\Delta\mu_1$, while Abe and Flory[124] showed that all these theoretical equations can be applied to mixtures of not only chain molecules but also spherical molecules (CCl_4, benzene, cyclohexane, neopentane, $TiCl_4$, $SnCl_4$, etc.).

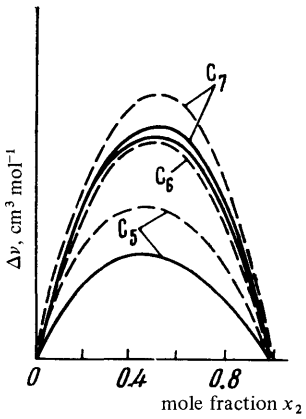


Figure 10. The volumes of mixing of benzene–alicyclic hydrocarbon systems[130]: continuous curves–experimental data; dashed curves–theoretical data.

The new Flory theory has been tested for a large number of mixtures of low-molecular-weight liquids and for solutions of polymers. It has been shown that, for mixtures of n-alkanes[121,122] and alkanes with cyclic hydrocarbons[124], mixtures of spherical molecules[124], mixtures of hydrocarbons with fluoro-derivatives, solution[3] of isooctane in CCl_4 and cyclohexane[126–129], and solutions of benzene and CCl_4 in toluene and xylene[55], the Flory theory always predicts the correct sign of the volume change and in most cases the calculated values of Δv^m are close to the experimental values (Fig.10). Fig.11 shows that the theory describes satisfactorily the experimental data also for solutions of polymers: in particular, the values of Δv^m for the natural rubber–benzene system[73], calculated by Eqn.(24), virtually agree with experiment; for solutions of poly-isobutylene in n-alkanes[74], the theory predicts the correct sign of the volume of mixing, but the values of Δv^m do not agree. An even greater discrepancy between the experimental and calculated Δv^m has been observed for solutions of polystyrene[76], although the theory predicts correctly the sign of Δv^m.

All the foregoing considerations show that the mixing of liquids and the dissolution of polymers are accompanied by a volume change which makes a significant contribution to all the thermodynamic potentials. Even a small contribution of the volume change can induce marked effects, for example, phase separation when the solution is heated.

The contraction effect on mixing liquids and on dissolving polymers leads to the occurrence of concentration fluctuations in solution, whose further growth leads to the formation of organised structures such as associated species or solvates. These organised structures, which are formed spontaneously, are classified as the so-called dissopative structures, considered in the modern thermodynamics of irreversible processes[130–131].

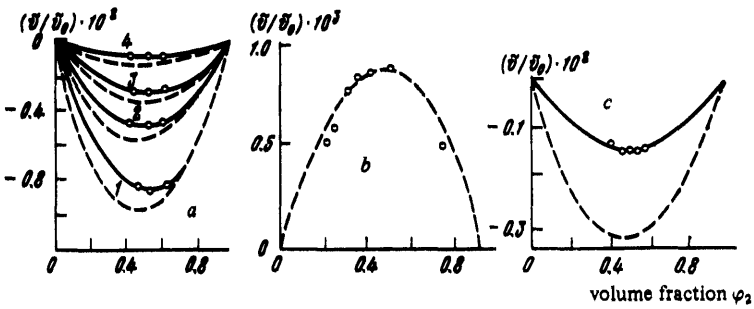


Figure 11. The relative volumes of mixing for different solutions: *a*) of polyisobutylene in n-alkanes[74] [1) in n-hexane; 2) in n-octane; 3) in n-decane; 4) in n-hexadecane]; *b*) of natural rubber in benzene[75]; c) of polystyrene in cyclohexane[76]. Continuous lines—experimental data; dashed lines—calculation based on the Flory theory.

REFERENCES

1. D.I.Mendeleev, "Osnovy Khimii" (Fundamentals of Chemistry), GosNTIkhimlit, Moscow–Leningrad, 1947, Vol.1.
2. D.I.Mendeleev, "Sochineniya" (Collected Works), ONTI, Khimteoret, Leningrad, 1937, Vol.4.
3. H.Hildebrand, "Solubility of Non-Electrolytes" (Translated into Russian), GONTI, 1938.
4. J.S. Rowlinson, "Liquids and Liquid Mixtures", Butterworth, London 1959.
5. A.F.Ioffe and N.N.Semonov, "Kurs Fiziki" (A Physics Course), GONTI, 1933, Vol.4.
6. H.Morawetz, "High Polymers", Vol.XXI, "Macromolecules in Solution" (Translated into Russian), Izd. Mir, Moscow, 1967.
7. J.S.Rowlinson and P.I.Freeman, Pure Appl.Chem., 2, 329 (1961).
8. P.I.Freeman and J.S.Rowlinson, Polymer, 1, 20 (1960).
9. J.H.Hildebrand, Discuss Faraday Soc., No.15, 9 (1953).
10. A.Bondi, J.Phys.Chem., 58, 929 (1954).
11. A.I.Kitaigorodskii, "Molekulyarnye Kristally" (Molecular Crystals), Izd.Nauka, Moscow, 1971.
12. Ya.I.Frenkel', "Sobranie Izbrannykh Trudov" (Collection of Selected Works), Izd.Akad.Nauk SSSR, 1952, Vol.3.
13. R.P.Rastogi, I.Nath, and I.Misra, J.Phys.Chem., 71, 1277 (1967).
14. R.K.Nigam and P.P.Singh, Trans.Faraday Soc., 65, 950 (1969).
15. R.Battino, Chem.Rev., 71, 1 (1971).
16. I.Prigogine and V.Mathot, J.Chem.Phys., 20, 49 (1952).
17. V.Mathot and A.Desmiter, J.Chem.Phys., 20, 782 (1953).
18. R.Thacer and J.S.Rowlinson, J.Chem.Phys., 21, 2242 (1953).
19. R.Thacer and J.S.Rowlinson, Trans.Faraday Soc., 50, 1036 (1954).
20. K.N.Marsh, Trans.Faraday Soc., 64, 883 (1968).
21. K.N.Marsh, J.Chem.Thermodynam, 2, 359 (1969).
22. P.I.Levien and K.N.Marsh, J.Chem.Thermodynam, 2, 227 (1970).
23. V.P.Belousov and A.G.Morachevskii, "Teploty Smesheniya Zhidkostei" (Heats of Mixing of Liquids), Izd.Khimiya, Leningrad, 1970.
24. H.F.Stoecki, I.G.Fernandez-Garcia, and C.G. Boissonas, Trans.Faraday Soc., 62, 3044 (1966).
25. I.N.Brønsted and I.Koefoed, Mat.-fys.medd.Kgl. danske vid.sels kab., 22, 1 (1946).
26. A.Desmiter and I.H.Van der Waals, Rec.Trav.chim. 77, 53 (1958).
27. I.D.Ibanies and C.T.Liu, J.Phys.Chem., 67, 1388 (1963).
28. T.Holleman, Physica, 27, 585 (1963).
29. Ch.Harrison and I.Winnick, J.Chem.Eng.Data, 12, 174 (1967).
30. M.L.Sims and I.Winnick, J.Chem.Eng.Data, 14, 164 (1969).
31. M.L.Shane'a and F.B.Canfield, Trans.Faraday Soc., 64, 2281 (1968).
32. A.Blinowska and W.Brostow, J.Chem.Thermodynam., 7, 787 (1975).
33. L.M.Duc, Z.Abdellan, and H.F.Stoecki, Helv.Chim. Acta, 56, 2513 (1973).
34. M.B.Ewing and K.N.Marsh, J.Chem.Thermodynam., 6, 1087 (1974).
35. P.Meares, Trans.Faraday Soc., 45, 966 (1949).
36. K.Nakanishi, H.Touhara, K.Sato, and M.Madao, Bull.Chem.Soc.Japan, 41, 2536 (1968).
37. I.P.E.Grolier, D.Ballet, and A.Viallard, J.Chem. Thermodynam., 6, 895 (1974).
38. M.L.McGlashan, J.E.Prue, and I.E.J.Sainsbury, Trans.Faraday Soc., 50, 1284 (1954).
39. G.P.Johari, J.Chem.Eng.Data, 14, 470 (1969).
40. G.C.Pimentel and A.L.McClellan, "The Hydrogen Bond" (Translated into Russian), Izd.Mir, Moscow, 1964.
41. H.C.Van Ness, C.Soczek, and N.Kochar, J.Chem. Eng.Data, 12, 346 (1967).
42. K.N.Marsh and C.Burfitt, J.Chem.Thermodynam., 7, 955 (1975).
43. S.Otin, M.Gracia, and C.Gutterres Losa, J.Chim. Phys.et Phys.Chim.Biol., 70, 1232 (1973).
44. K.Nakanishi and M.Shirai, Bull.Chem.Soc.Japan, 43, 1634 (1970).
45. G.C.Paraskevopoulos and R.W.Missen, Trans.Faraday Soc., 58, 869 (1962).

46. I.E.Otterstedt and R.W.Missen, Trans.Faraday Soc., **58**, 879 (1962).
47. P.Boule, Compt.rend., **C268**, 5 (1969).
48. D.A.Brandzeth, S.D.O'Neill, and R.W.Missen, Trans. Faraday Soc., **62**, 2355 (1966).
49. A.E.Pope, H.D.Pflug, B.Dacre, and G.C.Benson, Canad.J.Chem., **45**, 2665 (1967).
50. O.Ya.Samoilov, "Struktura Vodnykh Rastvorov Elektrolitov i Gidratatsiya Ionov" (The Structure of Aqueous Electrolyte Solutions and Ion-Hydration), Izd.Akad.Nauk SSSR, 1957.
51. A.I.Altsybeeva, V.P.Belousov, and A.G.Morachevskii, Symposium, "Khimiya i Termodinamika Rastvorov" (The Chemistry and Thermodynamics of Solutions), Izd.Leningrad.Gos.Univ., p.45.
52. A.G.Mitchell and W.F.H.Winne-Jones, Discuss. Faraday Soc., No.15, 161 (1963).
53. H.S.Frank and M.L.Evans, J.Chem.Phys., **13**, 507 (1945).
54. G.Namethy and M.A.Schraga, J.Chem.Phys., 36, 3382 (1962).
55. J.Singh, H.D.Pflug, and G.C.Benson, J.Phys. Chem., **72**, 1939 (1968).
56. L.Romani and M.I.Paz Andrade, Anales de Quimica, **70**, 422 (1974).
57. T.M.Letcher, J.Chem.Thermodynam, 7, 205 (1975).
58. M.D.Pena and J.N.Delgado, Anales de Quimica, 70, 678 (1974).
59. S.E.Wood and J.P.Prusie, J.Amer.Chem.Soc., **67**, 480 (1945).
60. J.R.Goates, R.J.Sullivan and J.B.Ott, J.Phys. Chem., **63**, 589 (1959).
61. W.Woycicki and K.W.Sadovska, Bull.Acad.Polon Sci., Ser.Sci.Chim., **16**, 147 (1968).
62. W.Woycicki and K.W.Sadovska, Bull.Acad.Polon Sci., Ser.Sci.Chim., **16**, 329 (1968).
63. W.Woycicki and K.W.Sadovska, Bull.Acad.Polon Sci., Ser.Sci.Chim., **16**, 365 (1968).
64. W.Woycicki and K.W.Sadovska, Bull.Acad.Polon Sci., Ser.Sci.Chim., **16**, 413 (1968).
65. No ref. given in the original (Ed of Translation).
66. W.Woycicki and K.W.Sadovska, Bull.Acad.Polon Sci., Ser.Sci.Chim., **16**, 531 (1968).
67. K.N.Marsh and C.Burfitt, J.Chem.Thermodynam, **7**, 955 (1975).
68. A.A.Tager, A.Smirnova, and N.Sysueva, Nauch. Dokl.Vys.Shkoly, 1, 135 (1958).
69. U.Bianchi and G.Guniberty, Polymer, **7**, 151 (1966).
70. C.H.Baker, W.B.Brown, and G.Gee, Polymer, **3**, 215 (1962).
71. A.A.Tager, L.V.Adamova, M.V.Tsilipotkina, and G.I.Frolova, Vysokomol.Soed., **A13**, 654 (1971).
72. G.Delmas, D.Patterson, and T.Somcynsky, J.Polymer Sci., **57**, 79 (1962).
73. B.E.Eichinger and P.J.Flory, Trans.Faraday Soc., **64**, 2035, 2053, 2061, 2066 (1968).
74. P.J.Flory, I.L.Ellenson, and B.E.Eichinger, Macromolecules, **1**, 279 (1968).
75. P.J.Flory and H.Hocker, Trans.Faraday Soc., **67**, 2258 (1971).
76. H.Hocker and P.J.Flory, Trans.Faraday Soc., **67**, 2270 (1971).
77. H.Hocker, H.Shih, and P.J.Flory, Trans.Faraday Soc., **67**, 2275 (1971).
78. I.S.Clunie, I.F.Goodman, and P.S.Symons, Trans. Faraday Soc., **65**, 287 (1969).
79. A.Teramoto, S.Kusamizu et al. Macromol.Chem., **90**, 78 (1966).
80. R.W.Kershaw and G.N.Malcolm, Trans.Faraday Soc., **64**, 323 (1967).
81. O.R.Bruce and G.N.Malcolm, J.Chem.Thermodynam., 1, 183 (1963).
82. A.A.Tager, L.V.Adamova, Yu.S.Bessonov, V.N. Kuznetsov, T.A.Plyusnina, V.V.Soldatov, and M.V. Tsilipotkina, Vysokomol.Soed., **A14**, 1991 (1972).
83. G.N.Malcolm, C.E.Baird, G.R.Bruce, K.G. Kheyne, R.W.Kershaw, and M.C.Pratt, J.Polymer Sci., **A2**, 7, 1945 (1969).
84. A.I.Davenport, I.S.Rowlinson, and G.Saville, Trans. Faraday Soc., **62**, 322 (1966).
85. A.A.Tager, "Fiziko-Khimiya Polimerov" (The Physical Chemistry of Polymers), Izd.Khimiya, Moscow, 1978.
86. I.A.Friend, I.A.Larkin, A.Maroudas, and M.L. McGlashan, Nature, **198**, 683 (1963).
87. Th.Holleman, Physica, **29**, 275 (1963).
88. A.I.Davenport and I.S.Rowlinson, Trans.Faraday Soc., **59**, 78 (1963).
89. D.Patterson, Rubber Chem. Technol., **40**, 1 (1967).
90. A.H.Liddel and F.L.Swinton, Discuss.Faraday Soc., No.49, 115 (1970).
91. I.B.Kinsinger and L.E.Ballard, J.Polymer Sci., **B2**, 879 (1964).
92. I.M.Bardin and D.Patterson, Polymer, **10**, 247 (1969).
93. G.Delmas and D.Patterson, Polymer, **7**, 513 (1966).
94. G.Allen and C.H.Baker, Polymer, **6**, 181 (1965).
95. A.A.Tager, A.A.Anikeeva, V.M.Andreeva, T.Ya. Gumarova, and L.A.Chernoskutova, Vyskomol.Soed., **A10**, 1661 (1968).
96. V.M.Andreeva, A.A.Anikeeva, S.A.Vshivkov, and A.A.Tager, Vyskomol.Soed., **B12**, 789 (1970).
97. C.D.Marat and I.S.Rowlinson, Polymer, **7**, 525 (1966).
98. D.Patterson, G.Delmas, and T.Somcynsky, Polymer, **8**, 503 (1967).
99. L.S.Bolotnikova, T.I.Samsonova, and S.Ya.Frenkel', Vysokomol.Soed., **B10**, 235 (1968).
100. V.M.Andreeva, A.A.Tager et al, Vysokomol.Soed., **B11**, 555 (1969).
101. I.Prigogine and R.Defay, "Chemical Thermodynamics" (Translated into Russian), Izd.Nauka, Novosibirsk, 1966.
102. B.I.Lirova, A.L.Smolyanskii, P.A.Savchenko, and A.A.Tager, Vysokomol.Soed., **B14**, 265 (1972).
103. A.A.Tager, A.A.Anikeeva et al, Vysokomol.Soed., **B13**, 231 (1972).
104. A.A.Tager, A.I.Podlesnyak, and L.V.Demidova, Vysokomol.Soed., **B10**, 601 (1968).
105. A.A.Tager, A.I.Podlesnyak, M.V.Tsilipotkina, L.V. Adamova, A.A.Bakhareva, and L.V.Demidova, Vysokomol.Soed., **A12**, 1320 (1970).
106. E.Jenkel and K.Gorke, Z.Elektrochem., **60**, 579 (1956).
107. H.Daust and M.Rinfret, Canad.J.Chem., **32**, 492 (1054).
108. A.A.Tager and L.V.Adamova, Symposium, "Trudy po Khimii i Khimicheskoi Tekhnologii" (Collected Papers on Chemistry and Chemical Engineering), Gorky, 1972, No.2(31), p.112.
109. J.H.Hildebrand, J.M.Prausnitz, and R.L.Scott, "Regular and Related Solutions", Van Nostrand–Reinhold, Princeton, N.J., 1970.
110. M.I.Shakhparonov, "Vvedenie v Molekulyarnuyu Teoriyu Rastvorov" (Introduction to the Molecular Theory of Solutions), Gos.Izd.Tekh.-Teoret.Lit., Moscow, 1956.
111. I.Prigogine et al, "The Molecular Theory of Solutions", Amsterdam, 1957.

112. I.Prigogine, N.Trappeniers, and V.Mathot, Discuss. Faraday Soc., No.15, 93 (1953).
113. I.Prigogine, A.Bellemans, and C.Naar-Colin, J. Chem.Phys., **26**, 751 (1957).
114. J.Hijmans, Physica, **27**, 433 (1961).
115. S.N.Battacharyya, D.Patterson, and T.Somcynsky, Physica, **30**, 1276 (1964).
116. A.D.Patterson and A.A.Tager, Vysokomol.Soed., **A11**, 1814 (1967).
117. R.Simha and A.J.Havlik, J.Amer.Chem.Soc., **86**, 197 (1964).
118. V.S.Nanda and R.Simha, J.Chem.Phys., **41**, 3870 (1964).
119. R.Simha and R.F.Boyer, J.Chem.Phys., **37**, 1003 (1962).
120. V.S.Nanda, R.Simha, and T.S.Somcynsky, J.Polymer Sci., **C12**, 277 (1966).
121. P.I.Flory, R.A.Orwoll, and A.Vrij, J.Amer.Chem. Soc., **86**, 3507, 3515 (1964).
122. R.A.Orwoll and P.I.Flory, J.Amer.Chem.Soc., **89**, 6814, 6822 (1967).
123. P.I.Flory, J.Amer.Chem.Soc., **87**, 1833 (1965).
124. A.Abe and P.I.Flory, J.Amer.Chem.Soc., **87**, 1838 (1965).
125. L.Tonks, Phys.Rev., **50**, 955 (1936).
126. R.Battino, J.Phys.Chem., **70**, 3408 (1966).
127. L.Washington and R.Battino, J.Phys.Chem., **72**, 4496 (1968).
128. R.Battino, J.Phys.Chem., **72**, 4503 (1968).
129. G.C.Benson and J.Singh, J.Phys.Chem., **72**, 1347 (1968).
130. P.Glansdorff and I.Prigogine, "Thermodynamic Theory of Structure, Stability, and Fluctuations" (Translated into Russian), Izd.Mir, Moscow, 1973.
131. I.Prigogine and R.Lefever, Experimentia Suppl., **18**, 101 (1971)

Faculty of Chemistry,
The Urals State University,
Sverdlovsk

Translated from *Uspekhi Khimii*, **49**, 637-678 (1980) U.D.C. 547.46.052.3

Advances in the Chemistry of Pernitriles

N.S.Zefirov and D.I.Makhon'kov

The problems of a formal systematic treatment of nitrogen-carbon structures as well as the methods of synthesis, chemical properties, and applications of the most familiar representative of the class of nitrogen-carbon compounds, namely pernitriles, are examined.
The bibliography includes 298 references.

CONTENTS

I.	Introduction	337
II.	A formal systematic treatment of nitrogen-carbon structures	337
III.	Percyanoalkanes	338
IV.	Percyanoalkenes	339
V.	Percyanoalkynes	347
VI.	Percyanoarenes	349
VII.	Percyano-derivatives of nitrogen heterocycles	349
VIII.	Pernitriles with a nitrogen-carbon skeleton	350
IX.	Appendix	352

I. INTRODUCTION

Approximately 30 organic compounds, whose molecules consist solely of nitrogen and carbon atoms, and approximately the same number of anions of percyanohydrocarbon derivatives containing one or several acid C–H bonds—the so-called cyanocarbonic acids (see Appendix)—are now known. However, it is of interest that, although the majority of these acids form stable salts, for example dicyanamide, pentacyanocyclopentadiene etc., it has so far been impossible to synthesise compounds such as hexacyanocyclopentadiene, or tricyanamide, which are extremely interesting from both theoretical and possibly practical points of view.

Analysis of literature data shows that during the last 15 years the number of compounds of the "nitrogen–carbon" class synthesised has not only increased almost by a factor of nine[1], but every year there is an increase in the number of publications devoted to the investigation of the physicochemical and chemical properties of these compounds.

By virtue of advances in synthesis, the majority of representatives of this class have become relatively readily available and the intense development of quantum-chemical methods permitted a theoretical prediction of the existence of molecules of this type. This applies primarily to polycyano-compounds or pernitriles, which have recently become the objects of constant attention by investigators. The unusual properties of polynitriles are associated with the unique properties of the cyano-group, which combines powerful electron-accepting properties with a small bulk. Being linear and containing a cylindrical π-electron system, the cyano-group is capable of conjugation with a wide variety of π-electron systems, being favoured in this respect compared with other strong electron-accepting substituents such as the nitro- and sulphonyl groups.

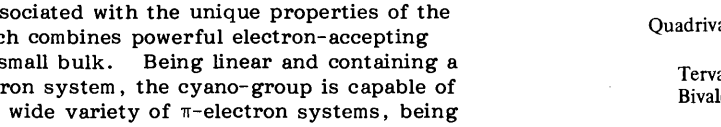
As an illustration, we may note that the electrical conductivities of salts of the tetracyanoquinodimethane radical-ion are virtually equal to the conductivity of graphite, pentacyanocyclopentadiene is a stronger acid than perchloric acid, tetracyanoquinone oxidises water, and tetracyano-oxiran adds to olefins and even to aromatic compounds, like ozone[2].

Despite the relative novelty of nitrogen–carbon compounds, certain representatives of this class of compounds have become quite familiar chemically. For example, the bibliography on the chemistry of tetracyanoethylene already numbers more than a thousand studies and there has been no slackening of the interest in this compound. Furthermore, each year new types of reactions of tetracyanoethylene are reported. On the other hand, the chemistry of many polynitriles has been studied very superficially, although it is of considerable theoretical and even practical interest.

The present review is devoted to advances in the chemistry of pernitriles and covers the literature up to 1976 inclusive. The section devoted to the systematic treatment of nitrogen–carbon molecules deals with an examination of literature data.

II. A FORMAL SYSTEMATIC TREATMENT OF NITROGEN–CARBON STRUCTURES

We shall consider a formal combinatorial approach to structures consisting of carbon and nitrogen atoms. Both these elements have coordination numbers ranging from unity to four depending on the oxidation state and are capable of forming double and triple bonds. On this basis, it is easy to deduce all possible monatomic fragments, which are illustrated below:



Any structure of a nitrogen–carbon compound can be obtained by scanning all possible combinations of these fragments, provided that the following requirements are fulfilled: all the valences are saturated and the molecule is electrically neutral overall. The role of the homologous modulus (cm^3)

† The list does not include bivalent carbon, because isonitriles can be described in terms of the fragment $-N\equiv\overline{C}$.

can be fulfilled either by homogroups of the type $-C\equiv C-$ and $-N=N-$ (there is also a possibility of the formation of cumulene carbon chains) or by heterogroups such as, for example, $-N=C=N-$. Among these, only the azo-group has a geometry suitable for inclusion in a ring and for the formation of cyclic azaheterocycles. It is readily seen that the combination of the above atomic fragments permits a large variety of nitrogen–carbon skeletons, which can be divided into two types: (1) those with single free valences and (2) those with unused double bonds ("exo-double bonds").

The fundamental problem in the determination of molecular structures consists in finding the end group. Evidently, only two monatomic fragments, $Y\equiv$ and $Z=$, can play the role of an end group and neither is univalent. A bivalent end group can be derived from the diatomic fragment $=X=Z$; the diazo-group $=\overset{+}{N}=\overline{N}$ corresponds to such a fragment. In hydrocarbons the terminal valence is usually saturated by a univalent atom—hydrogen. Evidently, in a systematic treatment of nitrogen–carbon compounds it is essential to find univalent fragments capable of "covering" the unused valences; a nitrogen–carbon structure can then be derived by means of a systematic treatment of hydrocarbons involving the replacement of hydrogen atoms by the appropriate univalent nitrogen–carbon group. Among diatomic electrically neutral combinations, it is possible to obtain only one, $-X\equiv Y$, satisfying the requirement for a univalent state. The $-C\equiv N$ and $-\overset{+}{N}\equiv C^-$ functional groups, i.e. the nitrile and isonitrile groups, correspond to this combination. The azido-group $N\equiv\overset{+}{N}-\overline{N}- \leftrightarrow N=\overset{+}{N}=N-$ corresponds to the univalent triatomic fragments $Y\equiv X-Z-$ or $Z=X=Y-$. Thus the molecules of nitrogen–carbon compounds (with the exception of unsaturated cyclic structures consisting of azo- and acetylenic groups) should belong to the class of diazo-compounds, nitriles, isonitriles, and azides.

Molecules containing more than two isonitrile or diazo-groups are apparently unknown. On the other hand, pernitriles and perazides have been described in the literature. However, whereas there are only isolated publications on perazides[4–9], the literature on pernitriles is fairly extensive; the properties of pernitriles are the subject of the succeeding sections of the review.

III. PERCYANOALKANES

1. Tetracyanomethane

The only stable representative of the percyanoalkane series is tetracyanomethane (TCM). The first attempt to synthesise TCM from silver tricyanomethide and chlorocyanogen was undertaken by Schmidtmann[10] in 1896. Three years later Hantzch and Osswald[11] tried to obtain TCM by Schmidtmann's method having replaced chlorocyanogen by iodocyanogen. The attempts to synthesise TCM from bromotricyanomethane and potassium cyanide[12] and from the compounds $C(CH_2N{=}CHC_6H_5)_4$ and $C(CH_2NCl_2)_4$ were also unsuccessful[13].

It was not until 1969 that Mayer[14] succeeded in synthesising TCM in accordance with Schmidtmann's scheme:

$$AgC(CN)_3 + ClCN \xrightarrow{100^\circ} AgCl + C(CN)_4 \ . \qquad (1)$$

Mayer's product was a colourless crystalline compound, soluble in polar solvents, and decomposing fairly rapidly on storage with formation of an unidentified orange-yellow amorphous substance. Mayer described certain chemical properties of TCM, in particular its alkaline and acid hydrolysis:

$$C(CN)_4 + 2OH^- \rightarrow C(CN)_3^- + OCN^- + H_2O \ ,$$
$$C(CN)_4 + 2H_2O \rightarrow C(CN)_3^- + NH_4^+ + CO_2 \ .$$

Systematic study of the chemistry of TCM began as soon as it was shown[15] that the stability of this compound depends greatly on the conditions of its synthesis, particularly on the absence of traces of chlorine in chlorocyanogen and of traces of moisture in silver tricyanomethide (which catalyse the trimerisation of chlorocyanogen). The presence of an admixture of cyanuric chloride was in fact responsible for the instability of the first TCM specimens. The enthalpy of formation of TCM from the elements has been determined[16], its molecular geometry has been studied by electron diffraction[17] and X-ray diffraction[18], and its photoelectron[19], ^{13}C NMR[13,20], and infrared and Raman spectra[21] have been studied.

As was to be expected, TCM proved to be extremely reactive in relation to nucleophiles. Comparison of the thermochemical properties of TCM and polyhalogenomethanes showed that the accumulation of four cyano-groups at a saturated carbon atom leads to an appreciable destabilisation of the TCM molecule. The "bond separation" energy, the existence of which is reflected in a tendency towards reaction involving the formation of the nitrile cation and the tricyanomethyl anion, is 23.5 kcal mol^{-1}.[20]

Tetracyanomethane reacts readily with inorganic chlorides, for example:

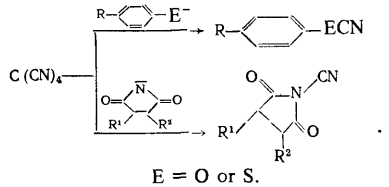
$$C(CN)_4 + LiCl \rightarrow LiC(CN)_3 + ClCN \ .$$

Formally, this reaction can be regarded as electrophilic substitution at a saturated carbon atom (the cyano-group is replaced by the lithium cation). However, the "cyanophilic" mechanism, involving attack by the nucleophile on the carbon atom of the cyano-group, is believed nowadays to hold for these reactions:

$$B^- + N\equiv C-C(CN)_3 \longrightarrow B-CN + C(CN)_3^- \ .$$

This mechanism is related to that of the so-called "halogenophilic" reactions of polyhalides[15,22,23].

The reaction of TCM with caesium fluoride has been used successfully as a method for the preparation of fluorocyanogen[24], but attempts to synthesise dicyanogen oxide by the analogous reaction with potassium and caesium cyanates led to the isolation of an unidentified polymer[25]. The reactions of TCM with the anions of dibasic acid imides[23] and phenoxide and thiophenoxide anions[22] take place under mild conditions (THF, 10–15 min) and lead respectively to *N*-cyanoimides, cyanates, and thiocyanates:



E = O or S.

Thus TCM behaves as a powerful cyanating agent in reactions with nucleophiles of this type.

The reactions of TCM with tertiary amines and phosphines, which in most cases lead to unidentified mixtures of products, proceed in a much more complex manner. It is believed[15] that in this case the primary reaction products are trisubstituted *N*-cyanoammonium or *P*-cyanophosphonium tricyanomethides [mechanism (2)]—extremely reactive compounds which undergo subsequent hydrolysis with elimination of the cyano-group from the cation or undergo intramolecular transformations involving attack on the cation by the ambident cyanoform anion:

$$R_3E + C(CN)_4 \rightarrow [R_3\overset{+}{E}CN]\,\bar{C}(CN)_3 \ ; \qquad (2)$$
$$E = N \text{ or } P \ .$$

The products of secondary reactions of the first type—tribenzylammonium and triphenylphosphonium tricyanomethides—have been isolated in yields of 90 and 20% respectively[15]. The reaction of TCM with triphenylphosphine complexes of transition metals have been reported[26] to proceed via the mechanism

$$Pt(Ph_3P)_4 + C(CN)_4 \rightarrow 2Ph_3P + Pt(Ph_3P)_2(CN)C(CN)_3 \ .$$

However, in the light of later studies of the reactions of TCM with nucleophiles, the above reaction probably requires a more detailed investigation.

The ability of an electrophile such as TCM to react with compounds which are usually classified as electrophiles (hydrogen chloride and the halides of sulphur and phosphorus acid) was very much unexpected[15]:

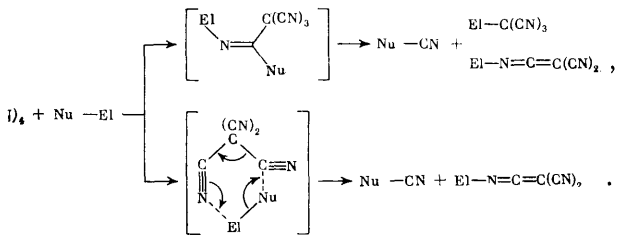
$$C(CN)_4 + HCl \rightarrow ClCN + HC(CN)_3 \xrightarrow{HCl} (NC)_2C{=}C\langle^{NH_2}_{Cl} \ ,$$

$$C(CN)_4 + SO_2Cl_2 \rightarrow ClCN + ClC(CN)_3 + SO_2 \ ,$$

$$C(CN)_4 + SOCl_2 \rightarrow ClCN + (NC)_2C{=}C\langle^{N{=}S{=}O}_{Cl} \ ,$$

$$C(CN)_4 + PCl_5 \rightarrow ClCN + (NC)_2C{=}C\langle^{N{=}PCl_3}_{Cl} \ .$$

Alternative mechanisms of the above reactions are presented below[15]:



us TCM is a unique compound in which a regular tetral structure and the consequent equivalence of all the ›-groups are combined with a high mobility of one of the ›-groups, since TCM reacts with equal ease with both nucleophiles and electroph'les.

Reactions of the first type are particularly useful when anions of different kinds are used as nucleophiles. The transfer of the cyano-group to an atom with a negative charge takes place under extremely mild conditions and leads to cyanation products in almost quantitative yields.

Reactions of the second type with compounds containing a mobile chlorine atom are also extremely convenient for the synthesis of compounds having four electron-accepting groups at a saturated carbon atom (for example, of chlorotricyanomethane) and derivatives of the keten imine form of the tricyanomethide anion such as thionylamino- and phosphazo-2,2-dicyanoethylenes.

2. Hexacyanoethane

In 1928 the first and unsuccessful attempt was made to obtain hexacyanoethane (HCE) by treating silver tricyanomethide with chlorine[27]. The synthesis of HCE was achieved in 1968 by the reaction of chlorocyanogen with pentacyanoethylsodium, obtained by treating tetracyanoethylene with sodium cyanide[28]. The yield of product was only 17%. The discoverers of this synthesis note that the success of the reaction depends on the absence of a solvent (apart from chlorocyanogen itself). The best results were obtained in the presence of aluminium chloride. Both in solutions and in crystalline state HCE decomposes rapidly (the process is catalysed by bases) with formation of tetracyanoethylene. As in many other reactions of pernitriles, dicyanogen, which theoretically should be formed in this reaction, could not be detected[28].

IV. PERCYANOALKENES

1. Tetracyanoethylene (TCE)

A number of reviews, both general[2,29] and concerned with certain specific questions, for example, the reactions of TCE with amines and aminoacids[30], the alkylation of TCE[31], transition metal complexes of pernitriles[32], the properties of polymeric compounds of metallic derivatives of TCE[33], and molecular complexes[34], have been devoted to the chemistry of tetracyanoethylene. The present review therefore deals solely with the most interesting studies carried out in the last eight years.

Vigorous investigation of the synthetic aspects of the chemistry of TCE led to the publication of new reports on the physicochemical properties of this compound. Thus the molecular constants[35] and molecular orbitals[36] of TCE have been calculated and studies have been made on the NMR[37] and NQR[38] spectra, mass spectra (of negative ions)[39], photoelectron spectra[40], and the relation between the ionisation potentials and electron affinities, on the one hand, and the reactivity of TCE, on the other[41].

(a) Molecular Complexes of TCE

The presence of four powerful electron-accepting groups is responsible for the extremely high tendency of TCE to form molecular complexes with a wide variety of classes of electron-donating molecules, among which complexes with aromatic compounds[34] and polymeric complexes of TCE have been most thoroughly investigated[42].

The formation of complexes of TCE with π-donors precedes as a rule the cycloaddition, tricyanovinylation, and cyanation reactions. Thus the interaction of TCE with ferrocene is not limited to the formation of a π-complex, which was believed for a long time, but leads to a mixture of cyanoferrocene (40%) and tricyanovinylferrocene (16%) (150 °C, sulpholane or acetonitrile as solvents)[43]. The analogous reaction with ferrocenylmercury chloride yields mainly tricyanovinylferrocene and the absence of the directing effect in the reaction with ethylferrocene indicates a radical mechanism of this reaction[43].

In the presence of bases TCE reacts with 2,4,6-trinitroanisole and 1,3,5-trinitrobenzene to form anionic σ-complexes, whose structure has been confirmed by NMR[44]. It has been shown recently that TCE forms molecular complexes also with saturated compounds of Group IVB metals (permethylpolysilanes[45], polygermanes[46], hexa-alkyldistannanes[46], and tetraalkyl derivatives of germanium, tin, and lead[47]) and even with saturated hydrocarbons—hexamethylethane, cyclohexane, bicyclohexyl, decalin, adamantane, and 1,1-biadamantyl[48].

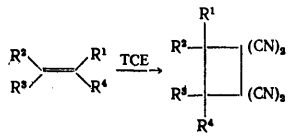
(b) Reactions Involving Addition to the C=C Bond of TCE

The vast majority of reactions of TCE (probably with the sole exception of reactions involving the cyano-group and the cracking reaction) include the stage in which the substrate adds to the C=C bond of TCE, leading as a rule to a zwitterionic intermediate, which then cyclises intramolecularly or undergoes intermolecular reactions, frequently accompanied by fragmentation processes of different types. In particular, this factor is responsible for the wide variety and complexity of the chemistry of TCE.

Another type of addition reaction (in the presence of a mobile hydrogen atom in the substrate molecule) involves the formation of substituted tetracyanoethanes, which are in many instances the final products, but which usually decompose with elimination of an HCN molecule, malononitrile, or tetracyanoethane.

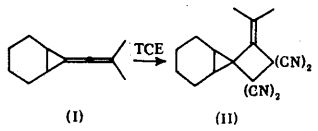
The reactions of TCE with olefins, the principal pathway of which in the case of monoalkenes involves the formation of cyclic 1,2-adducts, have apparently been most thoroughly investigated. When the molecule contains a large number of double bonds (particularly conjugated double bonds or bonds with a suitable steric arrangement), the reaction products are 1,*n*-adducts. In the simplest case of conjugated donors $n = 4$ (the Diels–Alder reaction), but in more complex systems there is a possibility of the formation of adducts with $n = 3$, 5, 6, 8, and higher values, the reactions being usually accompanied by different kinds of rearrangements and leading as a rule to mixtures of isomers. The study of reactions of this type is extremely interesting for the investigation of problems of reactivity.

1,2-Cycloaddition reactions. The activation of the double bond by steric strain or by electron-donating substituents entails addition to TCE with formation of cyclobutane derivatives. Vinyl sulphides, *N*-vinylamides, *N*-vinylsulphonamides[29], vinyl ethers, and vinylcyclopropanes react via the general mechanism



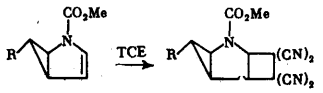
(3)

In the last case, however, the reaction is complicated by the ability of TCE to react with cyclopropane via the $[2\pi + 2\sigma]$ mechanism (see below). Nevertheless, the reaction with allene (I) yields both isomers of the spiro-compound (II):[49]



(I) (II)

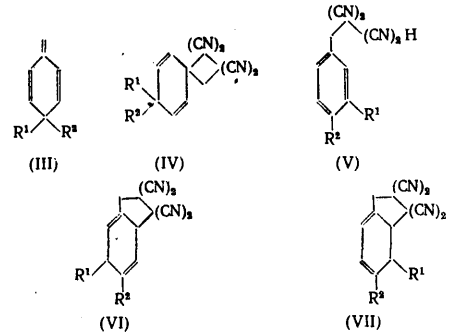
Nor is the three-membered ring involved in reactions of derivatives of 2-azabicyclo[3,1,0]hex-3-ene[50]:



Aryl-substituted olefins, namely styrenes[51], acenaphthylene[52,53], 1-vinylpyrene[53], as well as indene and vinylferrocene react with TCE in accordance with the $[2\pi + 2\pi]$ mechanism[53,54]. However, in many cases the reaction involves the aromatic system and leads to 1,4-addition products (see below).

1,3-Dienes incapable of undergoing the Diels–Alder reaction (for example, cyclic olefins with an exomethylene group and polymethylated butadienes) also form 1,2-adducts as a rule. Reactions of this kind have been reviewed[55].

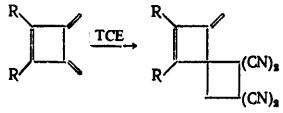
The reaction of TCE with 6,6-disubstituted 3-methylenecyclohexa-1,4-dienes greatly depends on the structure of the triene. Whereas the dimethyl derivative (IIIa) forms adducts (IV) and (V) [adduct (IV) rearranges to adduct (V) in polar solvents], the corresponding aryl derivatives (IIIb) and (IIIc) give rise to adduct (V) and a further two adducts (VI) and (VII), the relative amounts of which depend on the polarity of the solvent[56]:



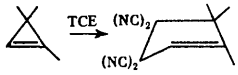
(III) (IV) (V) (VI) (VII)

(a) $R^1 = R^2 = CH_3$; (b) $R^1 = Ph$, $R^2 = CH_3$; (c) $R^1 = R^2 = Ph$.

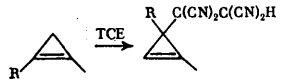
The reactions of diphenyl- and dimethyl-dimethylenecyclobutenes take place via the 1,2-cycloaddition mechanism[29]:



The reaction of TCE with cyclopropenes depends on the presence or absence of an allylic hydrogen atom. In the latter case ring opening occurs (via the stage involving the addition of TCE to the double bond), while in the former case a substituted tetracyanoethane is produced[57]:

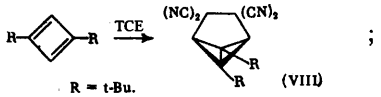


;



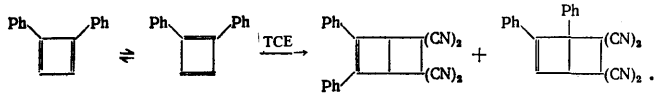
.

1,3-Di-(t-butyl)cyclobutadiene reacts with TCE to form a derivative of dihydrobenzvalene (VIII) in a high yield[58]:



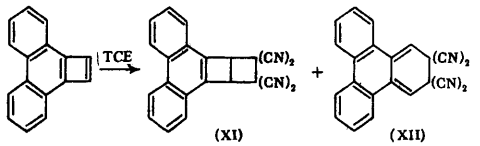
;

On the other hand, the existence of *o*-diphenylcyclobutadiene as an equilibrium mixture of two isomers was confirmed by the formation of adducts (IX) and (X) in proportions of 1 : 7:[59]



(IX) (X)

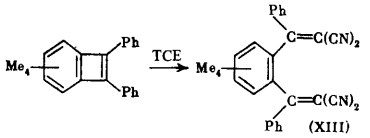
The reaction of phenanthro[*l*]cyclobutadiene with TCE leads to a mixture of adducts (XI) and (XII), the former being unstable and rearranging to the latter on heating[60]:



(XI) (XII)

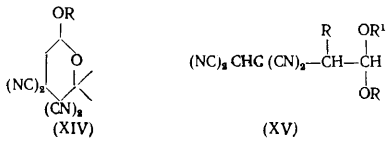
The reaction of benzocyclobutenes proceeds differently[61,62]. The addition of one equivalent of TCE leads to the formation

of adducts with structure (XIII)[62]:



(XIII)

The cycloaddition of TCE to vinyl ethers proceeds via the stage of a 1,4-dipolar intermediate, which has been convincingly demonstrated by Schug and Huisgen[63], who isolated compound (XIV) after the reaction of ethoxyethylene with TCE in acetone[63]. Tetrahydropyridines and piperidines respectively are formed analogously in the presence of nitriles and amines[63]. The products (XV) of the reaction of the zwitter-ionic intermediate with alcohols have also been isolated and conformational and kinetic studies on this process have been carried out[64,65]:



(XIV) (XV)

The cyclobutanes obtained by the reaction of TCE with ring-substituted phenyl vinyl ethers decompose slowly with loss of HCN and the formation of 4-aryloxy-1,1,2-tricyanobuta-1,3-dienes[66]. Metalloalkylolefins (XVI), containing Group IV elements, behave analogously to vinyl ethers[67]:

$$CH_2{=}CH{-}CH_2{-}MR_3 \ (M = Si,\ Ge,\ or\ Sn;\ R = Me\ or\ Ph)\ .$$

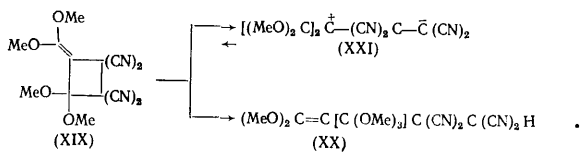
(XVI)

The coordination of an olefin to transition metals (Fe, Co, ', Mo)[68] leads, as in the case of polyenes (see below), to a ange in the reaction pathway and to the formation (for yl and allenyl derivatives) of rearranged products of types VII) and (XVIII):



(XVII) (XVIII)

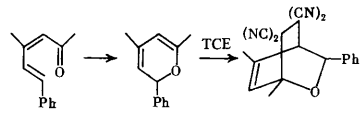
The reaction of TCE with tetramethoxyethylene leads to the normal [2 + 2]-adduct[69], while the analogous reaction with tetramethoxyallene gives an equilibrium mixture of compound (XIX) [which gives rise to compound (XX) on treatment with methanol] and the betaine (XXI)—the principal component at room temperature[70]:



(XIX) (XXI) (XX)

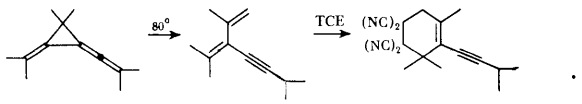
Conjugated dienes and polyenes. After it had been found that TCE is such a powerful dienophile that it can be used for the quantitative determination of dienes[71], the formation of the corresponding adducts became a virtually permanent feature of studies on the synthesis of compounds containing a diene or heterodiene fragment. This led to the publication of a whole series of reports dealing with the study of the mechanism, kinetics, and thermochemistry of the Diels–Alder reaction with TCE[72–77].

TCE proved to be extremely useful for the trapping of various kinds of intermediates containing a diene system [for example, the pyran (XXII), formed in the isomerisation of 4-methyl-6-phenylhexa-3,5-dien-2-one, was identified in this way[78] (scheme (IV)] and also for the investigation of problems of electrocyclic tautomerism (particularly for the quantitative estimation of the content of isomers):

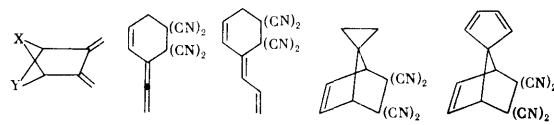


(XXII) (4)

As an example, mention may be made of studies by Huisgen and coworkers on the cycloaddition of TCE to substituted cyclo-octatetraenes[79–81]. TCE has found extensive applications for the identification of unstable dienes formed in thermal, photochemical, or catalytic isomerisation reactions. An interesting example of this kind is provided by the thermal isomerisation of 1-dimethylvinylidene-2-isopropylidene-3,3-dimethylcyclopropane[82]:



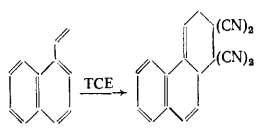
Among the dienes introduced into the Diels–Alder reaction with TCE, a wide variety of systems have been investigated: phenafulvenes to which TCE adds in the 8- and 10-positions[83], dimethylene derivatives of bi- and tri-cyclic hydrocarbons having the general formula (XXIII)[84–86], thioacetals[87], phencyclone[73,88], *N*-methylisoquinolinone[89], dialkyl butadien-2-yl phosphates[90], biscyclopentadienylmercury[91], as well as divinylallene[92], 1,2,3,5-hexatetraene[93], spiro[2,4]heptatriene[94], and spiro[4,4]nonatriene[95], which combine with only one equivalent of TCE [adducts (XXIV)–(XXVII)]:



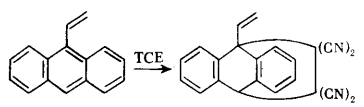
(XXIII) (XXIV) (XXV) (XXVI) (XXVII)

The diene and ene synthesis reactions involving polyene systems have also been studied in relation to derivatives of vitamin A_1 and steroid alkenes[96,97].

Aryl-substituted olefins give rise as a rule to [2 + 2]-adducts (see above). On the other hand, 1-vinyl- and 2-vinyl-naphthalenes react via the Diels–Alder mechanism[29,53], for example:

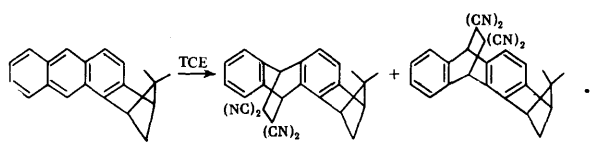


while 9-vinylanthracene[53] reacts like anthracene itself[98], combining with TCE in the 9- and 10-positions, i.e. the vinyl group is not involved in the reaction. Adduct (XXVIII) dissociates readily in solution:



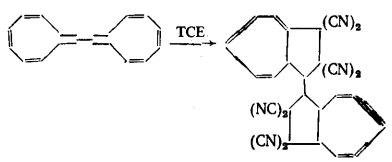
(XXVIII)

The reaction of TCE with apopinanthracene reacts anomalously—the addition to the sterically hindered part of the molecule takes place preferentially [(XXIX) : (XXX) = 1.5][99]:

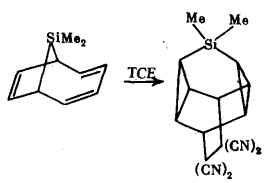


(XXIX) (XXX)

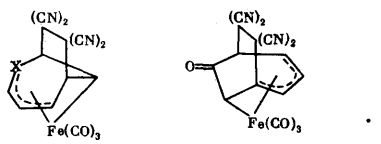
The reaction of 8,8-biheptafulvenyl with TCE leads to a mixture of adducts, which has not been separated, believed to contain, on the basis of spectroscopic data, the products of [8 + 2]-cycloaddition[100]:



Among unusual reactions of TCE, mention may also be made of the reaction with 9,9-dimethyl-9-silabicyclo[4,2,1]nona-2,4,7-triene[101]:



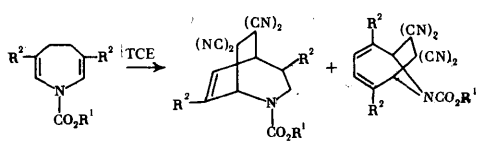
The reactions of TCE with polyene systems are also of special interest for the study of the influence of transition metals on the reactivity of coordinated olefins. Investigations[102–104] have shown that tricarbonyliron complexes of cycloheptatriene and cyclooctatetraene readily undergo 1,3-exo-cycloaddition with formation of the σ,π-complexes (XXXI) and (XXXII) respectively:



(XXXI), X = CH_2; (XXXII), X = —CH=CH— (XXXIII)

while the reaction of troponetricarbonyliron with TCE gives the 1,5-cycloaddition product (XXXIII).

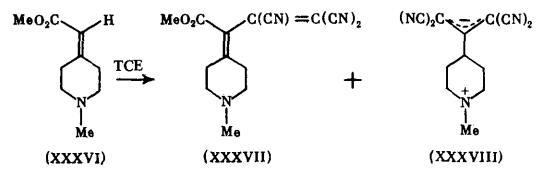
The addition of TCE to azepines[105–107] proceeds via mechanism (5), the formation of the 1,6-adducts (XXXV) being observed only for 3,6-di(isopropyl or t-butyl)azepines; it has been shown[107] that it is a kinetically controlled process, the 1,4-adducts (XXXIV) being thermodynamically more stable:



(5)

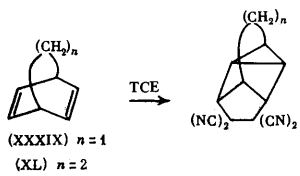
(XXXIV) (XXXV)

It is of interest that the formation of cyclic adducts is not observed at all in the reaction with dihydropyridine (XXXVI). The principal reaction products are compounds (XXXVII) and (XXXVIII)[108]. The mechanism of this reaction has not been studied:



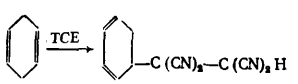
(XXXVI) (XXXVII) (XXXVIII)

Homodiene structures. The study of the interaction of homoconjugated dienes with TCE showed that the reactivity of bicyclo[2,2,*n*]alkadienes (*n* = 1,2,3, or 4) decreases with increasing *n* and that, whereas compounds (XXXIX) and (XL) react with TCE via the [2*s* + 2*s* + 2*s*] mechanism [Eqn. (6)], cyclohexa-1,4-diene forms adduct (XLI), which readily loses a molecule of tetracyanoethane to form benzene[109] [mechanism (7)]:



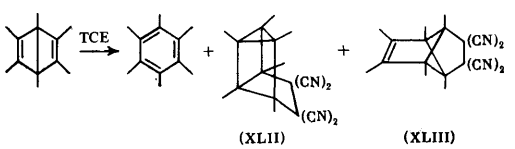
(XXXIX) *n* = 1
(XL) *n* = 2

(6)



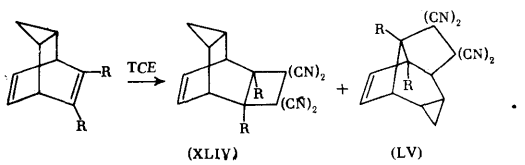
(7)

The reaction with hexamethylbicyclo[2,2,0]hexadiene gives a mixture of hexamethylbenzene (12–15%) and adducts (XLII) and (XLIII) in proportions of 10 : 1:[110]



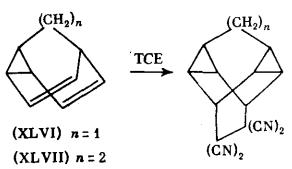
(XLII) (XLIII)

The photoaddition of TCE to tricyclo[3,2,2,$0^{2,4}$]nonadiene derivatives leads to a mixture of adducts (XLIV) and (XLV)[111]:



(XLIV) (LV)

Bridged homotropylidenes combine with TCE via the mechanism of the Diels–Alder reaction. Thus barbaralane (XLVI) and dihydrobullvalene (XLVII) react with TCE via the following mechanism[112]:

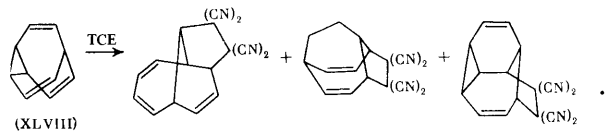


(XLVI) *n* = 1
(XLVII) *n* = 2

The photochemical reaction with barbaralone proceeds analogously[113].

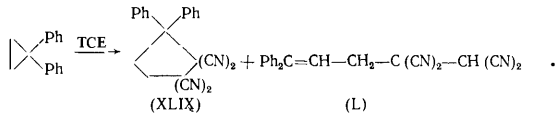
The reaction of bullvalene (XLVIII) with TCE leads to the formation of products whose relative amounts depend on the

polarity of the solvent#:



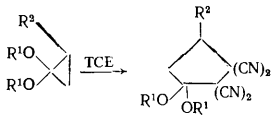
(XLVIII)

Reactions with strained hydrocarbons. Whereas cyclopropane itself does not react with TCE, the reaction with 1,1-diphenylcyclopropane leads to a mixture of products (XLIX) and (L) in proportions of 1 : 1.3[114]:

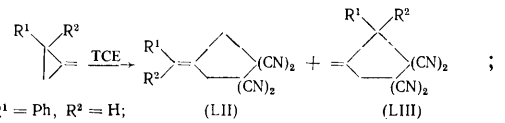


(XLIX) (L)

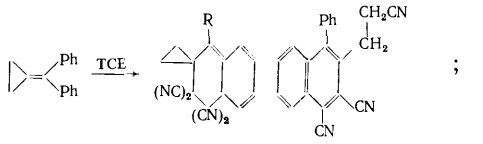
The cycloaddition of cyclopropanone and phenylcyclopropanone acetals proceeds via the $[2\sigma + 2\pi]$ mechanism[115]:



Methylenecyclopropanes (LIa) and (LIb) react with TCE to form the 1 : 1 adducts (LII) and (LIII); the introduction of aromatic substituents into the methylene component of the molecule of (LIV) leads (via a zwitter-ionic intermediate) to adduct (LV)[116]:



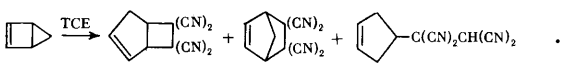
(LI) (a) $R^1 = Ph$, $R^2 = H$; (LII) (LIII)
(b) $R^1 = R^2 = Ph$.



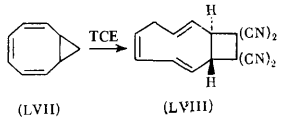
(LIV) (a) R = H; (LV) (LVI)
(b) R = Ph.

It has been shown[117] that compound (LVb) is then aromatised with the opening of the three-membered ring and the loss of HCN; the final product has the structure (LVI).

The reaction of TCE with bicyclo[2,1,0]pent-2-ene in THF leads to a mixture of products via the following mechanism[118]:

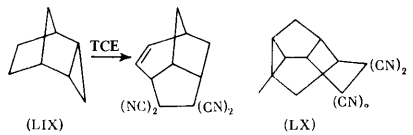


The electrophilic addition of TCE to *cis*-bicyclo[6,1,0]nonatriene (LVII) also proceeds with the simultaneous expansion of both rings[119]. Kinetic measurements have shown that compound (LVII) does not react directly with TCE; the latter adds to the valence isomer of this compound—1-*cis*, 3-*trans*, 5-*cis*, 7-*cis*-cyclononatetraene, with formation of adduct (LVIII)[120]:



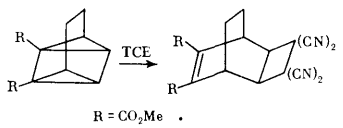
(LVII) (LVIII)

The non-concerted polar cycloaddition of TCE to *endo*-tricyclo[3,2,1,$0^{2,4}$]oct-6-ene (LIX) proceeds with the opening of the three-membered ring[121]. It is of interest that the introduction of a methyl group in the 2-position of compound (LIX) results in the formation of an adduct having the structure (LX)[122]:



(LIX) (LX)

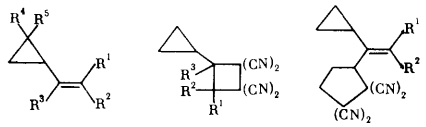
The reaction of TCE with tetracyclo[4,2,$0^{2,8}$,$0^{5,7}$]octane-1,6-dicarboxylate[123] leads to the stereospecific addition to the bis(homocyclobutane) system:



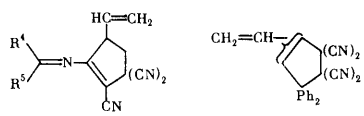
R = CO_2Me.

The reaction with quadricyclane proceeds in the same way[124]. On the other hand, the structure of the adduct with hexamethylprismane[125] has not so far been established.

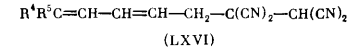
Cyclopropylalkenes. The mode of reaction of TCE with cyclopropylethylenes has been found to depend markedly on the structural characteristics of the latter. Whereas the reaction with cyclopropylethylene (LXIa) and 1,1-dicyclopropylethylenes (LXI, b and c) leads exclusively to the products of [2 + 2]-cycloaddition (LXII), the replacement of the methyl groups by phenyl groups or cyclopropyl groups [compounds (LXI, d and e)] gives rise to adducts having the structure (LXIII). The reaction of compound (LXIf) leads to a 7 : 1 mixture of compounds (LXIV) and (LXV), while the reaction of compound (LXIg) yields, apart from adduct (LXIV), also compound (LXVI) [the reaction with compound (LXIh) proceeds analogously].



(LXI) (LXII) (LXIII)



(LXIV) (LXV)



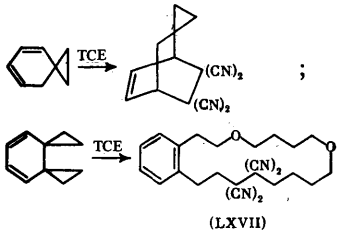
(LXVI)

(a) R = H; (b) R = H, R^3 = cyclopropyl; (c) R = H, $R^1 = R^2$ = Me,
R^3 = cyclopropyl; (d) R = H, $R^1 = R^2 = R^3$ = cyclopropyl;
(e) R = H, $R^1 = R^2$ = Ph, R^3 = cyclopropyl; (f) R = H, $R^4 = R^5$ = Ph;
(g) R = H, $R^4 = R^5$ = *o*-biphenylene; (h) R = H, R^3 = Me, R^4, R^5 = *o*-biphenylene.

The latter finding suggests that cycloadditions of this type take place with formation of a zwitter-ionic intermediate[126-128]. However, the formation of a TCE radical-anion in reactions with cyclopropylethylenes has been confirmed spectroscopically in a number of instances[127].

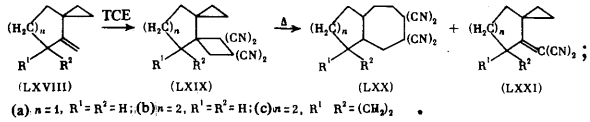
See P.Cernuschi, C.De Micheli, and R.Gandolfi, Tetrahedron Letters, 3667 (1977).

The reaction of spiro[2,5]octa-4,6-diene with TCE[129] led to the normal [4+2]-adduct, while the reaction of dispiro-[2,0,2,4]deca-7,9-diene in THF is accompanied by the opening not only of both three-membered rings but also of two solvent molecules, so that structure (LXVII) has been assigned to the final product[130]:



(LXVII)

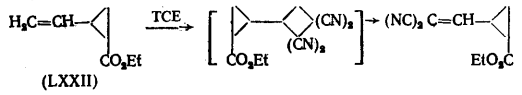
Vinylcyclopropanes (LXVIII, a–c) react with TCE to form the [2+2]-adducts (LXIX) whose thermal rearrangement results in a mixture of compounds (LXX) and (LXXI), the relative amounts of which depend strongly on the nature of the solvent[131,132]:



(LXVIII) (LXIX) (LXX) (LXXI)

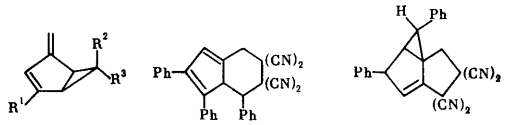
(a) $n=1$, $R^1=R^2=H$; (b) $n=2$, $R^1=R^2=H$; (c) $n=2$, R^1 $R^2=(CH_2)_2$.

A metathetical reaction, analogous to the conversion of (LXVIII) into (LXXI), also takes place in the case of cyclopropylethylene (LXXII)[133]:



(LXXII)

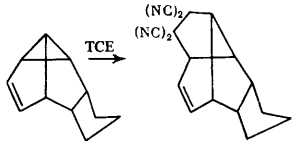
The mode of reaction of TCE with homofulvenes depends markedly on the structure. Whereas compound (LXXIIIa) gives rise to adduct (LXXIV), the reaction with compound (LXXIIIb) leads to adduct (LXXV)[134]:



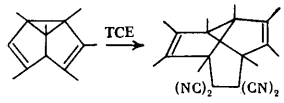
(LXXIII) (LXXIV) (LXXV)

(a) $R^1=R^3=Ph$, $R^2=H$; (b) $R^1=R^3=H$, $R^2=Ph$.

The cycloaddition of TCE to 3,7-*endo*-1-methoxytetracyclo-[6,3,0,$0^{2,11}$,$0^{3,7}$]undec-9-ene proceeds via the [$\pi_\sigma^2+\sigma_s^2+\pi_s^2$] mechanism[135]:

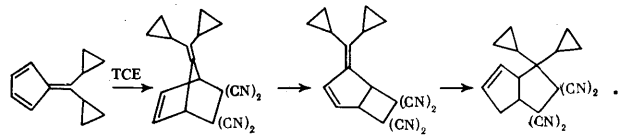


The reaction of octamethylsemibulvalene with TCE leads to adduct (LXXVI)[136]:



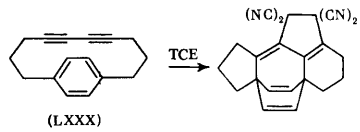
(LXXVI)

The study of the competitive reactivities of diene, ene, and cyclopropyl systems in relation to the reactions of TCE with dicyclopropylfulvene led to the discovery of the phenomenon of the "reaction cascade": the product of the [4+2] diene synthesis (LXXVII) rearranges to the more stable [2+2]-adduct (LXXVIII), which then isomerises quantitatively to the [2+6]-adduct (LXXIX)[137]:



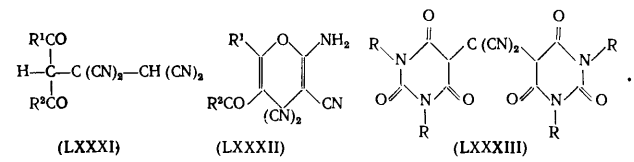
(LXXVII) (LXXVIII) (LXXIX)

Reactions with alkynes. The only example of a reaction of TCE with conjugated diynes is the reaction with compounds of type (LXXX) via the [$\pi 1s+\pi 2s+\pi 2s+\pi 2a$] mechanism[138]:



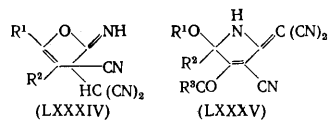
(LXXX)

Reactions with carbonyl compounds and their analogues. The reactions of TCE with active methylene compounds lead to the formation in the first stage of non-cyclic Michael adducts (LXXXI), which then undergo at least four different types of reactions. Reactions with cyclic β-diketones (4-hydroxycoumarin, 4-hydroxycarbostyril[139], dimedone, and cyclohexane-1,3-dione)[140] lead to derivatives of the 4*H*-pyran (LXXXII). The analogous reaction with barbituric acid derivatives leads to the simultaneous formation of the bipyrimidyl derivative (LXXXIII), whose content increases with increasing reaction temperature, although adduct (LXXXII) is not converted into (LXXXIII) on heating[141]:



(LXXXI) (LXXXII) (LXXXIII)

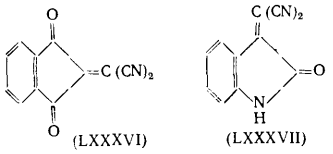
The reactions with 1,3-disubstituted 5-pyrazolones[141] and 2-indanone[142] also involve the formation of disubstituted malononitriles of type (LXXXIII). The reaction of TCE with acetylacetone yields adduct (LXXXI) in ethanol, but in acetonitrile the product is adduct (LXXXII)[143]. On the other hand, when the reaction was carried out in benzene, the only product proved to be the dihydrofuran (LXXXIV), which rearranges to dihydropyrrole (LXXXV) on heating[144]:



(LXXXIV) (LXXXV)

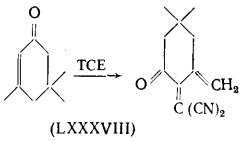
It has been shown[144] that the reactions of other acyclic β-diketones with TCE also lead to dihydropyrroles (LXXXV) via the stage involving the formation of dihydropyrans (LXXXIV), which cannot be isolated in most instances owing to their instability.

On the other hand, the reactions of TCE with indan-1,3-dione and oxindole[145,146] gives rise to the dicyanomethylene derivatives (LXXXVI) and (LXXXVII):

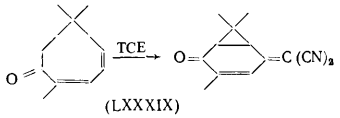


(LXXXVI) (LXXXVII)

The product of the reaction with anthrone in acetonitrile is the normal Michael adduct, but the latter is converted under the influence of a base into 10,10′-bianthrone, which is also formed directly when anthrone is acted upon by TCE in a neutral medium (ethanol–chloroform)[143]. The causes of the differences between these reactions of TCE have still not been completely elucidated. Cyclic α,β-unsaturated ketones do not give rise to bicyclic adducts despite the possibility of enolisation to a planar diene. The reactions of TCE with isophorone[147] and eucarvone[148] proceeds in an acid medium and lead to the formation of the dicyanomethylene derivatives (LXXXVIII) and (LXXXIX), the reaction in the latter case being accompanied by the formation of a three-membered ring:



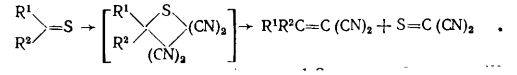
(LXXXVIII)



(LXXXIX)

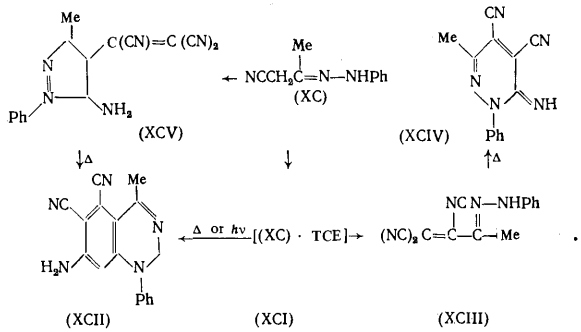
On the other hand, 5-substituted cyclohexa-2,4-dienones do not react with TCE, which is believed to be due to steric factors[149].

Thioketones react with TCE via a cycloaddition–cyclofragmentation mechanism with formation of dicyanomethylene derivatives:



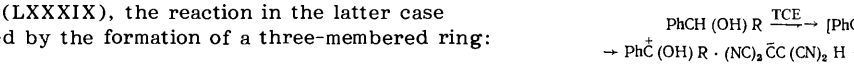
Reactions of this type have been described for 5-aryl-1,2-dimercapto-3-thiones[150], tropothione[151], and thioacetals of thioacylketens[152].

The mode of reaction of TCE with cyanoacetone hydrazones depends markedly on the nature of the solvent and the reaction temperature. Thus the corresponding phenylhydrazone (XC) gives rise in benzene to a 1 : 1 complex (XCI), which is converted into pyrazolopyridine (XCII), either thermally or under irradiation, whereas in ethanol or acetonitrile (at 20 °C) it loses a malonitrile molecule to form the hydrazone (XCIII), which cyclises to compound (XCIV) on heating. On the other hand, the reaction in boiling ethanol leads directly to compound (XCII)—it is believed to proceed via adduct (XCV), undergoing thermal cyclisation to compound (XCII), and not via a stage involving the formation of the complex (XCI)[153]:



(XCV) (XC) (XCIV) (XCII) (XCI) (XCIII)

Dehydrogenation reactions. The reactions of TCE with alkylarylmethanols, tetrahydroquinoline, and 2,5-dihydrofuran lead to the formation of tetracyanoethane and the corresponding dehydrogenated compound, in many instances in almost quantitative yield (the yield of furan is 95%)[154]. It has been shown that the reaction with alcohols proceeds via the mechanism[154]



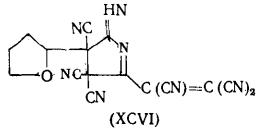
The dehydrogenation reactions of 1,4-dihydrobenzene[109] [see Scheme (7) above] and 9(11)-dihydroergosteryl acetate[155] belong to the same type.

Other addition reactions. The use of TCE as an inhibitor of the radical polymerisation of olefins is based on its ability to combine with free radicals, for example, via the mechanism



(8)

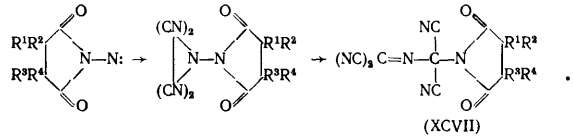
It is believed that the photoaddition of tetrahydrofuran to TCE takes place via a radical mechanism; the structure



(XCVI)

has been assigned to the final product[156].

Carbenes[2,157] and imidonitrenes[158] readily add to TCE to form respectively cyclopropanes and unstable aziridines, which rearrange quantitatively to imines of type (XCVII):

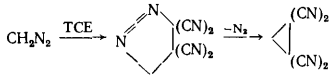


(XCVII)

TCE is hydrogenated to tetracyanoethane[159] and is oxidised by hydrogen peroxide in acetonitrile[160] to tetracyano-oxiran. Tetracyano-oxiran can also be obtained from TCE and primary ozonides[161]. This also results in the formation of the corresponding aldehydes and ketones and in higher yields than in the standard ozonisation procedure, which makes the above reaction particularly useful in structural studies with the aid of ozonolysis.

The addition of chlorine[162] is catalysed by chloride ions, which confirms the electrophilic nature of the bond in TCE. The reaction of TCE with diazomethane[163], leading to pyrazoline which loses a nitrogen molecule on heating, is of interest from the standpoint of the synthesis of nitrogen–carbon

compounds:

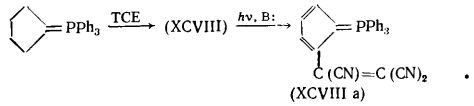


Sulphuric acid and bisulphites add reversibly to TCE even in water[159]. The reactions of alkali metal cyanides leads to the formation of the corresponding pentacyanopropanides[2].

(c) Reactions Involving the Substitution of a Cyano-Group in TCE

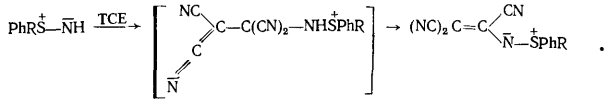
Treatment of TCE with alcohols and primary and secondary aliphatic amines can lead to the successive elimination of one or two HCN molecules and the formation of tricyanovinyl or dicyanomethylene derivatives[2]. However, in the majority of cases the reactions of TCE involving the elimination of a cyano-group stop at the first stage and lead to tricyanovinylation products. Such reactions take place with ammonia and hydrazine, *o*-alkylphenols, pyrrole, phenanthrene, phenylhydrazones, 2-methylfuran, and azulenes[2].

The reaction of TCE with cyclopentadienylphosphorane in the presence of bases leads to tricyanovinylation in the sterically hindered 2-position[164]. In the absence of bases the reaction yields the unstable product (XCVIII), which is converted photochemically or under the influence of bases into compound (XCVIIIa). It has not so far been possible to determine the structure of compound (XCVIII)[164].

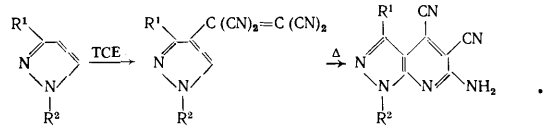


(XCVIII a)

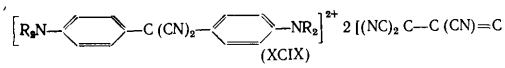
The interaction of TCE with *N*-unsubstituted arylsulphilimines proceeds via an addition–elimination mechanism[165]:



The reaction of 3-aminopyrazoles with TCE also leads to the elimination of HCN and the formation of tricyanovinylpyrazoles, which cyclise on heating to pyrazolo[3,4-*b*]pyridines[141]:



Whereas treatment of aniline with TCE leads to *N*-tricyanovinylaniline (it is believed to proceed via a stage involving the formation of a π-complex, which then reacts with one or two aniline molecules[166]), the product of the reaction with *N*,*N*-dimethylaniline (DMA) is *N*,*N*-dimethyl-4-(tricyanovinyl)-aniline, while *N*,*N'*-dialkylanilines with a higher molecular weight react with TCE to form complex mixtures containing bispentacyanopropenides of substituted malononitriles of type (XCIX) as the main components[167]:

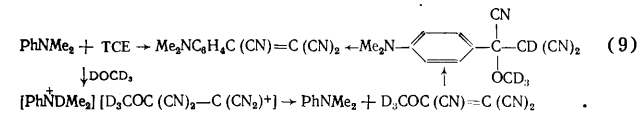


(XCIX)

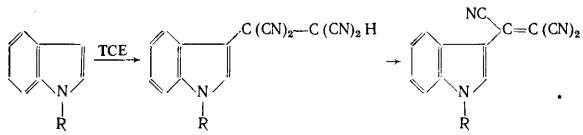
Compounds of this kind have also been detected as admixtures in TCE–DMA reaction mixtures[167].

EPR data indicate the formation of the TCE radical-anion in reactions with *N*,*N*-disubstituted anilines and its virtually complete absence in the case of aniline[166].

The study of the reaction of TCE with DMA in deuteromethanol[168] led to the detection of the intermediates indicated below:



On the other hand it has been shown synthetically and spectroscopically that the intermediate in the reaction of TCE with DMA is not a zwitterion, as was believed previously, but a neutral substituted tetracyanoethane[169]. The same intermediate is formed in the tricyanovinylation of indoles[170]:

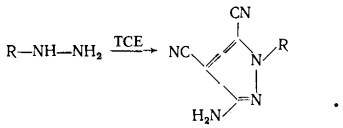


The detailed mechanism of these reactions is still the subject of controversy[171].

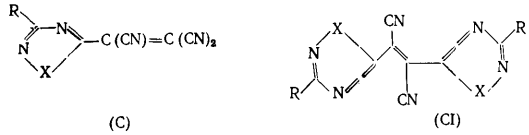
(d) Reactions Involving Addition to a Cyano-Group of TCE

Only a small number of reactions involving addition to a cyano-group of TCE are known. At first sight, this appears unexpected, because a cyano-group in TCE is formally linked to the strongly electron-accepting tricyanovinyl group and should therefore be more reactive than, for example, in dicyanogen. However, the even greater reactivity of the double bond in TCE is responsible for the preferential occurrence of reactions involving this bond.

The reaction of TCE with monosubstituted hydrazines leads to the formation of 3-amino-4,5-dicyanopyrazoles[172,173] and not 5-amino-3,4-dicyanopyrazoles as reported previously[2]:



Nitrile sulphides and nitrile oxides undergo 1,3-dipolar addition to a cyano-group of TCE with formation of mono- and bis-thiadiazoles and mono- and bis-oxadiazoles [(C) and (CI)][157]:



(C) (CI)

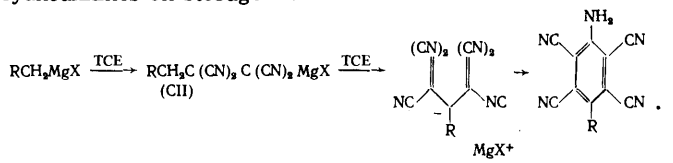
X = O or S.

It is believed that these reactions proceed via a concerted mechanism[174].

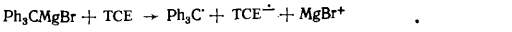
(e) Mixed Reactions

Reactions with Grignard reagents. Treatment of Grignard reagents with one equivalent of TCE leads to adduct (CII), whose treatment with trifluoroacetic acid results in the formation of a high yield of substituted tetracyanoethanes, while

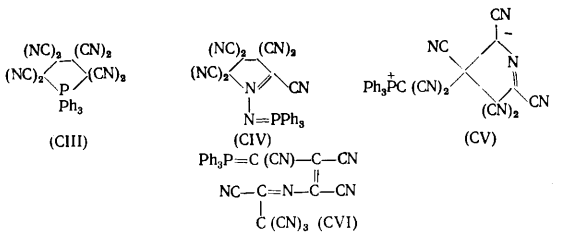
interaction with a second equivalent of TCE gives rise to 3-substituted hexacyanopentadienides, which rearrange to tetracyanoanilines on storage[175]:



The reaction of TCE with phenyl-, isopropyl-, and t-butylmagnesium halides proceeds analogously in the first stage but reaction of adducts (CII) with a second TCE molecule leads to complex mixtures containing, apart from the TCE radical-anion, tricyanovinylbenzene in the case of phenylmagnesium bromide and 3-amino-6,6-dimethylhexacyanocyclohexene in the case of isopropylmagnesium bromide. An electron transfer stage has been discovered in the reaction of TCE with tritylmagnesium bromide[176]:



Reactions with aromatic phosphines. The reactions of TCE with triarylphosphines lead to the formation of 2 : 1 adducts, which hydrolyse to tetracyanoethane and racemic phosphine oxides (in the case of optically active phosphines)[177]. It has been suggested that the hydrolysis involves a stage in which a phosphinium radical-cation is formed[177]. The structure of the adduct of TCE with triphenylphosphine still remains unknown. Instead of the phosphole structure (CIII) proposed initially, which is inconsistent with ^{31}P NMR data[178], the aminoylid structure (CIV) and the betaine structures (CV) and (CVI) are nowadays considered as the most likely[177]:



(f) Polymerisation of TCE

Compared with acrylonitrile and vinylidene cyanide, TCE polymerises with much more difficulty. However, when TCE is heated to a sufficiently high temperature in the presence of metals, metal complexes, alcohols, phenols, amines, and amides, it undergoes degradation with formation of dark-coloured polymeric materials with semiconducting and catalytic properties[2].

A careful study of this type of polymerisation has been carried out[179] for a series of salts of polycyanohydrocarbons, which on heating also undergo spontaneous rearrangements with rupture of the $-C\equiv N$ triple bond and the formation of black powders with a crystalline lustre. Studies by differential thermal analysis showed that the first stage probably involves the formation of radical-ions which then undergo thermal rearrangements.

The polymerisation of TCE in the presence of organotin catalysts takes place with formation in the first stage of addition products having Sn—N bonds and subsequent chain growth as a result of the reaction of these bonds with the cyano-groups[180]. TCE itself can also serve as a catalyst of the polymerisation reaction; thus tricyanoethanol containing TCE initiates the polymerisation of alkyl vinyl ethers[181] [while pure TCE reacts to form cyanobutanes (see above)]. TCE is added in the synthesis of thermostable polyoxymethylenes[182] and in the cationic copolymerisation of olefins (to increase the reactivity of the less reactive component[183]), and also in order to inhibit anionic polymerisation processes[184].

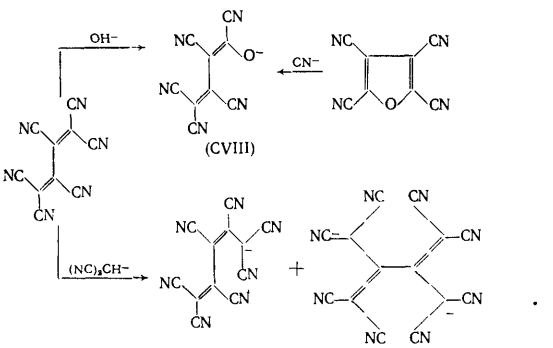
2. Hexacyanobutadiene

The condensation, catalysed by the addition of tetracyanoethane and tricyanoethylene, of the tetracyanoethanedi-ide anion, formed when TCE is treated with sodium hydride in acetonitrile, gives rise to the hexacyanobutenedi-ide anion (CVII), which can also be readily obtained by heating salts of the TCE radical-anion in solution[185]:



The oxidation of the anion (CVII) with bromine or concentrated nitric acid leads to the formation of hexacyanobutadiene (HCBD)—the only known example of the series of percyanoalkadienes.

Being a strong π-acid, HCBD undergoes the diene synthesis reaction as a dienolphile[185] and forms readily complexes with aromatic compounds as well as an unusual complex with tetrathiafulvalene (TTF), in which TTF exists in two oxidation states (0 and +1) and which exhibits a high electrical conductivity at room temperature (its resistivity is $10^{-3}\ \Omega$ cm)[186]. The HCBD radical-ion is formed readily even in the presence of mild agents such as sodium bromide and metallic mercury[185]. Treatment of HCBD with aqueous sodium bicarbonate leads to substitution of one of the terminal cyano-groups by a hydroxy-group. It is of interest that product (CVIII) is also formed when tetracyanofuran reacts with the cyanide ion[185]:



On the other hand, the reaction of HCBD with the malononitrile anion yields products of the substitution of the cyano-groups in both 1- and 2-positions[2,185].

A number of physicochemical properties of HCBD and its radical-anion have been reviewed[2].

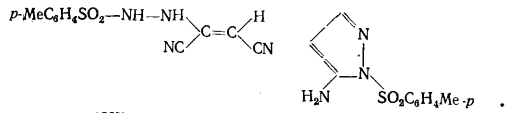
V. PERCYANOALKYNES

The chemistry of dicyanoacetylene (DCA) and dicyanodiacetylene (DCDA), synthesised before all other percyanohydrocarbons (1908), has been developing most vigorously only in the last 15 years. The sharply increased interest in these compounds can be explained not only by the great variety of their chemical properties and of their synthetic possibilities but also by their ability to generate ultrahigh temperatures on combustion in oxygen or ozone. The latter

factor stimulated a detailed investigation of the reactions of DCA not only with oxygen[187-189] but also with active nitrogen[190].

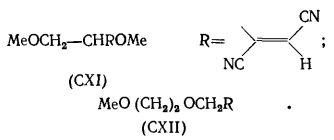
The review of cyanoacetylenes[191] published in 1977 gives a virtually exhaustive description of studies on the physical chemistry and chemistry of DCA and DCDA, so that the list of the main types of reactions of percyanoalkynes can only be supplemented by certain data not considered in the above review and new results.

It has been shown recently that DCA is capable of adding not only to alcohols, thiols, and aromatic amines[191] but also to tosylhydrazine[192]. The adduct has the structure (CIX), while the analogous reaction with cyanoacetylene yields mainly the cyclic adduct (CX)[191]:



(CIX) (CX)

Ethers, normally employed as solvents (tetrahydrofuran, diethyl ether, and monoglyme) also add to DCA. For example, the reaction with monoglyme leads to a 1:1 mixture of compounds (CXI) and (CXII)[193]:



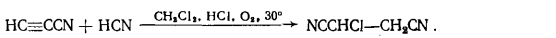
(CXI)

(CXII)

It is believed that the reaction is preceded by the formation of a charge-transfer complex.

The reactions of cyanoacetylenes with hydrogen halides and halogens are more unexpected. The addition of HX (X = Cl or Br) to the acetylenic bond takes place even at room temperature with formation of a mixture of isomers of dicyanohalogenoethylene[194,195]. The addition of bromine to DCA also takes place at room temperature with formation of dibromofumaronitrile[196]. The addition of iodine is much slower even in the presence of iron iodide[196]. The mechanism of this reaction is obscure; it has been suggested[2] that it is more likely to proceed via a radical than an ionic mechanism.

The attempt to obtain DCA from HCN and cyanoacetylene also led to the formal addition of HCl and HCN to cyanoacetylene:



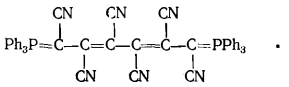
The mechanism of this reaction has still not been elucidated[197]. Bearing in mind the known electrophilic properties of the molecule, the ready formation of a 1:1 complex of DCA with aluminium bromide is fairly unexpected[198]. Although the structure of the complex is unknown, by analogy with many complexes of nitriles with Lewis acids[2] the complex is believed to involve the coordination of aluminium bromide to the cyano-group. The complex is extremely sensitive to moisture and readily reacts with dienes, giving rise to Diels–Alder products.

The study of the ultraviolet spectra of colourless solutions of DCA in aromatic hydrocarbons demonstrated the absence of charge-transfer complexes even for hexamethylbenzene, which forms intensely coloured complexes with tetracyanoethylene[2].

On the other hand, it has been reported[199] that solutions of DCDA in benzene are blue. However, since toluene, being a stronger π-base, gives rise to a blue solution much more slowly, it is believed that the colour of the benzene solution is caused by some other factors, for example, the presence of impurities[2].

DCA reacts vigorously with metal compounds: it is reduced by tributylstannane in methanol, is inserted in the C–Au bond in the reaction with the ferrocenylgold–triphenylphosphine complex, combines with mercury(II) chloride in aqueous solution (in proportions of 2:1), and forms compounds containing C–Co bonds with pentacyanocobalt and octacarbonyldicobalt[191].

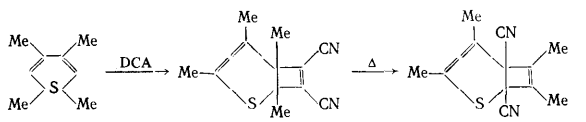
The 3:2 adduct of DCA with triphenylphosphine, formed at room temperature, is believed to have structure (CXIII)[2]:



(CXIII)

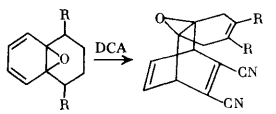
The 1,4-cycloaddition of DCA to dienes has been studied most extensively at the present time and is frequently used to synthesise a wide variety of polycyclic compounds[2,191]. Apart from aliphatic dienes and cyclodienes, DCA reacts with aromatic compounds (benzene, naphthalene, and anthracene) and with heterocycles (derivatives of furan and pyridine). Thiophens are an exception; the structures of thiepins and [2+2]-adducts have been attributed to the products of their reactions with DCA[200].

The latest studies have shown that the adduct of DCA with tetramethylthiophen undergoes the Cope thermal rearrangement, so that the final product has structure (CXIV)[200]:



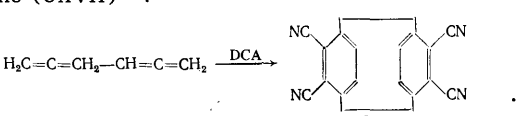
(CXIV)

Arene oxides of type (CXV) react with DCA to form the tricyclic adducts (CXVI)[201]:



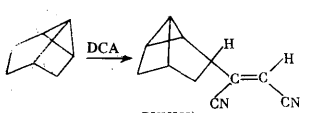
(CXV) (CXVI)

The reaction with hexa-1,2,4,5-tetraene leads to [2,2]paracyclophane (CXVII)[202]:



(CXVII)

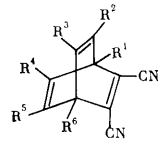
Like TCE, DCA is capable of transannular addition to norbornadiene and barrelene and of reactions, involving ring opening, with strained alicyclic systems of the type of bicyclo[2,1,0]pentane[191]. However, the reaction with tricyclo[4,1,0,$0^{3,7}$]heptane leads to a substituted maleonitrile (CXVIII) and not to a cyclic adduct[203]:



(CXVIII)

A study of the ultraviolet spectra of adducts of DCA with aromatic hydrocarbons (CXIX) revealed the presence of absorption bands corresponding to the formation of intramolecular charge-transfer complexes, where the dicyanoethylene bridge functions as the acceptor and the remaining two double

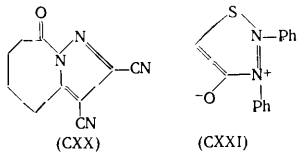
bonds are donors[29]:



(CXIX)

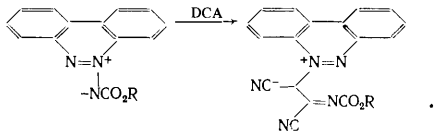
Being an active dipolarophile, DCA undergoes 1,3-cycloaddition reactions with diazomethane, diazocyclopentadienes, ethyl diazoacetate, benzonitrile oxide, and isoquinolinium ylids; it also reacts with 1,4-dipoles—for example, with 2-hydroxy-1,6,8-trimethyl-4-oxopyrimido[1,2-*a*]pyrimidinium[191].

The reaction of DCA with 2-diazocyclohexanone, which proceeds via a 1,3-dipolar addition stage, includes a sigmatropic (1,5)-acyl shift and leads to 1,10-diazabicyclo[5,3,0]deca-7,9-dien-2-one (CXX)[204]:



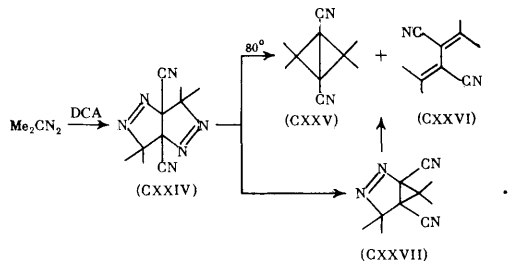
(CXX) (CXXI)

Phosphoryldiazo-compounds[205], anhydro-4-hydroxythiazolium hydroxide (CXXI)[206], and azimines [for example, compound (CXXII)] have also been made to react with DCA as 1,3-dipoles. In the last instance the resulting [1,3]-adduct undergoes a spontaneous electrocyclic opening of the triazoline ring and is converted into the azomethine (CXXIII)[207]:



(CXXII) (CXXIII)

Treatment of DCA with an excess of dimethyldiazomethane gives rise to pyrazoline (CXXIV) and the latter loses on heating two nitrogen molecules with formation of a mixture of products whose main components are the dicyclobutane (CXXV) and the diene (CXXVI):



(CXXIV) (CXXV) (CXXVI) (CXXVII)

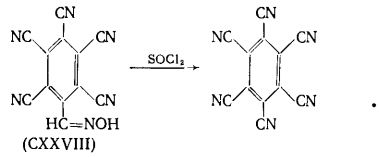
The latter is formed quantitatively when compound (CXXIV) is irradiated and particularly in the thermolysis of compound (CXXV). When the bisadduct (CXXIV) was heated cautiously, it was possible to obtain also cyclopropanopyrazoline (CXXVII), whose thermolysis also gives rise to a mixture of compounds (CXXV) and (CXXVI) but with a higher content of the diene[208].

Cyanoacetylenes have attracted particular attention as potential monomers for semiconducting polymers. Thus DCA–olefin copolymers[209] have semiconducting properties and are thermally stable, which permits their use in the manufacture of transistors, thermoelectric devices, and as casings for rocket engines.

Furthermore, DCA polymers proved to be convenient objects for the study of the electrophoretic behaviour of polyconjugated systems[210].

VI. PERCYANOARENES

The only example of aromatic percyanohydrocarbons is hexacyanobenzene (HCB), which was synthesised for the first time in 1963 by the dehydration of the oxime (CXXVIII) in accordance with the reaction[211]:



(CXXVIII)

The synthesis of HCB from 1,3,5-tricyano-2,4,6-trifluorobenzene and calcium cyanide in dimethylformamide in a yield of approximately 50% was described later[212].

Treatment of 2,4,6-trichloro-1,3,5-tricyanobenzene with sodium methoxide or ethoxide (at −20 °C) followed by treatment with sodium cyanide (at −5 °C) and refluxing in a $POCl_3$–pyridine mixture gives rise to a mixture of HCB and chloropentacyanobenzene (in proportions of 1 : 9 in the former case and 1 : 3 in the latter)[213].

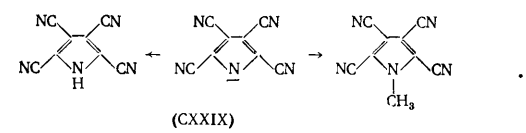
The molecular orbitals of HCB were calculated by Shwarts[214]. HCB readily forms coloured complexes with aromatic hydrocarbons[211] and a black 1 : 2 complex with pyrene[215].

Spectroscopic studies on complexes of this composition with aromatic methoxy- and methylthio-compounds led to the establishment of the following series based on the strength of "electron-accepting" properties: tetracyanoquinodimethane > TCE > HCB > tetracyanobenzene[216]. The hydrolysis of HCB leads to the formation of pentacyanophenol—a very strong acid whose methylation with diazomethane yields pentacyanoanisole and whose halogenation gives rise to the corresponding halogenopentacyanobenzenes[217]. The reactions of HCB with alcohols and amines take place even at room temperature[218,219]. In the former case there is slow formation of alkoxypentacyanobenzenes, which react with the excess alcohol even following a moderate temperature rise, forming the corresponding ether and pentacyanophenol[218]. The reactions of HCB with ammonia and dimethylamine also proceed under exceptionally mild conditions and lead to products of mono- and 1,3-di-substitution in the aromatic ring. However, the analogous reaction with aniline and o-diaminobenzene requires heating to 80 °C.[219]

As regards condensed aromatic percyano-systems, there have been no reports of compounds containing more than two cyano-groups, with the exception of tricyanoperylene[220].

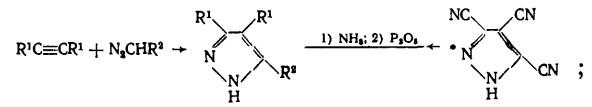
VII. PERCYANO-DERIVATIVES OF NITROGEN HETEROCYCLES

Although salts of tetracyanopyrrole (CXXIX) can be obtained by treating tetracyano-1,4-dithiine with azide ions[221] and can be converted into the corresponding pyrrole (on ion exchange resins) and *N*-methylpyrrole, the percyano-compound has not so far been synthesised:



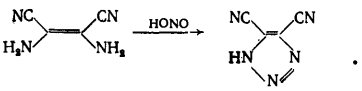
(CXXIX)

Tetracyanopyrazole and tricyanotriazole have not been synthesised either, although 3,4,5-tricyanopyrazole has been prepared in two ways[222]:



(a) R^1=CN, R^2=CO_2Et;
(b) R^1=CO_2Et, R^2=CN .

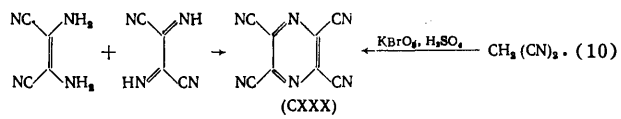
It is of interest that it is not impossible to carry out the direct synthesis (for $R = R^1 = CN$)[222]. 4,5-Dicyanotriazole can be obtained by treating diaminomaleonitrile with nitrous acid[223-227]:



Both compounds are strong acids and readily form stable salts.

The reports of the synthesis of pentacyanopyridine have not so far been confirmed by the description of the relevant experiment, although the pentacyanopyridine radical-anion was studied by EPR in 1966.[228]

Tetracyanopyrazine (CXXX) can be obtained by the condensation of diaminomaleonitrile and diiminosuccinonitrile[229] or by the direct oxidation of malononitrile[230] via reaction (10). In both cases 1-aminotricyanopyrazine and 1,2-diaminodicyanopyrazine are formed simultaneously:

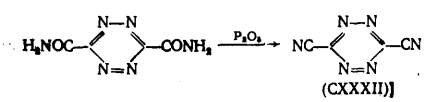


(CXXX)

Tetracyanopyrazine itself is used as a regulator of plant growth[231] and derivatives of 3,5-diamino-2,4-dicyanopyrazine, obtained by treating compound (CXXX) with ammonia and primary and secondary amines, are used to synthesise fluorescent materials, dyes, and "ladder" polymers[232,233]. The reaction of compound (CXXX) with *N,N*-disubstituted anilines leads to the corresponding 2-(4-aminophenyl)-3,5,6-tricyanopyrazines, which are used as dyes[234]. The mass spectra of polycyanopyrazines have been investigated[235].

The most thoroughly investigated six-membered heterocyclic pernitrile, which has been known for a long time, is tricyano-1,3,5-triazine[131]. In contrast to the usual method for the synthesis of *sym*-triazines, compound (CXXXI) cannot be obtained by the trimerisation of dicyanogen. It was synthesised in a very low yield in 1919 via the triamide of cyanuric acid[236]. Pyrolysis of compound (CXXXI) gives rise to dicyanogen[236,237] and treatment with alcohols leads to the successive substitution of cyano-groups by alkoxy-groups and the formation of the corresponding cyanurates[236,238]. Reduction with alkali metals or irradiation of a mixture of compound (CXXXI) and hexamethylmelamine results in a stable blue radical-ion[239,240].

The synthesis of 3,6-dicyano-1,2,4,5-tetrazine (CXXXII) was achieved in 1961[241] via the reaction



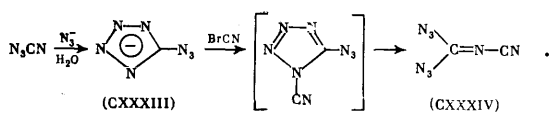
(CXXXII)]

Compound (CXXXII) was obtained in an amount of 0.15 g and a yield of 12–18%; being extremely unstable, it decomposed fully after several days even in an atmosphere of argon and in the absence of moisture[241]. The latest studies are limited to a description of the mass-spectrum[242] and the calculation of the molecular orbitals of the radical-anion (CXXXII)[243].

VIII. PERNITRILES WITH A NITROGEN–CARBON SKELETON

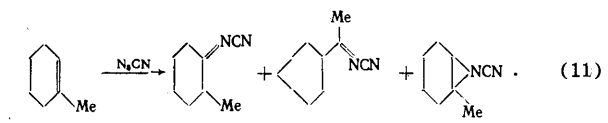
The simplest pernitrile of this series—tricyanamide—has not so far been synthesised. The attempt to obtain it from silver dicyanamide and chlorocyanogen was unsuccessful[244], while reports of the synthesis of this compound by the pyrolysis of mercury thiocyanate[245] and mercury dicyanamide[246] are apparently erroneous.

One of the most thoroughly investigated "azapernitriles", namely, cyanogen azide, is a colourless oily liquid which detonates on mechanical, electrical, and thermal shock and can be obtained in virtually quantitative yield when sodium azide is treated with chlorocyanogen in an anhydrous medium[247]. When cyanogen azide, obtained by the analogous reaction with bromocyanogen in an aqueous medium, is acted upon by the azide ion, the anion of 5-azidotetrazole (CXXXIII) is formed and reacts in its turn with bromocyanogen to form the *gem*-diazide (CXXXIV)—the product of the rearrangement of an unstable cyanazidotetrazole. Treatment of cyanogen azide with aqueous alkali at room temperature can also lead to the formation of the salt (CXXXIII). Hydrogen sulphide readily reduces cyanogen azide to cyanamide[247]:



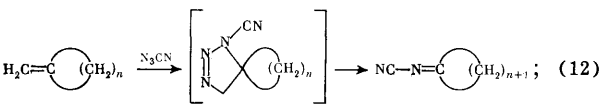
(CXXXIII) (CXXXIV)

Below 60 °C, cyanogen azide reacts as a powerful electrophilic azide, adding to olefins with formation of unstable triazolines, which decompose to alkylidenecyanamides and (or) *N*-cyanoaziridines, whose proportions can be varied within wide limits depending on the type of olefin and the solvent employed[248]:

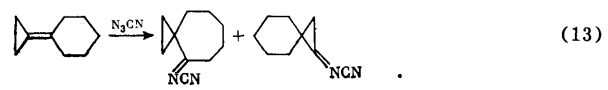


(11)

Cycloalkenes can also undergo ring contraction[248,249] [for example, via reaction (11)]; on the other hand, the reactions of methylenecycloalkanes are accompanied as a rule by ring expansion[243] [reaction (12)]. Alkylidenecycloalkanes give rise to a mixture of isomers [for example, via reaction (13)]:



(12)

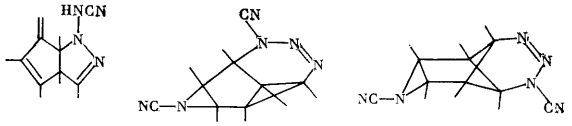


(13)

We may note that the attempt to catalyse these reactions by the introduction of silver ions did not lead to an increase of the rate of reaction, but altered (in many cases considerably) the proportions of the isomers formed[249]. Alkylidenecyanamides hydrolyse extremely readily to the corresponding ketones, which makes these reactions the basis of a valuable synthetic method.

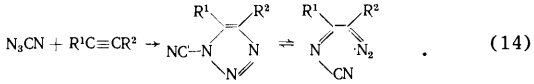
The time and temperature variation of the reaction of cyanogen azide with hexamethylbicyclo[2,2,0]hexadiene is of interest; the reaction gives rise to adduct (CXXXV) after 10 h at 20 °C, to compound (CXXXVI) at 0 °C over the same

period, and to compound (CXXXVII) at 0 °C after 20 min[250]:



(CXXXV) (CXXXVI) (CXXXVII)

The reaction of cyanogen azide with acetylenes leads to the formation of an equilibrium mixture of triazoles and diazoamines via the reaction[251]



(14)

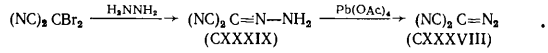
The photolysis and thermolysis of cyanogen azide above 50 °C[248,252,253] give rise to cyanonitrene, which is a convenient intermediate in processes involving the modification of polymers[254] and in the synthesis of aziridines, alkylidenecyanamides, and azepines from olefins and aliphatic and aromatic hydrocarbons respectively[248,255].

Cyanogen azide reacts with tertiary phosphines to form *N*-cyanophosphinimides which are effective repellents, insecticides and hematocides[256]. The reactions with aromatic arsines and phosphites proceeds similarly[257,258]. The method for the synthesis of *N*-alkoxyalkylcyanamides is based on the reaction of cyanogen azide with ethers and polyethers[259].

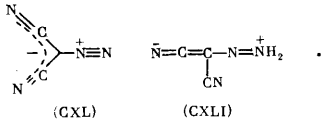
The molecular[260] and electronic[261,262] structures, ionisation potentials[263], and microwave[264,265], infrared[266,267], and Raman[267] spectra of cyanogen azide have also been calculated and investigated.

The pyrolysis of cyanogen azide in the gas phase at 200 °C leads to the formation (apparently as a result of the reaction of cyanonitrene with the unreacted cyanogen azide) of azodinitrile NC–N=N–CN[268]—a red-orange volatile explosive compound, which was subsequently synthesised from hydrazine and chlorocyanogen in the presence of sodium azide[269]. The study of the infrared and Raman spectra of this compound showed that it exists exclusively in the *trans*-form (it has been shown by calculation to be more stable than the *cis*-form by 20 kcal mol^{-1}[270–272]). Azodinitrile is a powerful dienophile, which reacts instantaneously (even at room temperature) with cyclopentadiene, 2,3-dimethylbutadiene, and even (albeit slowly) anthracene[268].

Dicyanodiazomethane (CXXXVIII) was first synthesised from dibromomalononitrile via the hydrazone (CXXXIX)[73]:

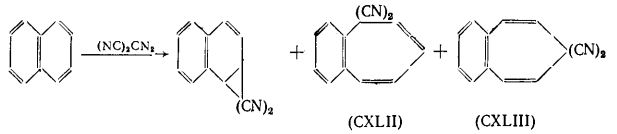


Here one should note the unusual stability of the hydrazone (CXXXIX). The high dipole moments of compounds (CXXXVIII) and (CXXXIX) (5.82 and 3.8 D respectively) together with NMR and ultraviolet spectroscopic data confirmed the contribution of the betaine structures (CXL) and (CXLI).



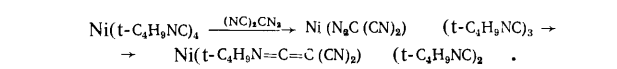
(CXL) (CXLI)

In contrast to other diazo-compounds, dicyanodiazomethane oxidises primary and secondary amines even at 20 °C, being itself reduced to the hydrazone (CXXXIX). While it is resistant to the action of even 2 *N* sulphuric acid, it readily reacts with nucleophiles such as triphenylphosphine and Grignard reagents[2]. The thermolysis and photolysis[2] of compound (CXXXVIII) yield dicyanocarbene, which makes it possible, for example, to obtain cyclopropanes by reaction with olefins[274] and norcaradiene derivatives from benzene and xylene[275]. However, it is of interest that the thermolysis of dicyanodiazomethane in naphthalene yields in addition products (CXLII) and (CXLIII)[275]:

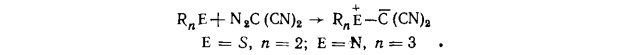


(CXLII) (CXLIII)

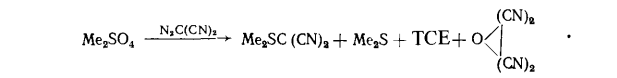
The reaction of compound (CXXXVIII) with isonitrile complexes proceeds via a substitution stage and leads to the formation of keten imines[276]:



A method for the synthesis of sulphonium and ammonium dicyanomethylides is based on the interaction of compound (CXXXVIII) with sulphides and amines[277,278]:



The reaction of compound (CXXXVIII) with dimethyl sulphoxide proceeds via the mechanism[277]



The infrared spectra of compound (CXXXVIII) and of the free radical $C(CN)_2$ have also been studied[279].

Treatment of TCE with sodium hydride in acetonitrile yields the hexacyanobutenediide anion (CVII), which cyclises in aqueous solutions to the aminotetracyanocyclopentadienide anion via 1-amino-2,3,4,5,5-pentacyanocyclopentadiene. The diazotisation of the cyclopentadienide anion yields diazotetracyanocyclopentadiene[280]—the initial compound for the synthesis of various salts of substituted tetracyanocyclopentadienes which are used as propellants, weed killers and pesticides, sensitisers and, dyes[281]—in particular the salts of pentacyanocyclopentadiene and cyanodiazotetracyanocyclopentadiene as well as the salts of azobis(tetracyanocyclopentadiene), which are used in the syntheses of organic conductors[282].

---o0o---

Thus analysis of the literature data shows that the chemistry of polycyano-compounds has been the subject of increasing attention by investigators for more than half a century and that approximately four-fifths of the total number of publications dealing with these compounds have appeared in the last fifteen years.

The range of reactions in which pernitriles can be involved is extremely wide. They can be reduced and oxidised, can undergo various kinds of fragmentation, are capable of undergoing reactions involving addition to double bonds (when these are present) and to cyano-groups, which can participate in their turn in substitution reactions. The majority of pernitriles are extremely sensitive to nucleophilic attack and readily give rise to radical-anions.

The stability of these compounds varies within very wide limits, ranging from that of tetracyanoethylene, which can be isolated from solution in fuming nitric acid, to compounds of the type of cyanogen azide or azodinitrile, which decompose explosively. The reactions of pernitriles proceed in most cases at room temperature, but the identification of certain products of these reactions is sometimes extremely difficult because of their instability or their tendency to polymerise.

Thus not a single instance of the identification of dicyanogen, formed in reactions of polynitriles, has been described hitherto and the products of the reactions of percyano-anions are frequently unidentified coloured amorphous substances which probably have a polymeric structure.

There is no doubt that further development of the chemistry of pernitriles may prove to be extremely fruitful for the synthesis of compounds with valuable properties (for example, organic conductors, ingredients of fuel mixtures, thermostable polymers, etc.), and for the development of new synthetic methods and methods for the investigation of problems in theoretical and physical organic chemistry.

IX. APPENDIX

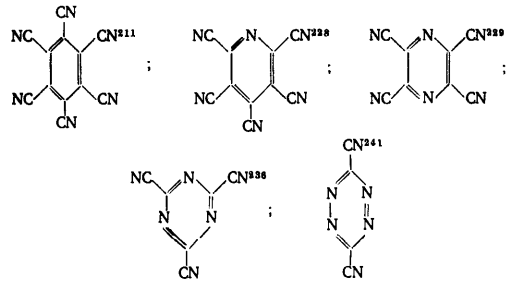
1. NITROGEN–CARBON COMPOUNDS§

I. Pernitriles:

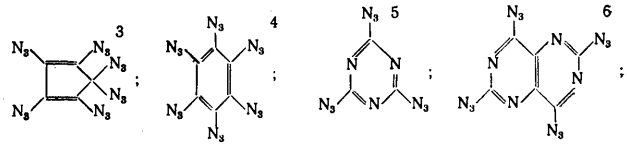
$(CN)_2^{263}$; $C(CN)_4^{14}$; $C_2(CN)_6^{28}$; $(NC)_2C{=}C(CN)_2^{264}$;

$(NC)_2C{=}C(CN){-}C(CN){=}C(CN)_2^{265}$;

$NCC{\equiv}CCN^{266}$; $NCC{\equiv}C{-}C{\equiv}CCN^{265}$; $NCN{=}C{=}NCN^{266}$; $NCN{=}NCN^{268}$;

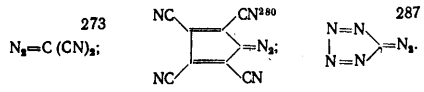


II. Perazides:

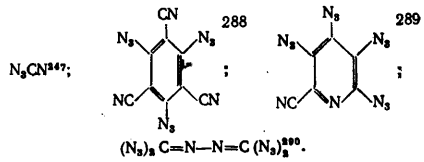


$(N_3)_2C{=}N{-}N{=}C(N_3)_2^7$.

III. Diazo-Compounds



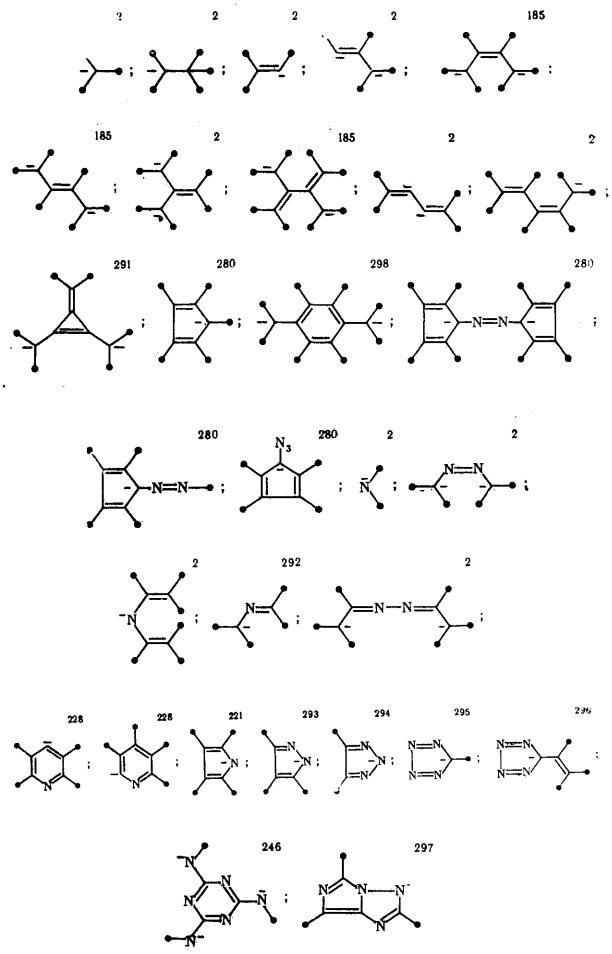
IV. Mixed Nitrogen–Carbon Compounds:



$(N_3)_2C{=}N{-}N{=}C(N_3)_2^{290}$.

§ The literature references are to publications in which the synthesis was described for the first time.

2. NITROGEN–CARBON PERCYANO-ANIONS¶



¶ The symbol ⇀ always designates the $-C{\equiv}N$ group.

REFERENCES

1. O.Griszkiewicz-Trochimowski, Bull.Soc.chim.France, 1437 (1961).
2. E.Ciganek, W.J.Linn, and O.W.Webster, in "The Chemistry of the Cyano Group" (Edited by Z.Rappoport), Intersci.Publ.London, 1970, p.427.
3. J.Senior, J.Org.Chem., **3**, 1 (1938).
4. US P.3217017 (1966); Chem.Abs., **64**, 1896 (1966).
5. J.G.Morse and L.P.Kuhn, US Clearing House Fed. Sci.Techn.Inform., No.713665 (1970); Chem.Abs., **75**, 19826 (1970).
6. "Beilsteins Handbuch der Organischen Chemie", Bd. 26, II. Springer-Verlag, Berlin, 1954, Vol.26, II, p.16.
7. N.B.Smirnova and I.Ya.Postovskii, Biol.Akt.Soed., 102 (1965).
8. US P.2990412 (1961); Chem.Abs., **55**, 25256 (1961).
9. E.W.Hughes, J.Chem.Phys., **3**, 1 (1935).
10. A.Schmidtmann, Chem.Ber., **29**, 1174 (1896).
11. A.Hantzch and G.Osswald, Chem.Ber., **32**, 641 (1899).

12. L.Birckenbach and K.Huttner, Chem.Ber., **62**, 160 (1929).
13. E.Griszkiewicz-Trochimowski and O.Griszkiewicz-Trochimowski, Mem.Poudres, **40**, 109 (1958).
14. E.Mayer, Monatsh., **100**, 462 (1969).
15. D.I.Makhon'kov, Candidate's Thesis, Moscow State University, 1977.
16. D.S.Barnes, C.T.Mortimer, and E.Mayer, J.Chem. Termodyn., **5**, 481 (1973).
17. H.Oberhammer, Z.Naturforsch., **26a**, 2042 (1971).
18. D.Britton, Acta Cryst., **30b**, 1818 (1974).
19. H.Bock, E.Haselbach, E.Mayer, and H.Stafast, Helv.Chim.Acta, **59**, 1035 (1976).
20. N.S.Zefirov, N.M.Sergeev, D.I.Makhon'kov, and L.Ya.D'yachkova, Zhur.Org.Khim., **13**, 3 (1977).
21. R.E.Hester, K.M.Lee, and E.Mayer, J.Phys.Chem., **74**, 3373 (1970).
22. N.S.Zefirov, N.K.Chapovskaya, and D.I.Makhon'kov, Zhur.Org.Khim., **12**, 617 (1976).
23. D.I.Makhon'kov, N.S.Zefirov, and L.Ya.D'yachkova, Zhur.Org.Khim., **13**, 968 (1977).
24. E.Mayer, Angew.Chem., **81**, 627 (1969).
25. E.Mayer, Monatsh., **101**, 846 (1970).
26. W.Beck, K.Schopp, C.Oetker, and R.Schlödder, Chem.Ber., **106**, 2145 (1973).
27. L.Birkenbach and K.Huttner, Chem.Ber., **62b**, 153 (1929).
28. S.Trofimenko and B.C.McKusick, J.Amer.Chem.Soc., **84**, 3677 (1962).
29. D.N.Dhar, Chem.Rev., **67**, 611 (1967).
30. R.Foster, Mol.Complexes, **2**, 251 (1974).
31. D.N.Dhar, Chem.Techn.Rep., 2 (1966).
32. W.H.Baddley, Inorg.Chim.Acta, **2**, 7 (1968).
33. A.A.Berlin and A.J.Sherle, Inorg.Macromol.Rev., 1, 235 (1971).
34. K.Koyama and M.Nishimura, Kagaku To Kogyo, **45**, 243 (1971); Chem.Abs., **75**, 109890 (1971).
35. K.Venkaterswarlu and M.K.Warrier, Bull.Soc.Roy. Sci.Liege, **38**, 766 (1969).
36. H.Stafast and H.Bock, Tetrahedron, **32**, 855 (1976).
37. O.A.Ganson, A.R.Burke, R.B.King, and M.S.Saran, Inorg.Nuclear Chem.Letters, **10**, 291 (1974).
38. I.Murgich and S.Pissanetzky, J.Chem.Phys., **62**, 92 (1975).
39. C.E.Brion and L.A.R.Olsen, Int.J.Mass Spectrom. Ion Phys., **9**, 413 (1972).
40. I.Ikemoto, K.Samizo, T.Fujikawa, K.Ishii, T.Ohta, and H.Kuroda, Chem.Letters, 785 (1974).
41. K.N.Houk and L.L.Munchausen, J.Amer.Chem.Soc., **98**, 937 (1976).
42. M.Rougee and C.Andre, J.Polymer Sci., **16c**, 3167 (1968).
43. V.P.Nefedov, B.P.Bespalov, and V.V.Titov, Zhur.Org.Khim., **10**, 1553 (1974).
44. S.M.Shein, T.V.Leshina, N.A.Geraseva, A.D.Khmelinskaya, and L.V.Bryukhovetskaya, Zhur.Org.Khim., **11**, 2538 (1975).
45. H.Sakurai and M.Kira, J.Amer.Chem.Soc., **95**, 6826 (1973).
46. V.F.Traven' and R.West, Zhur.Obshch.Khim., **44**, 1837 (1974).
47. H.A.Gardner and J.K.Kochi, J.Amer.Chem.Soc., **97**, 5026 (1975).
48. V.F.Traven', V.F.Donyagina, N.S.Fedotov, G.V.Everst, and B.I.Stepanov, Zhur.Obshch.Khim., **46**, 2761 (1976).
49. R.Gompper and D.Lash, Tetrahedron Letters, 2687 (1973).
50. S.R.Tanny and F.W.Fowler, J.Org.Chem., **39**, 2715 (1974).
51. S.Nishida and I.Moritani, J.Org.Chem., **38**, 1878 (1973).
52. Y.Shirota, I.Nagata, and H.Mikawa, Chem.Letters, 49 (1972).
53. Y.Shirota, I.Nagata, H.Mikawa, Y.Nakata, and T.Nogami, J.Chem.Soc., Perkin Trans.I, 14 (1977).
54. K.R.Berger, E.R.Bichl, and P.C.Reeves, J.Org. Chem., **39**, 477 (1974).
55. P.D.Barlett, Quart.Rev., **24**, 473 (1970).
56. N.K.Hamer and M.E.Stubbs, J.Chem.Soc., Perkin Trans.I, 2971 (1972).
57. O.A.Nesmeyanova, S.V.Zotova, and E.I.Vostokova, Izv.Akad.Nauk SSSR, Ser.Khim., **11**, 2639 (1976).
58. P.Reeves, J.Henery, and R.Pettit, J.Amer.Chem. Soc., **91**, 5889 (1969).
59. P.Reeves, T.Devon, and R.Pettit, J.Amer.Chem. Soc., **91**, 5890 (1969).
60. T.Miyamoto and Y.Odaira, Tetrahedron Letters, 43 (1973).
61. A.Huth, H.Straub, and E.Muller, Tetrahedron Letters, 2845 (1973).
62. F.Toda and N.Dan, Chem.Comm., 30 (1976).
63. R.Schug and R.Huisgen, Chem.Comm., 60 (1975).
64. R.Huisgen, R.Schug, and G.Steiner, Angew.Chem., **86**, 47 (1974).
65. I.Karle, J.Flippen, R.Huisgen, and R.Schug, J.Amer.Chem.Soc., **97**, 5285 (1975).
66. I.R.Dombroski, M.L.Hallensleben, and W.Regel, Tetrahedron Letters, 3881 (1971).
67. G.D.Hartman and T.G.Traylor, Tetrahedron Letters, 939 (1975).
68. A.Culter, D.Ehntholt, W.P.Giering, P.Lennon, S.Raghu, A.Rosan, M.Rosenblum, J.Tancrede, and D.Wells, J.Amer.Chem.Soc., **98**, 3495 (1976).
69. R.W.Hoffmann, U.Bressel, J.Gehlhaus, and H.Häuser, Chem.Ber., **104**, 873 (1971).
70. R.W.Hoffmann and W.Schaeffer, Angew.Chem.Int. Ed., 9, 733 (1970).
71. M.Ozolins and G.H.Schenk, Anal.Chem., **33**, 1035 (1961).
72. F.E.Rogers, J.Phys.Chem., 76, 106 (1972).
73. A.I.Konovalov, Ya.D.Samuilov, and Z.A.Khairullin, Zhur.Org.Khim., 8, 229 (1972).
74. A.I.Konovalov, Zhur.Org.Khim., **5**, 1713 (1969).
75. T.Kojima and T.Inukai, J.Org.Chem., **35**, 1342 (1970).
76. C.C.Thompson and D.D.Holder, J.Chem.Soc., Perkin Trans.II, 257 (1972).
77. A.I.Konovalov, V.N.Solomonov, and A.N.Ustyugov, Dokl.Akad.Nauk SSSR, **211**, 102 (1973).
78. P.Scheiss, Helv.Chim.Acta, **55**, 2365 (1972).
79. I.Gasteiger and R.Huisgen, Angew.Chem., Int.Ed., 11, 716 (1972).
80. L.A.Paquette, W.Kitching, W.E.Heyd, and R.H.Meisinger, J.Amer.Chem.Soc., **96**, 7371 (1974).
81. R.Huisgen, W.E.Konz, and G.A.Gream, J.Amer. Chem.Soc., **92**, 4105 (1970).
82. G.Köbrich and B.Rösner, Tetrahedron Letters, 2031 (1973).
83. N.Morita and T.Asao, Chem.Letters, 71 (1975).
84. D.N.Butler and R.A.Snow, Canad.J.Chem., **53**, 256 (1975).
85. H.Hogeveen and P.W.Kwant, Tetrahedron Letters, 3747 (1973).
86. G.Capozzi and H.Hogeveen, J.Amer.Chem.Soc., **97**, 1479 (1975).

87. F.A.Carey and A.S.Court, J.Org.Chem., **37**, 4474 (1972).
88. T.Sasaki, K.Kanematzu, and K.Jizuka, J.Org. Chem., 41, 1105 (1976).
89. N.J.Mruk and H.Tieckelmann, Tetrahedron Letters, 1209 (1970).
90. US P.3978171 (1976); Chem.Abs., **85**, 192180 (1976).
91. A.R.Bursies, P.Laszlo, M.Murray, F.Stone, and A.Gordon, J.Organomet.Chem., **111**, 31 (1976).
92. U.Moedlhammer and H.Hopf, Angew.Chem., **87**, 492 (1975).
93. H.Maurer and H.Hopf, Angew.Chem., **88**, 687 (1976).
94. H.Duerr, B.Ruge, and B.Weiss, Annalen, 1150 (1974).
95. M.F.Semmelhack, J.S.Foos, and S.Katz, J.Amer. Chem.Soc., **94**, 8637 (1972).
96. K.H.Pfoertner, Helv.Chim.Acta, **58**, 833 (1975).
97. A.M.Andrews, Diss.Abs., Int.B, **32**, 6286 (1972).
98. A.I.Konovalov, V.D.Kiselev, A.N.Ustyugov, and N.G.Gess, Zhur.Org.Khim., **12**, 2541 (1976).
99. G.J.Miller, A.Singermann, and L.Friedman, J.Amer. Chem.Soc., **93**, 7109 (1971).
100. S.Kuroda, M.Oda, and Y.Kitahara, Angew.Chem., **85**, 93 (1973).
101. J.T.Barton and M.Juvet, Tetrahedron Letters, 2561 (1975).
102. M.Green, S.Heathcock, and D.S.Wood, J.Chem. Soc., Dalton Trans., 1564 (1973).
103. L.A.Paquette, S.V.Ley, S.Maiorana, D.F.Schneider, M.J.Broadhurst, and R.A.Boggs, J.Amer.Chem.Soc., **97**, 4658 (1975).
104. Z.Goldschmidt and Y.Bakal, Tetrahedron Letters, 1229 (1976).
105. J.M.Photis, J.Heterocycl.Chem., 7, 1249 (1970).
106. R.A.Abramovitch, S.R.Challand, and E.F.V.Seriven, J.Amer.Chem.Soc., **94**, 1374 (1972).
107. J.M.Photis, J.Heterocycl.Chem., 8, 729 (1971).
108. R.M.Acheson and J.Woollard, J.Chem.Soc., Perkin Trans.I, 744 (1975).
109. E.Haselbach and M.Rossi, Helv.Chim.Acta, **59**, 2635 (1976).
110. H.Iwamura, Y.Tanabe, and H.Kobayashi, Tetrahedron Letters, 1987 (1976).
111. H.Prinzbach, H.Fritz, H.Hagemann, D.Hunkler, S.Kagabu, and G.Philippossian, Chem.Ber., **107**, 1971 (1974).
112. H.P.Loeffler, T.Martini, H.Musso, and G.Schroeder, Chem.Ber., **103**, 2109 (1970).
113. K.Kurabayashi and T.Mukai, Chem.Comm., 1016 (1972).
114. T.Martini and J.A.Kampmeier, Angew.Chem., Int. Ed., **9**, 236 (1970).
115. A.A.P.Noordstand, H.Steinberg, and T.I.DeBoer, Tetrahedron Letters, 2611 (1975).
116. R.Noyori, N.Hayashi, and M.Kato, J.Amer.Chem. Soc., **93**, 4948 (1971).
117. J.E.Baldwin and E.R.Peavy, J.Org.Chem., **36**, 1441 (1971).
118. J.E.Baldwin and R.K.Pinschmidt, Tetrahedron Letters, 935 (1971).
119. L.Paquette, M.J.Broadhurst, L.K.Read, and J.Clardy, J.Amer.Chem.Soc., **95**, 4639 (1973).
120. G.Boche, H.Weber, and J.Benz, Angew.Chem., **86**, 238 (1974).
121. M.E.Battiste, J.M.Coxon, G.P.Posey, W.R.King, M.Mathew, and G.J.Palenic, J.Amer.Chem.Soc., **97**, **947 (1975).**
122. J.Coxon, M.De Bruin, and C.K.Lau, Tetrahedron Letters, 337 (1975).
123. H.Prinzbach, G.Philippossian, and U.Scheidegger, Helv.Chim.Acta, **53**, 857 (1970).
124. D.M.Lemal and J.P.Lokemsgard, J.Amer.Chem.Soc., **88**, 593 (1966).
125. C.D.Smith, J.Amer.Chem.Soc., **88**, 4273 (1966).
126. N.Shimizu, S.Ishizuka, T.Takashi, and S.Nishida, Chem.Letters, 751 (1975).
127. S.Nishida, J.Moritani, and T.Teraji, J.Chem.Soc., D, 36 (1971).
128. F.Effenberger and O.Gerlach, Chem.Ber., 107, 278 (1974).
129. A.De Meijere, Chem.Ber., **107**, 1702 (1974).
130. D.Kaufmann, A.De Meijere, B.Hingerty, and W.Saender, Angew.Chem., 87, 842 (1975).
131. S.Sarel, A.Felzenstein, and J.Yovell, Chem.Comm., 859 (1973).
132. S.Sarel, A.Felzenstein, and J.Yovell, Chem.Comm., 753 (1974).
133. A.Felzenstein, S.Sarel, and J.Yovell, Chem.Comm., 918 (1975).
134. R.Askani and J.P.Chesick, Chem.Ber., 106, 8 (1973).
135. G.Subrahmanyam, Indian J.Chem., **14b**, 365 (1976).
136. R.Askani and M.Wieduwilt, Chem.Ber., 109, 1887 (1976).
137. A.Cornelis and P.Laszlo, J.Amer.Chem.Soc., 97, 244 (1975).
138. T.Kaneda, T.Ogawa, and S.Misumi, Tetrahedron Letters, 3373 (1973).
139. H.Junek, Monatsh., 96, 1421 (1965).
140. H.Junek and H.Aigner, Z.Naturforsch., 25b, 1423 (1970).
141. H.Junek and H.Aigner, Chem.Ber., **106**, 914 (1973).
142. O.S.Wolfbeis, G.Zacharias, and H.Junek, Monatsh., 106, 1207 (1975).
143. Z.Rappoport and D.Ladkani, J.Chem.Soc., Perkin Trans.I, 2595 (1974).
144. J.W.Ducker and H.J.Gunter, Austral.J.Chem., 26, 1551 (1973).
145. H.Junek and H.Sterk, Tetrahedron Letters, 4309 (1968).
146. H.Junek and H.Aigner, Monatsh., 102, 622 (1971).
147. A.Cornelis, P.Laszlo, and C.Pasquet, Tetrahedron Letters, 4335 (1973).
148. M.Acar, A.Cornelis, and P.Laszlo, Tetrahedron Letters, 3625 (1972).
149. G.Anderson, Acta Chem.Scand., 30b, 403 (1976).
150. A.Rouessac and J.Vialle, Bull.Soc.chim.France, 2054 (1968).
151. T.Machiguchi, K.Okuma, M.Hoshino, and Y.Kitahara, Tetrahedron Letters, 2011 (1973).
152. R.Okazaki, A.Kitamura, and N.Inamoto, Chem. Comm., 257 (1975).
153. H.Junek, A.Hermetter, H.Fischer-Colbrie, M.Wittmer-Metz, and A.M.Braun, Chem.Ber., 109, 1787 (1976).
154. T.Nishigushi, H.Sakakibara, and K.Fukuzumi, Chem.Letters, 649 (1976).
155. A.J.Andrews, R.C.Fort, and P.W.L.Quesne, J.Org.Chem., **36**, 83 (1971).
156. J.Dickmann and C.J.Pedersen, J.Org.Chem., **28**, 2879 (1963).
157. I.E.Franz, R.K.Hose, and H.K.Pearl, J.Org.Chem., 41, 620 (1976).
158. H.Person, A.Foucaud, K.Luauglath, and C.Fayat, J.Org.Chem., **41**, 2141 (1976).
159. W.J.Middleton, R.E.Heckert, and E.L.Little, J.Amer. Chem.Soc., 80, 2783 (1958).

160. W.J.Linn, O.W.Webster, and R.E.Benson, J.Amer. Chem.Soc., **85**, 2032 (1963).
161. R.Criegee and P.Gunther, Chem.Ber., **96**, 1564 (1963).
162. C.L.Dickinson and B.C.McKusick, J.Org.Chem., 29, 3087 (1964).
163. J.Bastus and J.Castells, Proc.Chem.Soc., 216 (1962).
164. C.W.Rigby, E.Lord, M.P.Naan, and C.D.Hall, J.Chem.Soc., **B**, 1192 (1971).
165. Y.Tamura, K.Sumoto, H.Matsushima, H.Tanigushi, and M.Ikeda, J.Org.Chem., **38**, 4324 (1973).
166. P.N.Ngo, Diss.Abs, Int.B, 4209 (1974).
167. P.Farrell and R.K.Wojtowski, J.Chem.Soc., C, 1394 (1970).
168. M.J.T.Robinson and S.M.Rosenfeld, Tetrahedron Letters, 1431 (1975).
169. P.Farrell and R.K.Wojtowski, J.Chem.Soc., (C), 1390 (1970).
170. S.Kusabayashi and H.Mikawa, Bull.Chem.Soc. Japan, **45**, 836 (1972).
171. T.Nogami, T.Hasegawa, Y.Shirota, and H.Mikawa, Bull.Chem.Soc.Japan, **48**, 3048 (1975).
172. D.D.Traficante, M.Sundaralingam, P.Prusiner, T.Ito, and T.Sakurai, J.Org.Chem., 40, 1815 (1975).
173. R.A.Earl, R.J.Pugmire, R.R.Ganopatti, and L.B.Townsend, J.Org.Chem., **40**, 1822 (1975).
174. Y.M.Chang, J.Sims, and K.N.Honk, Tetrahedron Letters, 4445 (1975).
175. H.C.Gardner and J.K.Kochi, J.Amer.Chem.Soc., **98**, 558 (1976).
176. M.N.Ponomarchuk, L.F.Kasukhin, and V.D.Pokhodenko, Zhur.Obshch.Khim., **41**, 43 (1971).
177. C.D.Hall, M.P.Naan, and R.L.Powel, J.Chem.Soc., (B), 1683 (1971).
178. M.A.Shaw, J.C.Tebby, R.S.Ward, and D.H.Williams, J.Chem.Soc.(C), 1609 (1968).
179. C.E.Looney and J.R.Downing, J.Amer.Chem.Soc., 80, 2840 (1958).
180. S.Freireich, D.Gertner, and A.Zilkna, Europ. Polymer J., **9**, 411 (1973).
181. R.F.Tarvin, S.Aoki, and J.K.Stille, Macromolecules, **5**, 663 (1972).
182. US P.3963676 (1978); Chem.Abs., **85**, 124681 (1976).
183. G.Heublein, O.Barth, and W.Roemer, Adv.Ionic Polymer Proc.Int.Symp., 175 (1972).
184. A.A.Berlin, A.I.Kadantseva, A.A.Ivanov, G.K.Goryacheva, and N.I.Vorob'eva, Dokl.Akad. Nauk SSSR, **228**, 1364 (1976).
185. O.W.Webster, J.Amer.Chem.Soc., 86, 2898 (1964).
186. F.Wudl and W.E.Southwick, Chem.Comm., 254 (1974).
187. J.A.Meyer and D.W.Setser, J.Phys.Chem., **74**, 3452 (1970).
188. W.C.Hand and M.R.Richard, J.Phys.Chem., **80**, 557 (1976).
189. W.C.Hand and H.R.Obenauf, J.Phys.Chem., **76**, 269 (1972).
190. R.H.Obenauf, Diss.Abstr.Int.B, **33**, 1075 (1972).
191. A.N.Volkov and A.N.Nikol'skaya, Uspekhi Khim., **46**, 712 (1977) [Russ.Chem.Rev., No.4 (1977)].
192. M.Franck-Neumann and G.Leclerc, Bull.Soc.chim. France, 247 (1975).
193. R.J.Bushby, J.Chem.Soc., Perkin Trans.I, 274 (1974).
194. C.Moureu and J.C.Bongrand, Ann.Chim., **14**, 5 (1920).
195. C.Moureu and J.C.Bongrand, Compt.rend., **170**, 1025 (1920).
196. E.Kloster-Jensen, Acta Chem.Scand., **17**, 1866 (1963).
197. S.Murahashi, T.Takizawa, and S.Kurioka, Nippon Kagaku Zasshi, **77**, 1689 (1956); Chem.Abs., **53**, 5163 (1959).
198. E.Ciganek, Tetrahedron Letters, 3321 (1967).
199. US P.2200689 (1940); Chem.Abs., **34**, 6455 (1940).
200. D.N.Reinhoudt and C.G.Kowenhoven, Tetrahedron, **30**, 2093 (1974).
201. F.G.Klaerner and E.Vogel, Angew.Chem., **85**, 864 (1973).
202. H.Hopf and E.T.Lenich, Chem.Ber., **107**, 1891 (1974).
203. P.G.Gassman and G.D.Richmond, J.Amer.Chem. Soc., **92**, 2093 (1970).
204. M.Martin and M.Regitz, Annalen, 1702 (1974).
205. A.Hartmann and M.Regitz, Phosphorus, **5**, 21 (1974).
206. K.T.Potts, E.Houghton, and U.P.Singh, J.Org. Chem., **39**, 3627 (1974).
207. S.R.Challand, S.F.Gait, M.J.Ranee, W.C.Rees, and R.C.Storr, J.Chem.Soc., Perkin Trans.I, 26 (1975).
208. M.Franck-Neumann and D.Martina, Tetrahedron Letters, 1767 (1975).
209. US P.3419537 (1968); Chem.Abs., **70**, 48028 (1969).
210. E.Machowska, Coll.Czech.Chem.Comm., 4395 (1968).
211. K.Wallenfels and K.Friedrich, Tetrahedron Letters, 1223 (1963).
212. K.Friedrich and S.Oeckl, Chem.Ber., **103**, 3951 (1970).
213. BRD P.2205226 (1973); Chem.Abs., **79**, 115334 (1973).
214. V.N.Shwarts, "Obshchaya i Prikladnaya Khimiya, Respublikanskii Mezhvedomstvennyi Sbornik" (General and Applied Chemistry. All-Republic Interdepartmental Collection), 1972, No.4, p.59.
215. BRD P.1183900 (1965); Chem.Abs., **62**, 9074 (1965).
216. A.Sucharda-Sobczyk and L.Syper, Roczniki Chem., **49**, 479 (1975).
217. K.Friedrich and S.Oeckl, Chem.Ber., **106**, 2361 (1973).
218. K.Friedrich and S.Oeckl, Chem.Ber., **106**, 3796 (1973).
219. K.Friedrich and S.Oeckl, Chem.Ber., **106**, 3803 (1973).
220. A.Zinke, A.Dadieu, and A.Pongratz, Monatsh. **50**, 77 (1928).
221. R.D.West and H.E.Simmons, US P.3221113 (1965); Chem.Abs., **64**, 8359 (1966).
222. C.D.Weis, J.Org.Chem., **27**, 3695 (1962).
223. L.E.Hinkel and G.O.Richards, J.Chem.Soc., 1432 (1937).
224. H.Bredereck and G.Schmotzer, Annalen, **600**, 95 (1956).
225. E.Griszkiewicz-Trochimowski, Roczniki Chem., 1, 468 (1921).
226. E.Griszkiewicz-Trochimowski, Zhur.Russ.Fiz.Khim. Obshch., **55**, 548 (1924).
227. E.Griszkiewicz-Trochimowski, Zhur.Russ.Fiz.Khim. Obshch., **55**, 551 (1924).
228. P.Neumann, Dissertation, University of Freiburg, 1967.
229. R.W.Begland, D.R.Hartter, and D.S.Donald, J.Org.Chem., **39**, 1235 (1974).
230. BRD P.2425928 (1974); Chem.Abs., **83**, 10144 (1975).
231. BRD P.2134946 (1972); Chem.Abs., **76**, 140884 (1972).

232. US P.3808209 (1974); Chem.Abs., **83**, 81219 (1975).
233. US P.3928351 (1975); Chem.Abs., **84**, 122557 (1976).
234. US P.3963715 (1976); Chem.Abs., **85**, 178975 (1976).
235. G.Holzmann, H.W.Rothkopf, R.Mueller, and D.Woehlire, Org.Mass Spectrom., **10**, 97 (1975).
236. E.Ott, Chem.Ber., **52**, 656 (1919).
237. I.B.Johns, E.A.McElhill, and J.O.Smith, J.Chem. Eng.Data, **7**, 277 (1962).
238. A.S.Bayley, B.R.Henn, and J.M.Langdom, Tetrahedron, **19**, 161 (1963).
239. A.Carrington, H.C.Longuet-Higgins, and P.F.Todd, Mol.Phys., **9**, 211 (1965).
240. M.T.Jones, J.Amer.Chem.Soc., **88**, 5060 (1966).
241. E.Griszkiewicz-Trochimowski and M.Bousquet, Compt.rend., **258**, 2992 (1961).
242. S.J.Weininger and E.R.Thornton, J.Amer.Chem. Soc., **89**, 2950 (1967).
243. J.A.Pople, D.Beveridge, and P.A.Dobosh, J.Amer. Chem.Soc., **90**, 4201 (1968).
244. C.Mauguin and L.J.Simon, Compt.rend., **170**, 993 (1920).
245. E.S.Franklin, J.Amer.Chem.Soc., **44**, 486 (1922).
246. W.L.Burdick, J.Amer.Chem.Soc., **47**, 1485 (1925).
247. F.D.Marsh, J.Org.Chem., **37**, 2966 (1972).
248. M.E.Hermes and F.D.Marsh, J.Org.Chem., **37**, 2969 (1972).
249. J.E.McMurry and A.F.Coppolino, J.Org.Chem., (**38**), 2881 (1973).
250. A.Anastssiou and S.W.Eachus, J.Chem.Soc., D, 429 (1970).
251. M.E.Hermes and F.D.Marsh, J.Amer.Chem.Soc., **89**, 4760 (1967).
252. H.Okabe and A.Mele, J.Chem.Phys., **51**, 2100 (1969).
253. H.W.Kroto, T.F.Morgan, and H.H.Sheena, Trans. Faraday Soc., **66**, 2237 (1976).
254. US Appl.620292 (1968); Chem.Abs., **71**, 22556 (1969).
255. A.G.Anastassiou, J.Amer.Chem.Soc., **87**, 5512 (1965).
256. US P.3896188 (1975); Chem.Abs., **83**, 164373 (1975).
257. US P.3776950 (1973); Chem.Abs., **81**, 63769 (1974).
258. J.I.G.Cadogan and I.Gosney, J.Chem.Soc., Perkin Trans.I, 460 (1974).
259. US P.3427323 (1969); Chem.Abs., **71**, 70149 (1969).
260. A.Almenningen, B.Bak, J.Peter, and T.G.Strand, Acta Chem.Scand., **27**, 1538 (1973).
261. K.Bolton, R.D.Brown, and F.R.Burden, Chem. Phys.Letters, **15**, 79 (1972).
262. V.V.Mel'nikov, S.A.Zacheslavskii, L.F.Baeva, and B.V.Gidaspov, Zhur.Org.Khim., **8**, 1805 (1972).
263. B.Bak, P.Jansen, and H.Stafst, Chem.Phys.Letters, **35**, 247 (1975).
264. G.L.Blackman, K.Bolton, R.D.Brown, F.R.Burden, and A.Mishra, J.Mol.Spectrosc., **47**, 457 (1973).
265. C.C.Costain and H.W.Kroto, Canad.J.Phys., **50**, 1453 (1972).
266. H.F.Shurvell and D.W.Hyslop, J.Chem.Phys., **52**, 881 (1970).
267. B.Bak, O.Bang, F.Nicolaisen, and O.Rump, Spectrochim.Acta, **27a**, 1865 (1971).
268. F.D.Marsh and M.E.Hermes, J.Amer.Chem.Soc., **87**, 1819 (1965).
269. B.Bak, R.Eskildsen, and P.Jansen, Acta Chem. Scand., **25**, 3181 (1971).
270. B.Bak, R.Eskildsen, and P.Jansen, J.Mol.Struct., 11, 25 (1972).
271. B.Bak and P.Jansen, J.Mol.Struct., 12, 167 (1973).
272. B.Bak, Dansk.Kem., 53, 81 (1972).
273. E.Ciganek, J.Org.Chem., 30, 4198 (1965).
274. Y.Tatsuno, A.Konishi, A.Nakamura, and S.Otsuka, Chem.Comm., 558 (1974).
275. E.Ciganek, J.Amer.Chem.Soc., 89, 1454 (1967).
276. D.J.Yarrow, J.A.Ibers, and Y.Tatsuno, J.Amer. Chem.Soc., **95**, 8590 (1973).
277. J.Rieser and K.Friedrich, Annalen, 641 (1976).
278. J.Rieser and K.Friedrich, Annalen, 669 (1976).
279. W.H.Smith and G.E.Leroi, Spectrochim.Acta, 25a, 1917 (1969).
280. O.W.Webster, J.Amer.Chem.Soc., 88, 4055 (1966).
281. US P.3536694 (1970); Chem.Abs., **74**, 65559 (1971).
282. R.C.Wheland and J.L.Gillson, J.Amer.Chem.Soc., **98**, 3916 (1976).
283. V.Migridichian, "The Chemistry of Organic Cyanogen Compounds", New York, 1947.
284. T.L.Cairns, R.A.Carboni, D.D.Coffman, R.E.Heckert, E.L.Little, B.C.McKusick, R.M.Scribner, and H.L.Winberg, J.Amer.Chem.Soc., 80, 2775 (1958).
285. C.Moureu and J.C.Bongrand, Bull.Soc.chim.France 846 (1909).
286. D.R.Williams and R.Damrauer, Theoret.Chim.Acta, **23**, 195 (1971).
287. R.Kuhn and H.Kainer, Angew.Chem., 65, 442 (195
288. E.Wassermann, K.Schueller, and W.Yager, Chem.Phys.Letters, 259 (1968).
289. C.Pannel, US P.3773774 (1973); Chem.Abs., 80, 59869 (1974).
290. C.V.Hart, J.Amer.Chem.Soc., 50, 1922 (1928).
291. T.Fukunaga, J.Amer.Chem.Soc., 98, 610 (1976).
292. L.Bucsis and K.Friedrich, Chem.Ber., **109**, 2469 (1976).
293. K.Friedrich and W.Ertel, Tetrahedron Letters, 4771 (1972).
294. C.D.Weis, J.Org.Chem., **27**, 3695 (1962).
295. L.E.Hinkel and G.O.Richards, J.Chem.Soc., 1432 (1937).
296. P.Scheiner, Tetrahedron Letters, 4489 (1971).
297. M.Brown, US P.3338915; Chem.Abs., **68**, 87299 (1970).
298. O.W.Webster, D.R.Hartter, R.W.Begland, W.A.Sheppard, and A.Cairncross, J.Org.Chem., **37**, 4134 (1972).

Faculty of Chemistry,
Lomonosov Moscow State University

Translated from *Uspekhi Khimii*, 49, 679 - 705 (1980) U.D.C. 547.4

Organometallic Derivatives of Diazoalkanes

O.A.Kruglaya and N.S.Vyazankin

The methods of synthesis and properties of organometallic derivatives of diazo-compounds are examined, attention being concentrated on the influence of the metal or the organometallic fragment on the structure and reactivity of the diazo-compounds. Studies on the use of metal-containing diazoalkanes as precursors of carbynes and α-metallated carbenes as well as studies on the reactivity of the latter are discussed.
The bibliography includes 165 references.

CONTENTS

I. Introduction 357
II. Methods of synthesis 357
III. Reactions without the evolution of nitrogen 359
IV. Reactions involving the intermediate formation of carbenes and carbynes 362
V. Structural and spectroscopic studies 366

I. INTRODUCTION

Two types of organometallic derivatives of diazoalkanes are known. The first includes only two compounds: 1-diazo-3-triethylsilyl-2-propanone and ferrocenyl(phenyl)diazomethane[1,2]; in these compounds the metal atom and the diazo-group are separated by hydrocarbon fragments. The second type includes α-metallated diazoalkanes in which one of the carbon atoms is linked both to the diazo-group and to the metal atom. The chemistry of these compounds is developing vigorously, because, apart from their continuously expanding applications in organometallic synthesis, they are a potential source of carbynes—unstable derivatives of univalent carbon. Furthermore, they are used extensively as precursors of α-metallated carbenes—short-lived species with a high and unusual reactivity. For example, singlet α-silylcarbenes frequently isomerise to sila-alkanes $R_2Si{=}CR'_2$—unstable intermediates with a $(p{-}p)\pi$ bond between the carbon and silicon atoms.

The considerable advances in the studies on the structure and reactivity of carbynes, α-metallated carbenes, and sila-alkanes are closely related to the progress in the chemistry of organometallic derivatives of diazo-compounds. The most complete compilation of data on the chemistry of α-metallated diazoalkanes (up to 1969) is given in Lappert and Poland's review[3]. Latest advances in the chemistry of organophosphorus diazo-compounds are discussed in other reviews[4,5].

II. METHODS OF SYNTHESIS

1. Metallation of Aliphatic Diazo-Compounds

In consequence of the enhanced CH acidity of diazoalkanes of the type $HC(N_2)R$, the latter are readily metallated by methyl-, n-butyl-, and phenyl-lithium. Diazomethyl-lithium[6-9], which is involved in a tautomeric equilibrium with lithium isocyanamide[10,11], trimethylsilyldiazomethyl-lithium[12-15], ethyl lithiodiazoacetate[16-20], and dialkyl lithiodiazomethylphosphonates[15] have been obtained in this way:

$$R'Li + HC(N_2)R \rightarrow LiC(N_2)R + R'H \quad ;$$
$$R{=}H,\ Me_3Si,\ COOEt,\ (MeO)_2P(O){-},\ \text{or}\ (EtO)_2P(O){-}$$

The metallation of diazoacetic ester requires low temperatures (between −110° and −65°C), while Me_3SiCHN_2 is smoothly metallated at 0 °C. The reaction of methyl-lithium with diazoethane in ether at 20 °C leads to a complex mixture of products[21]. Lithium diisopropylamide smoothly metallates α-diazoketones[17]. The reaction of the latter with butyl-lithium is complex:

$$\text{iso-Pr}_2NLi + HC(N_2)COR \xrightarrow[-70^\circ]{THF} LiC(N_2)COR \quad .$$

$Me_3SiC(N_2)K$ and $(EtO)_2P(O)C(N_2)K$ have been obtained by treating diazoalkanes with potassium t-butoxide[15].

Silver oxide metallates diazoacetic ester[22-24], diazoketones, and phosphorus-containing diazoalkanes[25,26], but the yield of silver derivatives depends greatly on the quality of the oxide[17]:

$$Ag_2O + 2HC(N_2)R \rightarrow H_2O + 2AgC(N_2)R \quad .$$

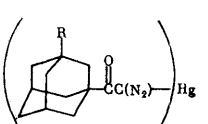
The reaction of silver acetylacetonate with dimethyl diazomethylphosphonate leads to a quantitative yield of $AgC(N_2)P(O)(OMe)_2$.[27] Treatment of silver acetate with an excess of CH_2N_2 in ether in the presence of pyridine at −5 °C yielded the complex $Ag_2CN_2.C_6H_5N$. When the complex is kept in vacuo at 25 °C, Ag_2CN_2, an explosive light-sensitive compound, is formed[28].

Diazoacetic ester is metallated at −70 °C by alkylmagnesium halides and dialkylmagnesium compounds[17], while at 0 °C Grignard reagents attack the diazo-group[29,30].

Yellow mercury(II) oxide reacts under mild conditions with the nitrile and esters of diazoacetic acid, diazoketones, and ethyl diazomethylphosphonate[25,31-37]:

$$HgO + 2HC(N_2)R \rightarrow H_2O + Hg[C(N_2)R]_2$$

Mercury derivatives of adamantoyldiazomethane (I) were obtained recently by this procedure[38]:



(I)

R = H, Cl, or Br .

Mercuration of dimethyl diazomethylphosphonate by mercury acetylacetonate leads to $Hg[C(N_2)P(O)(OMe)_2]_2$ in 80% yield[27].

Asymmetric alkyl- and aryl-mercuridiazoalkanes have been obtained by the reaction of diazo-compounds with arylmercury hydroxides[39], arylmercury silylamides[40], and organomercury

ethoxides[39]. The last compounds were synthesised *in situ* by treating RHgCl with alcoholic potassium ethoxide:

$$PhHgOH + HC(N_2)COMe \xrightarrow{-H_2O} PhHgC(N_2)COMe$$

$$RHgN(SiMe_3)_2 + HC(N_2)COOEt \rightarrow RHgC(N_2)COOEt + (Me_3Si)_2NH$$

$$RHgCl + EtOK \xrightarrow{+EtOH} RHgOEt \xrightarrow[-EtOH]{+HC(N_2)R'} RHgC(N_2)R' \quad ;$$

R = Me, t-Bu, $PhCH_2$, or Ph; R′ = CN, Me, Ph, COMe, COOMe, or COOEt.

We may note that the reactions of diazomethane with $RHgN(SiMe_3)_2$ and RHgOEt lead to crystalline readily detonated disubstituted derivatives of diazomethane regardless of the reactant ratio[39,40], for example:

$$2\,RHgN(SiMe_3)_2 + CH_2N_2 \rightarrow (RHg)_2CN_2 + 2(Me_3Si)_2NH \quad .$$

When bis[bis(trimethylsilyl)amide]mercury or mercury acetate is treated with diazomethane[40,41] in ether, the highly explosive polymeric diazomethylenemercury $(HgCN_2)_n$ is formed. According to Wright et al.[41], the latter reaction also leads to bis(diazomethyl)mercury $Hg(CHN_2)_2$, but attempts to repeat the synthesis of this diazomethane derivative were unsuccessful[33,40]. Polymeric diazomethylenezinc and diazomethylenecadmium have been obtained similarly[40]:

$$M[N(SiMe_3)_2]_2 + CH_2N_2 \rightarrow (MCN_2)_n + 2(Me_3Si)_2NH \quad ;$$

M = Hg, Zn, or Cd.

The above method of synthesis is fairly universal. Thus the interaction of diazomethane with organometallic compounds containing metal–nitrogen bonds leads to diazomethane derivatives of the type $(Me_nM)_2CN_2$, where M = germanium, arsenic, and their analogues, as well as thallium[6,40,42–45], for example:

$$(Me_2TlNMe_2)_2 + CH_2N_2 \rightarrow (Me_2Tl)_2CN_2 + 2Me_2NH \quad ;$$

$$2Me_2BiN(Me)SiMe_3 + CH_2N_2 \rightarrow (Me_2Bi)_2CN_2 + 2Me_3Si(Me)NH \quad .$$

Monometallated diazomethane derivatives Me_3GeCHN_2 and Me_2AsCHN_2 have been obtained in the same way but at controlled temperatures, using Me_3SnCl as the complex-forming agent and in the prsence of a large excess of diazomethane[44,46], for example:

$$Me_3GeNMe_2 + CH_2N_2 + Me_3SnCl \xrightarrow[-80°]{Et_2O} Me_3GeCHN_2 + Me_3SnCl \cdot Me_2NH \quad .$$

Diazo-compounds with two different organometallic fragments have been obtained analogously[47]:

$$R_nM{-}NR_2' + Me_2AsCHN_2 \rightarrow \begin{matrix} Me_2As \\ \diagdown \\ R_nM \end{matrix}\!\!>CN_2 + R_2'NH \quad ;$$

$R_nM = Me_3Si$, Me_3Ge, Me_3Sn, Me_3Pb, Me_2Sb, or Me_2Bi;

$$Hg[N(SiMe_3)_2]_2 + 2Me_2AsCHN_2 \rightarrow Hg[C(N_2)AsMe_2]_2 + 2(Me_3Si)_2NH \quad .$$

A large series of α-metallated diazocarbonyl compounds, derivatives of zinc-subgroup elements[40,48], germanium[40,45,49–53], and arsenic[43,54], have been obtained by treating compounds having metal–nitrogen bonds with α-diazoketones and diazoacetate esters, for example[50]:

$$R_{4-n}Sn(NR_2')_n + n\,HC(N_2)COOEt \rightarrow R_{4-n}Sn[C(N_2)COOEt]_n + n\,R_2'NH \quad ;$$

R = Me, Et, t-Bu, or Ph; R′ = Me or Et; n = 1, 2.

Methyl diazoacetate is readily metallated by trialkylmethoxystannanes[52], but this reaction requires more severe conditions than the previous ones (≥100 °C):

$$R_3SnOMe + HC(N_2)COOMe \rightarrow \underset{(85\%)}{R_3SnC(N_2)COOMe} + MeOH \quad ;$$

R = Et or n-Bu.

Bromotrimethylsilane silylates diazoacetate esters in the presence of amines[52], while chlorotrimethylsilane does not enter into similar reactions[6]:

$$Me_3SiBr + HC(N_2)COOR + Et_3N \xrightarrow[C_6H_6]{80°} Me_3SiC(N_2)COOR + Et_3N \cdot HBr \quad ;$$

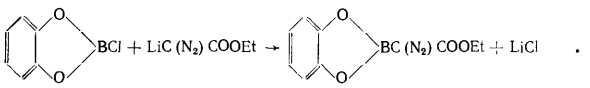
R = Me or Et.

2. Synthesis from α-Metallated Diazoalkanes

Ethoxycarbonyldiazomethyl-lithium reacts under mild conditions (below −50 °C) with halogenotrimethylsilanes, halogenotrimethylplumbanes, and chlorotributylstannane[16,17,49]:

$$R_3MCl + LiC(N_2)COOEt \xrightarrow{THF} R_3MC(N_2)COOEt + LiCl \quad .$$

A boron-containing diazoacetic ester has been obtained analogously[17]:



The interaction of trimethylsilyldiazomethyl-lithium $Me_3SiC(Li)N_2$ with Me_3SiCl in a pentane–hexane mixture at temperatures between −90° and −100 °C leads to bis(trimethylsilyl)diazomethane[14]. The reactions of diazomethyllithium with Ph_3GeCl, Me_3SnCl, and Ph_3SnBr also lead to dimetallated derivatives of diazomethane $(R_3N)_2CN_2$ (M = Ge or Sn).[6] It has been suggested[6] that the R_3MCHN_2 formed initially is metallated by a second mole of diazomethyl-lithium, this being followed by the reaction of $R_3MC(Li)N_2$ with the initial organogermanium or organotin halide. The attempts to obtain diazomethyl derivatives of zinc and cadmium by treating $ZnCl_2$ or $CdCl_2$ with diazomethyl-lithium were unsuccessful[33].

α-Mercurated diazoalkanes have been used widely for the synthesis of metal-containing diazo-compounds. Thus lithium-,[16,55] silicon-,[56–59] germanium-[49] and tin-containing[49,58] derivatives of diazoacetic ester have been obtained by transmetallation:

$$Hg[C(N_2)COOEt]_2 + 2RLi \xrightarrow[-70°]{THF} R_2Hg + 2LiC(N_2)COOEt$$

R = n-Bu, Ph, EtS, t-BuS.

$$Hg[C(N_2)COOEt]_2 + (R_3M)_2S \rightarrow HgS + 2R_3MC(N_2)COOEt \quad ;$$

$R_3M = Me_3Si$, Me_3Sn, or Ph_3Sn.

$$Hg[C(N_2)COOEt]_2 + 2R_3SiI \rightarrow HgI_2 + 2R_3SiC(N_2)COOEt \quad .$$

However the method of synthesis of $LiC(N_2)COOEt$ examined in the previous section is preferable.

A general method of the synthesis of α-metallated diazocarbonyl compounds which are derivatives of Group IVB elements is based on radical exchange reactions between bis(triethylsilyl)mercury or its analogues and mercurated diazocarbonyl compounds. In this case the exchange reactions are accompanied by demercuration[60–63]:

$$(R_3M)_2Hg + Hg[C(N_2)C(O)R']_2 \rightarrow 2R_3M{-}Hg{-}C(N_2)C(O)R' \rightarrow$$

$$\rightarrow 2Hg + 2R_3MC(N_2)C(O)R' \quad ;$$

$R_3M = Et_3Si$, $MePh_2Si$, Et_3Ge, or $(Me_3CCH_2)_3Sn$; R′ = Me, Et, OMe, OEt, or Ph.

The esters of stannylated diazoacetic acids react exothermically with trialkylhalogenosilanes, forming the corresponding silyl derivatives (yields 75–90%):[52]

$$R_3SnC(N_2)COOMe + R_3'SiBr \rightarrow R_3'SiC(N_2)COOMe + R_3SnBr \quad ;$$

R = Et or n-Bu; R′ = Me or Et.

3. Other Methods of Synthesis

Trimethylsilyldiazomethane can be obtained by treating with alkali *N*-(trimethylsilylmethyl)-*N*-nitrosourea[64,65,66] (a procedure analogous to the synthesis of diazomethane[67]) and

methyl[68] or ethyl[65] *N*-(trimethylsilylmethyl)-*N*-nitrosocarbamates and also by the decomposition of *N*-(trimethylsilylmethyl)-*N*-nitrosoacetamide with β-phenylethylamine[13,55]:

$$Me_3SiCH_2N(NO)CONH_2 \xrightarrow{20\%\ KOH} Me_3SiCHN_2\ (53—70\%)\ ;$$

$$Me_3SiCH_2N(NO)COOR \xrightarrow[Et_2O,\ 20^\circ]{NaOH} Me_3SiCHN_2\ (\sim 25\%)\ ;$$

$$Me_3SiCH_2N(NO)COMe \xrightarrow{PhCH_2CH_2NH_2} Me_3SiCHN_2\ .$$

Like the usual diazoalkanes[69], their α-silylated analogues have been obtained by oxidising hydrazones by metal oxides[57,70] and by treating *N*-tosylhydrazines with alkali[71]:

$$Ph_3SiCOPh + N_2H_4 \rightarrow Ph_3SiC(Ph)=NNH_2 \xrightarrow[or\ HgO]{MnO_2} Ph_3SiC(N_2)Ph\ ;$$

$$Ph_3SiCOR + TsNHNH_2 \rightarrow Ph_3SiC(R)=NNHTs \xrightarrow[or\ MeONa]{n\text{-}BuLi} Ph_3SiC(N_2)R\ ;$$

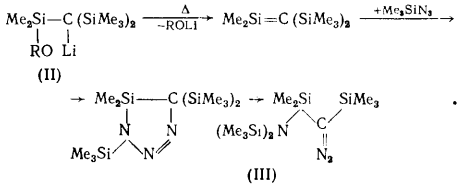
R=Me, Et, Ph, 4-FC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4, or $PhCH_2$.

Phenyl(triphenylgermyl)diazomethane, phenyl(trimethylsilyl)-diazomethane[71], and phenyl(trimethylsilyl)diazomethane labelled with ^{13}C at the diazo carbon atom have also been obtained using tosylhydrazine[72-74].

γ-Triethylsilylacetyldiazomethane has been synthesised by treating triethylsilylacetyl chloride with diazomethane[1]:

$$Et_3SiCH_2COCl + CH_2N_2 \xrightarrow[-5—0^\circ]{Et_2O} Et_3SiCH_2\overset{\overset{O}{\|}}{C}CHN_2\ .$$

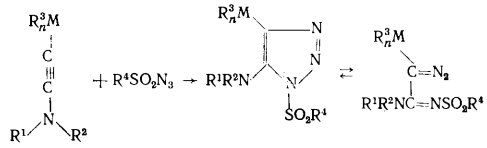
According to the data of Wiberg and coworkers[75], the thermolysis of compound (II) involves the intermediate formation of 1,1-dimethyl-2,2-bis(trimethylsilyl)-1-silaethylene. Its reaction with trimethylsilyl azide leads to a silicon-containing diazomethane (III) in a yield up to 50%:



(II) (III)

The second product of this unusual reaction is bis(trimethylsilyl)diazomethane.

It has been shown[76-78] that the reaction of sulphonyl azides with organometallic ynamines proceeds regiospecifically and leads to 5-amino-1,2,3-triazoles, which, depending on the nature of the substituents R^1, R^2, R^3, R^4, either wholly isomerise to α-metallated diazoacetamidines or are involved in a tautomeric equilibrium with the latter:



R^1, R^2, R^4 = alkyl, or aryl; $R^3_nM = R^1_2As$, R^1_2Sb, $Ph_2P(O)$—, $Ph_2P(S)$—, R^1_3Si, R^1_3Ge, or R^1_3Sn.

III. REACTIONS WITHOUT THE EVOLUTION OF NITROGEN

1. Reactions not Involving the Diazo-Group

Trimethylsilyldiazomethyl-lithium reacts with D_2O, forming Me_3SiCDN_2, which is of preparative interest[12]. Reactions with ketones in a mixture of tetrahydrofuran (THF) and pentane at −100 °C lead to 1-diazo-1-(trimethylsilyl)-2-alkanols—a new type of organosilicon bifunctional compound[13]:

$$Me_3SiC(Li)N_2 + RCOR' \xrightarrow[-100^\circ]{hydrolysis} Me_3SiC(N_2)C(OH)RR' \quad (65—85\%)\ ;$$

R=H, Me; R'=Me, Ph; or R, R'=$(CH_2)_5$.

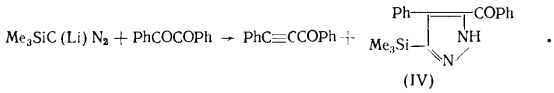
Benzophenone, whose reaction with $Me_3SiC(Li)N_2$ leads to diphenylacetylene (yield up to 85%), is an exception[15,79].

The reactions of the lithio-derivative of diethyl diazomethylphosphonate with diaryl ketones and with 2-benzoylthiophen and 3-benzoylpyridine proceed analogously:

$$(EtO)_2P(O)C(Li)N_2 + 4\text{-}RC_6H_4COPh \xrightarrow[-78\rightarrow 20^\circ]{THF} \xrightarrow{H_2O} 4\text{-}RC_6H_4C{\equiv}CPh \quad (66—94\%)\ ;$$

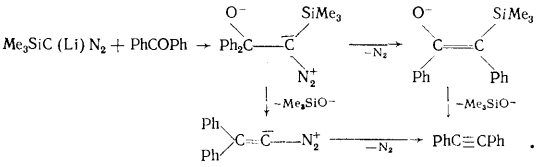
R=H, Cl, or MeO .

One of the products of the reaction of trimethylsilyldiazomethyl-lithium with benzil is pyrazole (IV)†:



(IV)

It has been suggested[15] that in these reactions the nucleophilic addition of the anion [for example, $Me_3SiC(N_2)^-$] to the carbonyl group is accompanied by the Wolff rearrangement, which involves the evolution of nitrogen and the elimination of the Me_3SiO^- anion (the sequence of these stages has not been elucidated):



A series of diazo-esters have been obtained in reactions of ethoxycarbonyldiazomethyl-lithium with alkyl halides, benzoyl chloride, benzaldehyde, and certain ketenes in THF at −50 °C or lower temperatures[16-18], for example:

$$LiC(N_2)COOEt + PhCOCl \rightarrow LiCl + PhCOC(N_2)COOEt\ ;$$

$$LiC(N_2)COOEt + RCOR' \rightarrow RR'C(OH)C(N_2)COOEt\ .$$

The yield of diazoesters $RR'C(OH)C(N_2)COOEt$ can be significantly increased when the reaction is carried out without the isolation of $LiC(N_2)COOEt$, by adding n-butyl-lithium to an equimolar mixture of diazoacetic ester and the carbonyl compound[17,19,20]:

$$HC(N_2)COOEt + RCOR' \xrightarrow[-60^\circ]{+BuLi} RR'C(OH)C(N_2)COOEt\ ;$$

R=H or Me, R'=Me or Ph; R, R'=$(CH_2)_4$, $(CH_2)_5$ or $(CH_2)_6$.

An analogous procedure has been proposed for the synthesis of β-hydroxy-α-diazoketones (yields up to 95%). In this case the lithio-derivative of the diazoketone is formed *in situ* on treatment with lithium diisopropylamide:

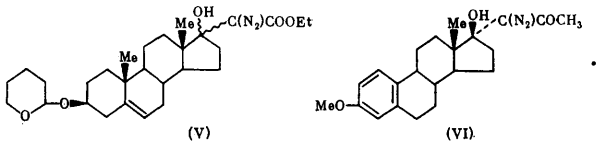
$$HC(N_2)\overset{\overset{O}{\|}}{C}R + R^1COR^2 \xrightarrow[-70^\circ]{iso\text{-}Pr_2NLi} R^1R^2C(OH)C(N_2)\overset{\overset{O}{\|}}{C}R$$

R=Me, Ph, 4-$MeOC_6H_4$, or t-Bu; R^1 = H or Me; R^2=Me, Ph, or PhCH=CH.

The diazoester (V) has been obtained in this way[17], i.e. by

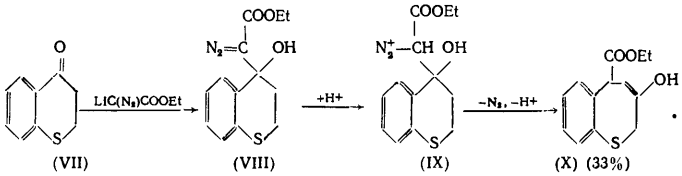
† The structure of a silylated enol was erroneously attributed to this product in a preliminary communication[79].

treating a mixture of 3β-(tetrahydro-2-pyranyloxy)-5(6)-androsten-17-one and diazoacetic ester with n-butyl-lithium, while treatment of a mixture of 3-methoxy-1,3,5,(10)-oestratrien-17-one and diazoacetone with lithium diisopropylamide leads to the diazoketones (VI):



(V) (VI)

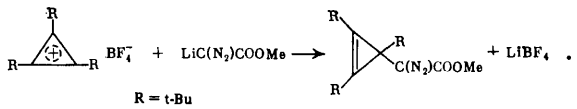
It has been shown recently[19] that the nucleophilic addition to $LiC(N_2)COOEt$ to the carbonyl group of 4-thiochromanone (VII) leads to the diazoester (VIII). Its treatment with a methanol solution of HCl generates the diazonium ion (IX)#, which then eliminates a nitrogen molecule and a proton, being converted into ethyl 2,3-dihydro-4-hydroxy-1-benzothiepin-5-carboxylate (X):



(VII) (VIII) (IX) (X) (33%)

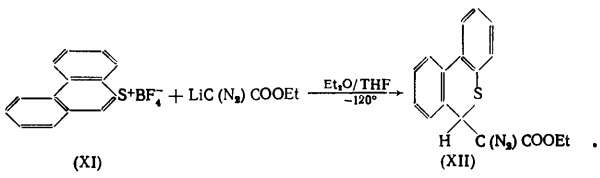
The ester of 1,3-dihydro-4-hydroxy-2-benzothiepine-5-carboxylic acid was synthesised similarly[19].

It is known[17] that the reactions of $LiC(N_2)COOEt$ with alkyl halides give low yields of compounds of the type $RC(N_2)COOEt$. On the other hand, tri-t-butylcylcopropenylium tetrafluoroborate reacts smoothly with methoxycarbonyldiazomethyllithium[81]:



R = t-Bu

A new synthesis of dienzo[*b*,*d*]thiepin[82,83], involving the reaction of dibenzothiopyrylium tetrafluoroborate (XI) with $LiC(N_2)COOEt$, has been described[82,83]; the diazo-compound (XII) is formed in 32% yield:



(XI) (XII)

The silver derivatives of diazoacetic ester[22,24], diazoketones[22], and diphenyl(diazomethyl)phosphorane[4] are readily alkylated by alkyl halides:

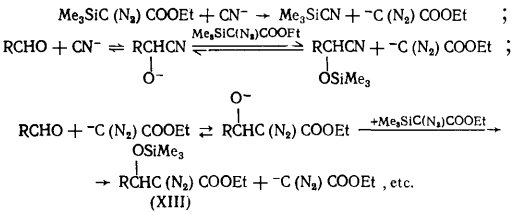
$$AgC(N_2)COOEt + BrCN \xrightarrow{Et_2O} BrC(N_2)COOEt + AgCN \quad .$$

The reactions of iodine or bromocyanogen with $AgC(N_2).COOEt$ and $AgC(N_2)P(O)(OMe)_2$ also do not involve the diazo-group[5,22], for example:

$$AgC(N_2)COR + R'X \rightarrow AgX + R'C(N_2)COR \quad .$$

Diazoesters of the $XC(N_2)COOEt$ (X = Cl, Br, or I) series have been obtained in addition by treating mercuribisdiazoacetic ester with thionyl chloride, bromine, or iodine[23,84]. However, the treatment of mercuribis(adamantoyldiazomethane) with a solution of ICl in chloroform (at ~10 °C) yielded adamantyl chlorodi-iodomethyl ketone as a result of the substitution of the diazo-group and the mercury atom by halogen atoms[85]. The reaction of $Hg[C(N_2)COOEt]_2$ with bromotriphenylmethane leads to the ethyl ester of 2-diazo-3,3,3-triphenylpropionic acid[22].

It has been shown recently[86] that ethyl α-(trimethylsilyl)-diazoacetate reacts exothermically with aliphatic and aromatic aldehydes, forming adducts (XIII) in nearly quantitative yields. The reaction is catalysed by the complex KCN.18-crown-6- and includes initiation and catalytic stages:



When trimethylsilyldiazoacetic acid ester interacts with ethyl chlorocarbonate at 100 °C, the Si–C bond is cleaved selectively[52]:

$$Me_3SiC(N_2)COOEt + ClCOOEt \rightarrow Me_3SiCl + N_2C(COOEt)_2 \quad .$$

The reaction of stannylated diazoketones with methanol results in the selective heterolysis of the Sn–C bond[52]:

$$Bu_3SnC(N_2)COR + MeOH \rightarrow Bu_3SnOMe + HC(N_2)COR \quad ;$$

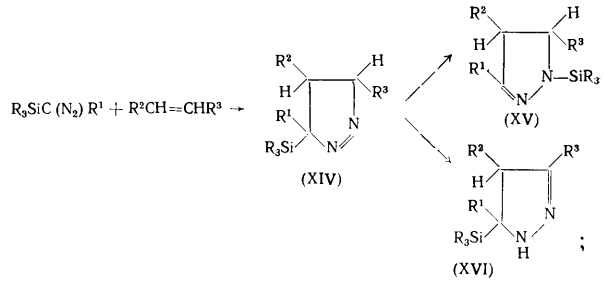
R = Me or Ph.

2. 1,3-Dipolar Cycloaddition Reactions

The formation of five-membered heterocycles in reactions with dipolarophiles is characteristic of the usual diazoalkanes[87,88] as well as their α-metallated analogues. In particular the cycloaddition of α-silyldiazoalkanes to diethyl fumarate, acrylonitrile, methyl acrylate, and analogous compounds with activated C=C bonds has been most thoroughly investigated[59,64,65,89–92]. It has been shown by ^1H NMR [89,92] that the primary products are 3-organosilyl-Δ^1-pyrazolines (XIV). The majority of Δ^1-pyrazolines are known to isomerise readily to Δ^2-pyrazolines[87,88,93]. The isomerisation of the heterocycles (XIV) leads to compounds (XV) as a result of the 1,3-migration of the R_3Si group or to their analogues (XVI) if the process is accompanied by the 1,3-transfer of a hydrogen atom. A rearrangement of the first type is characteristic of the diazoalkanes $R_3SiC(N_2)R^1$ with R^1 = Ph or COOEt, while that of the second type is characteristic of the

For details of the methods for the generation and reactions of aliphatic diazonium ions, see Kirmse's review[80].

diazoalkanes with $R^1 = H$ or Me:[65,89,92]



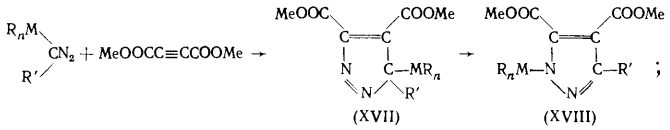
R = Me or Ph; R^1=Ph, COOEt, Me, or H;
R^2 = H or COOEt; R^3=CN, COMe, COOMe, or COOEt.

It has been shown for diethyl fumarate[92] that the relative rates of cycloaddition of diazoalkanes decrease in the sequence

$$\underset{1}{Me_3SiC(N_2)Me} > \underset{2\cdot10^{-2}}{Me_3SiC(N_2)Ph} > \underset{25\cdot10^{-4}}{Ph_3SiC(N_2)Me} > \underset{\sim2.5\cdot10^{-6}}{Ph_3SiC(N_2)Ph} > \underset{\sim2.5\cdot10^{-7}}{Me_3SiC(N_2)COOEt}.$$

The authors[92] believe that the rates of these reactions are determined by the degree of $(p \rightarrow d)_\pi$ interaction of the silicon and diazo-carbon atoms in the compound $R_3SiC(N_2)R^1$ (which was confirmed by CNDO/2 calculations) and also by the resonance-stabilising properties of R^1 and the steric conditions in the transition state of the cycloaddition reaction[92]. The rate of the isomerisation (XIV) → (XV) increases with enhancement of the electron-accepting properties of R^1: COOEt > Ph ≫ Me. The 1,3-migration of the hydrogen atom in the process (XIV) → (XVI) is accelerated under the influence of electron-accepting groups R^3 and in addition is catalysed by traces of water and amines[89,92].

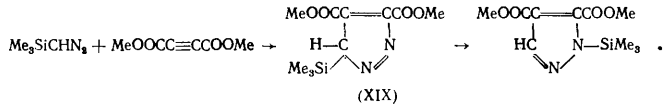
The reactions of ethyl triethylplumbyldiazoacetate with acrylonitrile, dimethyl maleate, tetracyanoethylene, and related compounds are analogous to those discussed above[94]. It has been shown[94,95] that the reactions of metallated diazoalkanes $R_nMC(N_2)R'$ with dimethyl acetylenedicarboxylate lead to isopyrazoles (XVIII) with 1,3-migration of the R_nM fragment:



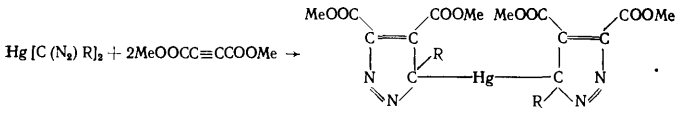
R_nM=Me_3Sn, Me_3Pb, Me_2Sb, Me_2Bi, MeHg.

HgC(N2)COOEt, or HgC (N2) COMe; R′=R_nM, COOEt, COMe, or COPh.

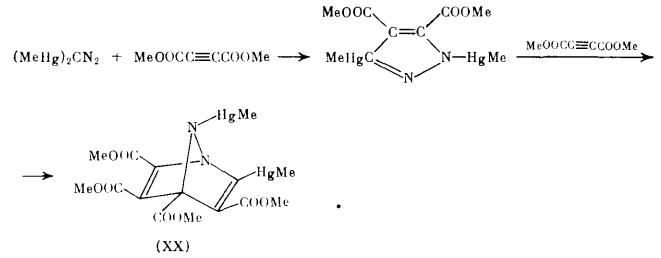
Me_2AsCHN_2, $(Me_2As)_2CN_2$, and $Me_2AsC(N_2)COOEt$ do not enter into this reaction, which can be explained by steric hindrance[95], nor does bis(dimethylthallium)diazomethane, which has an ionic structure[42]. Sigmatropic rearrangements of the type (XVII) → (XVIII) accompany also reactions involving the 1,3-dipolar cycloaddition of diazoalkanes $(Me_3Sn)_2CN_2$ and $Me_3SiC(N_2)R$ to MeOOCC≡CCOOMe, while the capacity of R for migration diminishes in the sequence[56,59] $Me_3Sn > Me_3Si > H > COOEt$. For example[14,91], in the isomerisation of isopyrazole (XIX) the Me_3Si group migrates and not the hydrogen atom as suggested previously[90]:



The reactions of mercuribis(diazoalkanes) of the type $Hg[C(N_2)R]_2$, where R = COOEtCOMe, with MeOOCC≡CCOOMe also proceed via the 1,3-cycloaddition mechanism[95]:

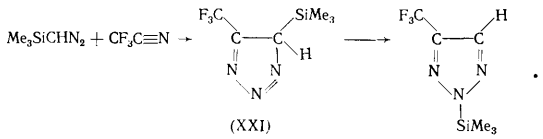


Bis(methylmercuri)diazomethane is converted in an analogous reaction into a mercurated pyrazole, which undergoes the Diels–Alder reaction with a second mole of MeOOCC≡CCOOMe, forming adduct (XX). On the basis of mass-spectrometric data, the structure of bis(methylmercuri)diazanorbornadiene was attributed to the latter[95]:



Dipolarophiles such as phenylacetylene, diphenylacetylene, sodium acetylenedicarboxylate[6,94], and bis(trimethylstannyl)-acetylene[95] do not react with α-metallated diazoalkanes or react sluggishly.

According to Crossman et al.[66], the reaction of trimethylsilyldiazomethane with trifluoroacetonitrile leads to adduct (XXI), which is converted into 4-trifluoromethyl-2-trimethylsilyl-1,2,3-triazole as a result of the migration of the Me_3Si group:

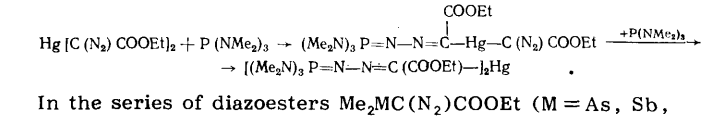


3. The Staudinger Reaction

It has been shown recently[44,46] that organometallic derivatives of diazo-compounds react with tris(dimethylamino)phosphine, which is highly basic, to form the corresponding phosphazines. In this reaction, discovered by Staudinger[96,97] for non-metallated analogues, the reactivity of the α-metallated diazoalkanes is determined by steric factors. Derivatives of diazomethane in the series Me_nMCHN_2 (M = Si, Ge, or As; $n = 3$ or 2) reacts spontaneously with $(Me_2N)_3P$; in the case of M = Si or As, a mixture of *cis*- and *trans*-phosphazines is formed:

$$Me_nMCHN_2 + (Me_2N)_3P \xrightarrow{Et_2O} Me_nMCH{=}N{-}N{=}P(NMe_2)_3 .$$

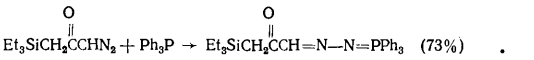
The analogous reaction with the compounds $MeHgC(N_2)R$, where R = COOEt, COMe, or COPh, takes place under mild conditions, while the interaction of mercuribisdiazoacetic ester can be carried out in stages:



In the series of diazoesters $Me_2MC(N_2)COOEt$ (M = As, Sb,

or Bi) phosphazines have been obtained only for the first two representatives. On the other hand, diazoalkanes with bulky substituents, for example compounds of the type $(Me_2M)_2CN_2$ (M = As or Sb), $(Me_3M)_2CN$, and $Me_3MC(N_2).COOEt$ (M = Si, Ge, Sn, or Pb) do not react with tris-(dimethylamino)phosphine[44,46]. Bis(dimethylthallium)diazomethane also does not react with $P(NMe_2)_3$, but this is due to the ionic structure of the diazoalkane[42].

We may note that 1-diazo-3-(trimethylsilyl)-2-propanone, in which the diazo-group is not shielded by the organometallic fragment, readily reacts with triphenylphosphine[1], like the usual diazo-compounds:



$$Et_3SiCH_2\overset{O}{\overset{\|}{C}}CHN_2 + Ph_3P \rightarrow Et_3SiCH_2\overset{O}{\overset{\|}{C}}CH{=}N{-}N{=}PPh_3 \quad (73\%)$$

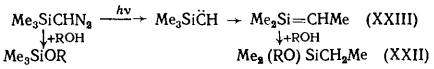
It has been suggested that in the transition states of these reactions the phosphine attacks the electrophilic α-N atom with subsequent rearrangement to Staudinger's β-N-adduct[44].

IV. REACTIONS INVOLVING THE INTERMEDIATE FORMATION OF CARBENES AND CARBYNES

1. Intramolecular Rearrangement of Carbenes

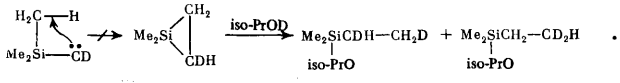
Kinetic and chemical evidence was obtained in 1967 [98,99] for the existence of the short-lived sila-alkenes $R_2Si{=}CR'_2$, in which the silicon atom has a coordination number of 3. This stimulated an intense development of methods for the generation of sila-alkenes as well as the study of their structure and reactivity (see the relevant reviews[100-102]). In particular, it was found that α-silyated diazoalkanes are available as precursors of sila-alkenes.

Thus photolysis of trimethylsilyldiazomethane in alcohols leads to alkoxydimethylethylsilanes (XXII).[12,103,104] Me_3SiOR is formed via a side reaction (non-photochemically):



$$Me_3SiCHN_2 \xrightarrow{h\nu} Me_3Si\ddot{C}H \rightarrow Me_2Si{=}CHMe \quad (XXIII)$$
$$\downarrow +ROH \qquad\qquad \downarrow +ROH$$
$$Me_3SiOR \qquad\qquad Me_2(RO)SiCH_2Me \quad (XXII)$$

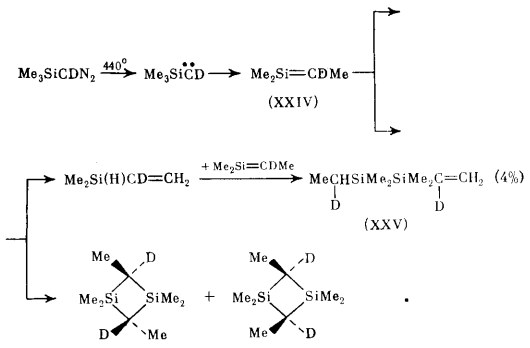
It has been suggested that the photolysis generates trimethylsilylcarbene, whose isomerisation leads to the sila-alkene (XXIII) as a result of the 1,2-shift of the methyl group to the carbene centre. The formation of the intermediate (XXIII) has been confirmed by the reaction with deuterated alcohols. For example, the photolysis of Me_3SiCDN_2 in iso-PrOD yielded isopropoxysilane $Me_2(iso\text{-}PrO)SiCD_2Me$, in which deuterium atoms are present only in the methylene group of the Et fragment[12]. This rules out the alternative mechanism—via the silacyclopropane intermediate:



$$H_2C{-}H \quad CH_2$$
$$Me_2Si{-}\ddot{C}D \rightarrow Me_2Si \quad CDH \xrightarrow{iso\text{-}PrOD} Me_2SiCDH{-}CH_2D + Me_2SiCH_2{-}CD_2H$$
$$\text{iso-PrO} \qquad\qquad \text{iso-PrO}$$

It has also been shown[103] that the photolysis of $Me_2PhSiCHN_2$ and $Me_2(PhCH_2)SiCHN_2$ in methanol leads to the carbenes $Me_2PhSi\ddot{C}H$ and $Me_2(PhCH_2)Si\ddot{C}H$. They isomerise to sila-alkenes via the 1,2-shift of one of the groups from silicon to the carbene centre. The ease of migration varies in the sequence Me > Ph ≅ $PhCH_2$.

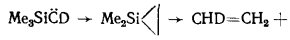
Judging from the composition of the products and their yield, the pyrolysis of Me_3SiCHN_2 (or Me_3SiCDN_2) in a flow system generates trimethylsilylcarbenes, which isomerise preferentially to a sila-alkene[12,104], for example:



$$Me_3SiCDN_2 \xrightarrow{440^\circ} Me_3Si\ddot{C}D \rightarrow Me_2Si{=}CDMe \quad (XXIV)$$

$$Me_2Si(H)CD{=}CH_2 \xrightarrow{+\,Me_2Si=CDMe} MeCHSiMe_2SiMe_2C{=}CH_2 \quad (4\%)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad D \qquad\qquad D$$
$$(XXV)$$

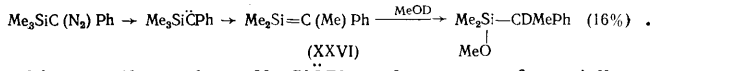
The sila-alkene (XXIV) dimerises to *cis*- and *trans*-disilacyclobutanes (overall yield >40%) and to a lesser extent rearranges to dimethylvinylsilane. The reaction of the latter with compound (XXIV) leads to adduct (XXV) in 4% yield. Furthermore, thermolysis gives rise to traces of ethylene and dimethylsilene as a result of a side reaction[104]:



$$Me_3Si\ddot{C}D \rightarrow Me_2Si\langle \rightarrow CHD{=}CH_2 + Me_2Si\,.$$

The intermediate formation of compound (XXIV) was confirmed by the pyrolysis of Me_3SiCHN_2 in the presence of 2-propanol. The latter traps sila-alkene with the formation of 2-propoxydimethylethylsilane (yield more than 67%).[12,104]

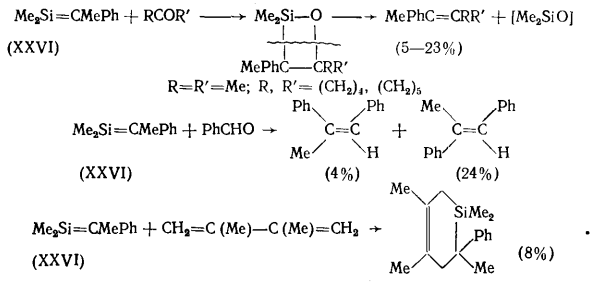
On the other hand, in the pyrolysis of phenyl(trimethylsilyl)diazomethane in the presence of alcohols the yield of sila-alkene (XXVI) was low[73]:



$$Me_3SiC(N_2)Ph \rightarrow Me_3Si\ddot{C}Ph \rightarrow Me_2Si{=}C(Me)Ph \xrightarrow{MeOD} Me_2Si{-}CDMePh \quad (16\%)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad (XXVI) \qquad\qquad\qquad\qquad\quad MeO$$

In this case the carbene $Me_3Si\ddot{C}Ph$ undergoes preferentially carbene–carbene rearrangement (see below).

The intermediate formation of sila-alkenes[105,106], including the intermediate (XXVI),[73,107] has been confirmed in addition by the reaction with ketones, which leads to olefins, by the reaction with aldehydes, in which mixtures of *cis*- and *trans*-alkenes are formed, and by the reaction with 2,3-dimethylbutadiene, which is known to trap sila-alkenes effectively[101] with formation of Diels–Alder adducts:

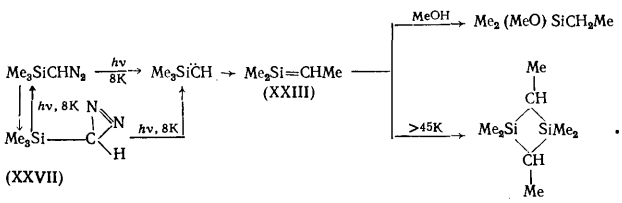


$$Me_2Si{=}CMePh + RCOR' \rightarrow Me_2Si{-}O \rightarrow MePhC{=}CRR' + [Me_2SiO]$$
$$(XXVI) \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (5\text{–}23\%)$$
$$MePhC{-}CRR'$$
$$R{=}R'{=}Me;\ R,\ R' = (CH_2)_4,\ (CH_2)_5$$

$$Me_2Si{=}CMePh + PhCHO \rightarrow \quad C{=}C \quad + \quad C{=}C$$
$$(XXVI) \qquad\qquad\qquad\qquad (4\%) \qquad\qquad (24\%)$$

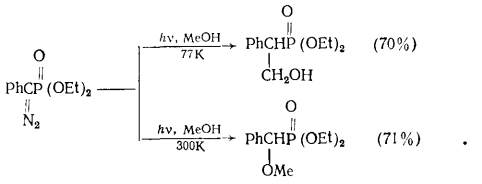
$$Me_2Si{=}CMePh + CH_2{=}C(Me){-}C(Me){=}CH_2 \rightarrow$$
$$(XXVI) \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (8\%)$$

In 1967 two groups of investigators[104,108,109] obtained simultaneously data for the mechanism of the photolysis of trimethylsilyldiazomethane, isolated in an argon matrix at 8 K:



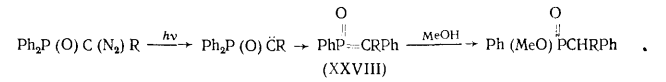
$$Me_3SiCHN_2 \xrightarrow[8K]{h\nu} Me_3Si\ddot{C}H \rightarrow Me_2Si{=}CHMe \quad (XXIII)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \xrightarrow{MeOH} Me_2(MeO)SiCH_2Me$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \xrightarrow{>45K} Me_2Si\langle CH(Me)$$
$$Me_3Si{-}C(N{=}N){-}H \quad h\nu, 8K$$
$$(XXVII)$$

It was shown by ultraviolet, ^{1}H NMR, and infrared spectroscopy that the primary photolysis product is trimethylsilyldiazirine (XXVII), which is stable at room temperature. Further photolysis of the mixture of Me_3SiCHN_2 and compound (XXVII) proceeds via the carbene to the sila-alkene (XXIII). The infrared spectra of compound (XXIII) (not entirely identical) were also published in other communications[108,109]. Furthermore, compound (XXIII) was identified on the basis of the formation of a mixture of *cis*- and *trans*-disilacyclobutanes by the reaction with methanol. It has been found by EPR that trimethylsilylcarbene has a triplet ground state[108]. This was confirmed by the formation of triplet carbenes in the photolysis of Me_3SiCDN_2, $Me_2(H)SiCHN_2$, and $(Me_3Si)_2CN_2$ in argon matrices at 8 K. At the same time it has been suggested that thermolysis of Me_3SiCHN_2 at ~420 °C and its photolysis at 25 °C leads to singlet trimethylsilylcarbene[108]. Two recently published interesting examples of the dependence of the spin state of carbenes on the conditions of their generation are consistent with this finding. Thus the photolysis of α-diazobenzylphosphonate in a methanol matrix at 77 K leads to triplet carbene and its photochemical decomposition in alcohols at 300 K leads to singlet carbene[110]. In the former case the reaction with the alcohol yields preferentially the C–H insertion product, while in the latter case the O–H insertion product is formed, in agreement with Kirmse's data[111]:



Similarly[112] the photolysis of phenyldiazomethane in 2-propanol at 20 °C results in the formation of benzyl 2-propyl ether (77%) as a result of the insertion of singlet phenylcarbene in the O–H bond of the alcohol molecule. On the other hand, if the photolysis is carried out in a 2-propanol matrix at −196 °C, then triplet phenylcarbene is generated (cf. Refs. 113–115) and reacts with the alcohol preferentially via the C–H insertion mechanism.

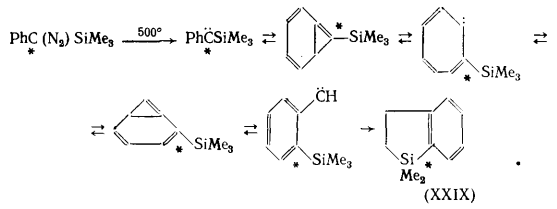
In conclusion of the discussion of the methods for the generation of sila-alkenes, we may note that the photolysis of the derivatives of diphenylphosphoryldiazomethane generates carbene which, like silylcarbenes, isomerise to unstable alkylideneoxophosphoranes (XXVIII) as a result of the 1,2-shift of the pH group from the hetero-element to the carbene centre[116,117]:



The intermediates (XXVIII) belong to a new class of heterocumulenes containing quinquevalent phosphorus having a coordination number of 3. They have been trapped successfully with methanol, aldehydes, and ketones[116,117].

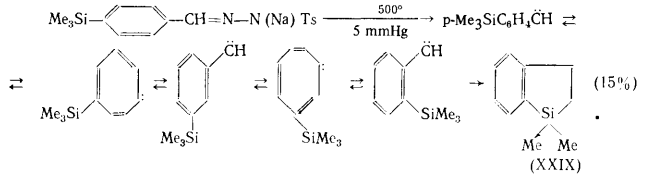
The reactions of phosphorylcarbenes, including their intramolecular rearrangements, have been discussed in reviews[4,118].

In the pyrolysis of $Me_3SiC(N_2)Ph$ and $Me_3SiC(Ph)$=N–N(Li)Ts in the gas phase[72–74,107,119] one of the products is 1,1-dimethyl-1-silaindan (XXIX) (yield up to 37%). It is assumed that the carbene Me_3SiCPh formed is in equilibrium with trimethylsilylheptatrienylidene and *o*-trimethylsilylbenzylidene (carbene–carbene rearrangement). The pyrolysis of the labelled compounds $Me_3Si^{13}C(N_2)Ph$ and $Me_3Si^{13}C(Ph)$=N–N(Li)Ts leads to indan (XXIX) with the label in the benzene ring, which confirms the following mechanism[72,73]:

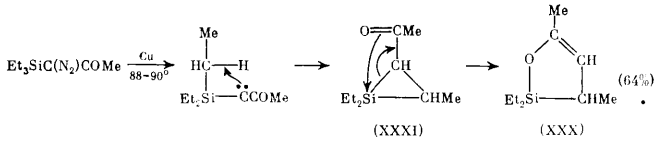


Side reactions lead to the isomerisation of the carbene $PhCSiMe_3$ to the sila-alkene (XXVI) (again see above) and to a lesser extent to 1,1-dimethyl-2-phenyl-1-silacyclopropane.

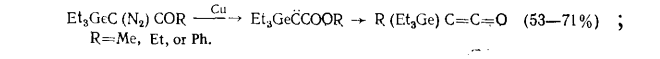
It is of interest that silaindan (XXIX) has also been obtained by the pyrolysis of the sodium salt of *p*-trimethylsilylbenzaldehyde tosylhydrazone[120], which generates the carbene p-$Me_3SiC_6H_4CH$, differing in structure from $PhCSiMe_3$. The reaction mechanism is analogous to that discussed above:



The copper-catalysed thermolysis of triethylsilyldiazoacetone in hexane leads to 1,1-diethyl-3,5-dimethyl-1-sila-2-oxa-3-cyclopentene (XXX). The carbenoid§ $Et_3SiCCOMe$ formed is probably inserted intramolecularly into the C–H bond of the Si–CH_2 fragment. This is followed by ring expansion[63,121,122] in the intermediate (XXXI):



The intermediate formation of silacyclopropanes in the rearrangements of carbenes has also been postulated in other studies[73,104]. On the other hand, the thermolysis of triethylgermyldiazoacetone and its analogues over copper generates the carbenoids $Et_3GeCCOR$, which undergo the Wolff rearrangement with formation of germylated ketens[63,123]:

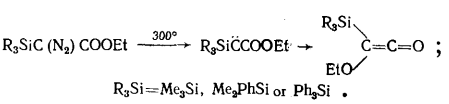


The thermolysis of the usual α-diazoketones over a copper catalyst is known to lead to ketocarbenoids which do not undergo the Wolff rearrangement[125], with a few exceptions[124].

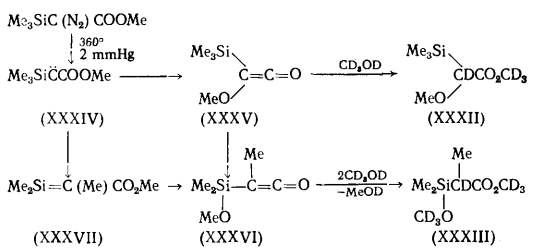
---

§ Following Marchand and MacBrockway[126], here and henceforth the term carbenoids is applied to the carbenes formed in the thermocatalytic decomposition of diazoalkanes on metals or their salts. There are data showing that the carbenoid is usually coordinated to the catalyst; as a result, the properties of the carbenoid can differ from those of the corresponding carbene.

We may note that the pyrolysis of α-silyldiazoacetates in a flow system leads to the Wolff rearrangement[127];

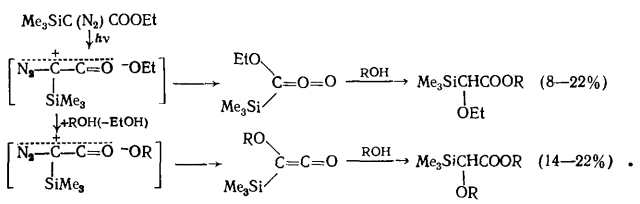


Ando and coworkers[128,129] showed that the esters (XXXII) and (XXXIII) are formed, together with other products, in the pyrolysis of methyl trimethylsilyldiazoacetate in a flow system in the presence of alcohols (for example, CD_3OD). They suggested that the pyrolysis leads to the carbene (XXXIV), which undergoes the Wolff rearrangement to the alkoxyketen(XXXV) and the latter can isomerise to the ketone (XXXVI). The reactions of (XXV) and (XXXVI) with the alcohol lead to esters:



Later the authors[129] suggested that the keten (XXXVI) is formed as a result of the rapid isomerisation of the silaalkene (XXXVII), which fails to react with the alcohol.

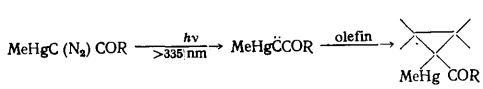
In its photochemical decomposition in alcohols[130,131] ethyl trimethylsilyldiazoacetate undergoes the Wolff rearrangement without the intermediate formation of carbenes (cf.Refs.132 and 133):



The photolysis of $MeHgC(N_2)COOMe$ [39] and $MeHgC(N_2)COMe$ [134] generates carbenes; the Wolff rearrangement is not typical for these compounds.

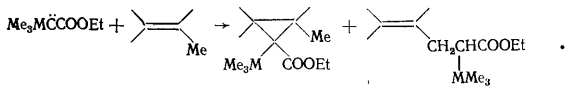
2. Addition to Multiple Bonds

The photolysis of α-metallated diazo-compounds under the usual conditions leads to carbenes in a singlet form. If the rate of their reaction with olefins is greater than the rate of their intercombination transition to the triplet state, stereospecific cycloaddition to the C=C bond and insertion in the C–H bond take place. The relative contributions of these reactions depend on many factors. For example[39,134], the yield of cyclopropanes is 70–90% in the photolysis of MeHgC.(N$_2$)COR (R = Me or OMe) in but-1-ene, 2-methylpropene, *cis*- or *trans*-but-2-ene, and buta-1,3-diene:



The reaction mixtures contain virtually no CH insertion products and the yield of products corresponding to the Wolff rearrangement is less than 4%.

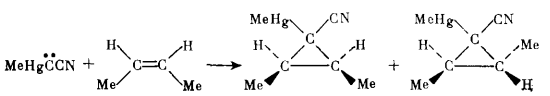
On the other hand, the photolysis of the diazoesters $Me_3MC(N_2)COOEt$ (M = Si, Ge, Sn, or Pb) leads to carbenes, which react with olefins less selectively: the formation of cyclopropanes is accompanied by the CH insertion[49,58,59,135]:



Steric factors have a considerable influence. Thus the interaction of the carbene $Me_3SiCCOOEt$ with isobutene entails the formation of only the cycloaddition product, while the reaction with the sterically hindered tetramethylethylene yields to the CH insertion product only[59]. The photolysis of Me_3SiCHN_2 generates trimethylsilylcarbene, whose reactions with ethylene and *trans*-but-2-ene give a low yield of cyclopropanes[136]. At the same time the carbene dimerises with formation of *trans*-1,2-bis(trimethylsilyl)ethylene. The latter reaction becomes the main one in the photolysis of Me_3SiCHN_2 in the presence of sterically hindered tetramethylethylene, tetrafluoroethylene, and perfluoropropene[136].

It has been shown by ^{1}H NMR that, on direct photochemical generation of the carbenes MeHgCCOMe, MeHgCCOOMe, Me_3SiCH, and $Me_3MCCOOEt$ (M = Si, Ge, Sn, or Pb),[49,59,134,136] their cycloaddition to *cis*- and *trans*-but-2-enes is mainly *cis*-stereospecific. This is evidence for the singlet state of the carbenes[111,137]. The contribution of the non-stereospecific cycloaddition of $Me_3SiCCOOEt$ is only 5%. The introduction of even small amounts of benzophenone into the reaction mixture[59] increases this contribution to 15% as a result of the sensitisation of the photolysis[111].

It has been shown recently[53] that the cyanocarbene HCCN, obtained by the direct photolysis of diazoacetonitrile, adds mainly *cis*-stereospecifically (to the extent of 94%) to *cis*-but-2-ene. Consequently, the contribution of triplet cyanocarbenes to this reaction is also low. On the other hand, both the direct benzophenone-sensitised photolysis of $MeHgC(N_2)CN$ in *cis*-but-2-ene leads to 1:1 mixtures of *cis*- and *trans*-dimethylcyclopropanes, which indicates the non-stereospecificity of the reaction

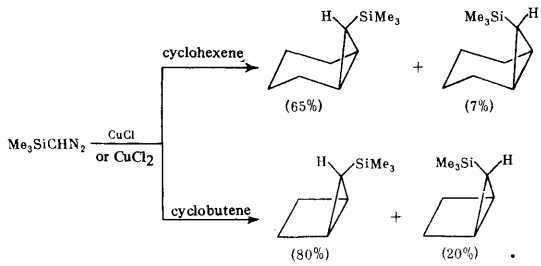


The difference between the properties of the carbenes HCCN and MeHgCCN has been explained[53] by the heavy atom effect. Both kinds of carbenes are generated in the singlet form, but, under the influence of the α-mercury atom, there is a rapid intercombination transition of MeHgCCN to the triplet state and the steady-state concentration of triplet carbenes increases.

The catalytic decomposition of trimethylsilyldiazomethane over copper salts in the presence of olefins leads to the carbenoid¶ Me_3SiCH. It is stabilised by cycloaddition to olefins and by dimerisation to *trans*- and *cis*-1,2-bis(trimethylsilyl)ethylenes[64,65,136,138]. The reaction with *trans*-but-2-ene takes place stereospecifically and leads to 1-trimethylsilyl-2,3-*trans*-dimethylcyclopropane (yield 13%).[136] The interaction with cyclohexene results in the formation of *anti*- and *syn*-7-trimethylsilylnorcarane[64,65]; the reaction with cyclobutene gives a mixture of *exo*- and *endo*-5-trimethylsilylbicyclo[2,1,0]pentanes[138], while the reaction with cyclohexa-1,3-diene leads to *exo*-7-trimethylsilylbicyclo[4,1,0]-hept-2-ene.[139] In the first two instances the cycloaddition

¶ For the role of the catalysts in the carbenoid decomposition of aliphatic diazo-compounds, see Mandel'shtam[140].

takes place with the preferential formation of the *exo*-isomers:

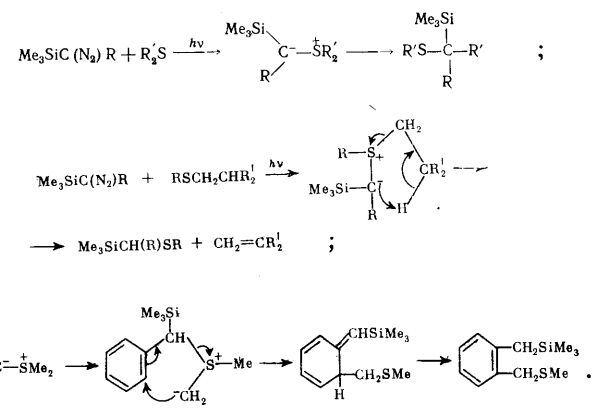


3. The Insertion of α-Metallated Carbenes in the O–H, C–H, C–O, C–S, C–Cl, Si–H, Si–Hg, and Ge–Hg σ-Bonds

Reactions of this type were investigated in relation to a large number of examples. It has been shown[39,59,71,119] that, in their reaction with alcohols, carbenes are usually selectively inserted in the O–H bonds, which makes it possible to use methanol and its deuterated derivatives for the identification of carbenes in the singlet state. For example, the photolysis of $MeHgC(N_2)COOMe$ in methanol leads to $MeHgCH(OMe)COOMe$ in 98% yield. The structure of the product was confirmed by its reduction (with $NaBH_4$ in ethanol) to $MeOCH_2COOEt$ and the photolysis of the initial diazoester in CD_3OD.[39]

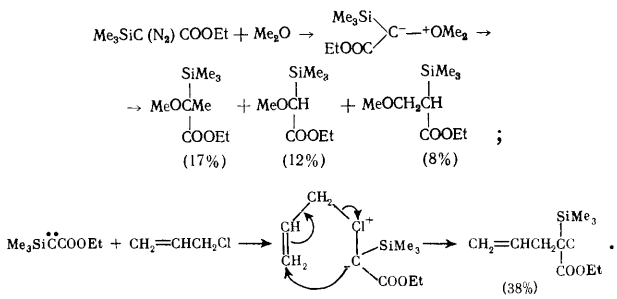
There is yet another reaction specific to singlet α-metallated carbenes—the insertion in the C–H bond[49,59,136]. Thus the photolysis ($\gamma > 300$ nm) of $Me_3SiC(N_2)COOEt$ in cyclohexane leads to ethyl cyclohexyltrimethylsilylacetate (yield 49%) while in n-butane at −30 °C a mixture of ethyl 2-trimethylsilylcaproate and ethyl 3-methyl-2-trimethylsilylvalerate is formed (overall yield 52%).[59] Furthermore, the rearrangements of certain carbenes, for example $Me_3SiC\ddot{P}h$ [72,119] and p-$Me_3SiC_6H_4$–$\ddot{C}H$ [120] include a stage involving the intramolecular insertion of the carbene group in the C–H bond (see Section IV).

It has been shown recently[131,141] that the photolysis of the diazoalkanes $Me_3SiC(N_2)R$ (R = COOEt or Ph) in dialkyl sulphides at ~20 °C leads to the carbenes $Me_3Si\ddot{C}R$, which react with R'_2S to form sulphonium ylids. This can be followed by stages involving insertion in the C–S bond, elimination, and the Sommelet–Hauser rearrangement (cf. Hauser et al.[142]):



The photolysis of $Me_3SiC(N_2)COOEt$ in dimethyl sulphide[141] at −78 °C leads to the stable ylid Me_2S^+–$^-C(COOEt)SiMe_3$ (m.p. 40 °C). Other evidence in support of the intermediate formation of ylids in such reactions has been presented in a review[143].

The reactions of α-silylated carbenes with ethers and alkyl halides also includes the ylid formation stage[131]:



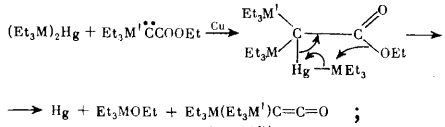
The insertion of the unusual carbenes[140,144,145] and their α-metallated analogues[136,147,148] in the Si–H bond is of synthetic interest. In the general case this bond is more carbenophilic than the C–H bond[136,146]. However, the yield of the Si–H insertion product can depend on the method of generation of the carbene. Thus the liquid-phase photolysis of a mixture of trimethylsilyldiazomethane and trimethylsilane leads to the Si–H insertion product $Me_3SiCH_2SiMe_3$ (yield 66%). On the other hand, this product is not formed in the liquid-phase thermolysis (in the photolysis of the same mixture in the gas phase)[136].

The catalytic decomposition of $Et_3GeC(N_2)COOEt$ over copper in benzene in the presence of triethylsilane or triethylgermane proceeds with the selective insertion of the resulting carbenoid in the Si–H or Ge–H bonds[147], for example:

$$Et_3Ge\ddot{C}COOEt + Et_3SiH \rightarrow Et_3Si(Et_3Ge)CHCOOEt\ .$$

In the analogous reaction with $Me(C_6F_5)_2SiH$ the insertion of $Et_3Ge\ddot{C}COOEt$ in the more inert Si–H bond does not occur[148]. The reaction leads to the azene $Et_3Ge(EtOOC)C{=}N{-}N{=}C(COOEt)GeEt_3$ (yield ~90%), which is known to be formed[60] via the addition of carbenoid $Et_3Ge\ddot{C}COOEt$ to a molecule of the initial diazoester.

It has been shown[149,150] that dihalogenocarbenes react non-selectively with bis(trimethylsilyl)- and bis(trimethylgermyl)-mercury. Dihalogenocarbenes are inserted both in the mercury–Group IVB element bond and in the newly formed Hg–C bond. On the other hand, the carbenoid $Et_3MCCOOEt$, formed in the catalytic decomposition of α-metallated diazoesters of the $Et_3M'C(N_2)COOEt$ (M' = Si, Ge, or Sn) series over copper in hexane or toluene in the presence of bis(triethylsilyl)- or bis(triethylgermyl)-mercury, is inserted in the Si–Hg or Ge–Hg bond. Successive demercuration ketens[61–63]:

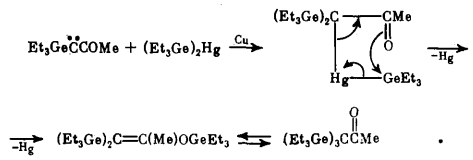


$$\rightarrow Hg + Et_3MOEt + Et_3M(Et_3M')C{=}C{=}O \quad ;$$

(58–92%)

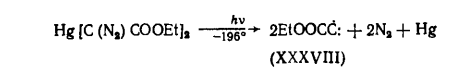
M = Si or Ge; M' = Si, Ge, or Sn.

The acetyltriethylgermylcarbenoid, generated by the thermocatalytic decomposition of $Me_3GeC(N_2)COMe$, is inserted selectively in the Ge–Hg bond in the reaction with bis(triethylgermyl)mercury. The reaction is also accompanied by demercuration[147]:



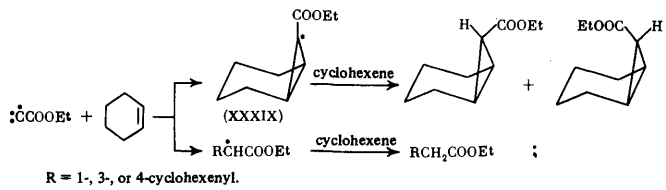
4. Methods of Generation and Reactivities of Carbynes

The chemistry of carbynes, which are derivatives of univalent carbon, has been developing vigorously in two directions. Studies have been made on the methods of synthesis and reactivities of transition metal complexes in which one of the ligands is a carbyne (see Fischer's review[111] review[151]). Methods for the generation of carbynes as kinetically independent species are being developed (see the short review of Strausz er al.[152]). In particular, ethoxycarbonylmethine (XXXVIII) is generated in the short-wavelength photolysis ($\lambda > 2100$ Å) of mercuribis(ethyl diazoacetate)[33,152] or alkylmercuridiazoacetates[39]:



(XXXVIII)

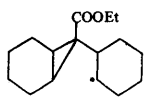
It was established that the carbyne (XXXVIII) is in the $^2\Pi$ ground state (↑↓↑ CCOOEt). Two parallel processes are characteristic of its reaction with cyclohexene: (1) addition to the double bond (concerted mechanism forbidden by orbital symmetry rules), leading to the formation of 7-ethoxycarbonyl-7-norcaranyl radicals (XXXIX); (2) insertion in the C–H bond (preferentially the allylic bond) with formation of alkyl radicals (XL):



(XXXIX)

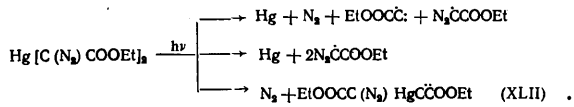
R = 1-, 3-, or 4-cyclohexenyl.

The radicals (XXXIX) and (XL) abstract hydrogen from cyclohexene. For (XXXIX), this process takes place stereospecifically with the preferential formation of the less stable ethyl *endo*-norcarane-7-carboxylate. Furthermore, the radicals (XXXIX) add to the double bond of cyclohexane and the resulting radicals (XLI) then disproportionate:



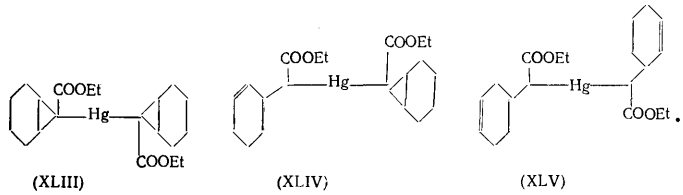
(XLI)

With increase of λ (for $\lambda > 2800$ Å), the yield of the carbyne (XXXVIII) falls owing to photolysis via competing pathways:



(XLII)

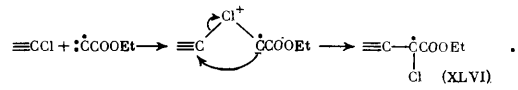
Under these conditions, the overall yield of the organomercury products (XLIII)–(XLV) increases to 38% with a simultaneous decrease of the yield of the non-mercurated products from 31 to 5%. Consequently the relative contribution of the mercury-containing carbenes [for example, (XLII)] in reactions with the solvent (cyclohexene) greatly increases:



(XLIII) (XLIV) (XLV)

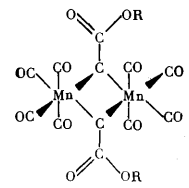
The regioselective insertion of the carbyne (XXXVIII) and the mercurated carbene (XLII) in the C–H bonds in the α-position with respect to the heteroatom has been observed in the photolysis of $Hg[C(N_2)COOEt]_2$ in heterocyclic compounds (tetrahydrofuran, tetrahydrothiophen, or pyrrolidine).[153] Judging from the proportions of the insertion products, the principal intermediate is the carbene (XLII), while the yield of the carbyne (XXXVIII) is 10–20%.

According to Patrick and Kovith[154], the photolysis of $Hg[C(N_2)COOEt]_2$ in the chloroalkanes $Me_{4-n}CCl_n$ ($n = 1$–4) at $\lambda < 2900$ Å leads to derivatives of ethyl chloroacetate and ethyl chloroacrylate. In this case the ethoxycarbonylmethine (XXXVIII) formed is inserted preferentially in the C–Cl bond with the intermediate formation of the chlorine-containing radical (XLVI). By analogy with the chemistry of the carbenes[126], it is suggested that the insertion step is preceded by the formation of an ylid radical:



(XLVI)

It is of interest to note that, in the reaction of $Mn(CO)_5Br$ with $Hg[C(N_2)COOR]_2$ (R = Et or t-Bu) in boiling ether, one of the products is the dimeric complex (XLVII) in which ethoxycarbonylmethine and t-butoxycarbonylmethine function is neutral three-electron bridge ligands[155,156].



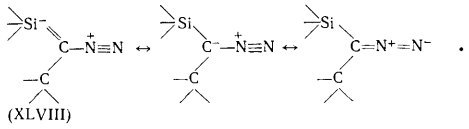
(XLVII)

The analogous complex is not formed in the reaction with $AgC(N_2)COOEt$. So far no analogies for this reaction are known[156].

V. STRUCTURAL AND SPECTROSCOPIC STUDIES

According to X-ray diffraction data[157], the $Ph_3SiC(N_2)Ph$ molecule is monomeric. It contains the linear C–N–N group and the planar Si–C(N_2)C fragment. The C–N bond is somewhat shorter and the N–N bond somewhat longer than in diazomethane (cf. Cox et al.[158]). The Si–C bond in the fragment is single (1.88 Å), which has been explained by the low contribution of structure (XLVIII) to the resonance

hybrid:



(XLVIII)

According to the same data[157], phenyl(triphenylgermyl)diazomethane has the same structure as its silicon analogue.

It has been shown[159,160] that all seven atoms of the $HgC(N_2)CO_2$ fragment in the crystals of t-BuHgC(N_2)COOEt and $Hg[C(N_2)COOEt]_2$ lie in the same plane. In the t-butyl derivative the carbonyl group is in the *cis*-position with respect to the diazo-group. This conformation is in general more stable than the transoid conformation[161]. It is particularly characteristic of aliphatic α-diazoalkanes[162].

It has been shown by NMR and infrared (IR) and Raman spectroscopic methods that bis(dimethylthallium)diazomethane is an ionic compound and that the anion $[CN_2]^{2-}$ has a linear structure[42]. In other compounds of the type $(R_nM)_2CN_2$ the metal–diazo-carbon bonds are covalent. The diazo-group gives rise to a distinct band in the IR spectra of these compounds in the range 1950–2050 cm^{-1}, due to the asymmetric stretching vibrations of the N–N bond[40,47]. The diazo-group in the compounds $(R_3Sn)_2CN_2$ absorbs in the region of 2000 cm^{-1} regardless of the nature of R. However, in the $(Me_3M)_2CN_2$ series the frequency $\nu_{as}(CN_2)$ decrease on average by 50 cm^{-1} in the following sequence of M: Si > Ge > Sn > Pb, which reflects the inductive effect of the Me_3M groups[40]. An analogous shift of the absorption band in the region of low frequencies has been observed in the spectra of the following series of compounds: $Me_2As(Me_3Ge)CN_2$ (2020 cm^{-1}), $Me_2As(Me_3Sn)CN_2$ (2000 cm^{-1}), and $Me_2As.(Me_3Pb)CN_2$ (1985 cm^{-1}).[47]

The introduction of the Me_2M fragment (M = As, Sb, or Bi) at the α-carbon atom of ethyl diazoacetate reduces the frequency by 45–55 cm^{-1}. It has been suggested[43] that this effect is due to the mass of the substituent and to a lesser extent the nature of the metal. An analogous conclusion was reached in the analysis of the IR spectra of $Me_3MC(N_2)COOEt$ (M = Si, Ge, Sn, or Pb) and certain related compounds[40].

As regards the stretching vibrations of the carbonyl group, an appreciable bathochromic shift is observed only after the introduction of the Me_3Sn, Me_3Pb, MeHg, and EtHg fragments, whereupon, according to the authors[40,43], the carbonyl group is coordinated intramolecularly to the metal atom. On the other hand, if such coordination does not occur in the compounds $Me_nMC(N_2)COOEt$ (M = Si, Ge, As, Sb, or Bi), the band shifts only very slightly[40,43].

Analogous effects are characteristic also of α-metallated diazoketones. For example, the carbonyl absorption band in the spectra of the compounds $Hg[C(N_2)COR]_2$ (R = alkyl, adamantyl, or aryl)[33,35,38] undergoes a 25–45 cm^{-1} bathochromic shift relative to the non-mercurated analogues.

The ultraviolet spectra of mercuridiazoacetates $RHgC(N_2).COOR'$ (R and R' = alkyl) contain two absorption bands: at 374–377 nm ($\varepsilon \cong 44$–59) and at 268–274 nm ($\varepsilon \cong 8600$–10 000). The introduction of the alkylmercuri-group in $HC(N_2)COOR'$ causes a 20–25 nm shift of the short-wavelength maximum and reduces its intensity by 40%. The position of the long-wavelength maximum changes only slightly (by 2–3 nm), but its intensity increases by a factor of three[39]. Similar features are characteristic of α-mercurated diazoketones[33,35].

Organometallic derivatives of diazo-compounds are also widely investigated by pulse $^{13}C\{^1H\}$ Fourier transform NMR.[43,163] In particular, $^1J(H-C)$ and the chemical shifts $\delta(^{13}CN_2)$ of the diazo-carbon atom in the compounds Me_nMCHN_2, $(Me_nM)_2CN_2$, and $Me_nMC(N_2)COOEt$ (M = Hg, Si, Ge, Sn, Pb, As, Sb, or Bi; $n = 1$, 2, or 3) have been determined. It has been found[163] that the substitution of the hydrogen atom in diazomethane or ethyl diazoacetate by the Me_3M fragment entails a downfield shift of the $^{13}CN_2$ signal, the magnitude of the signal increasing in the sequence Si < Ge < Sn < Pb.

In their analysis of the $^{13}C\{H\}$ NMR spectra of compounds in the $(Me_3M)_2CN_2$ series (M is a silicon subgroup element), Lorberth and coworkers[43,163] established that the carbon atom linked to the diazo-group is shielded owing to the diamagnetic influence of the neighbouring Me_3M fragments. The atom is particularly strongly shielded in bis(trimethylstannyl)diazomethane [$\delta(^{13}CN_2) = 5.8$ p.p.m.] and bis(trimethylplumbyl)diazomethane [$\delta(^{13}CN_2) = 1.9$ p.p.m.]. To account for this effect, the compound $(Me_3Sn)_2CN_2$ was investigated in detail by photoelectron spectroscopy, ^1H, ^{13}C, ^{15}N, and ^{119}Sn NMR, as well as ^{119} ^{119}Sn-Mössbauer spectroscopy[164]. It was established that the Me_3Sn groups function in this case as very powerful electron donors, as a result of which the CN_2 fragment acquires an enhanced electron density, which is distributed fairly uniformly over all three atoms of this group. Analysis of the Mössbauer spectra of solid specimens of $(Me_3Sn)_2CN_2$ led to the conclusion that tetracoordinate tin atoms, deshielded by the CN_2 group, are present[164].

A similar effect of the Me_3M groups (M = Si, Ge, or Sn) had been observed previously by ^{13}C NMR in dimetallated ketens $(Me_3M)_2C{=}C{=}O$.[165] In the diazoesters $Me_3MC(N_2)COOEt$ the shielding of the α-carbon atom is less marked [$\delta(^{13}CN_2) = 37.8$–42.9 p.p.m.].[163,164]

REFERENCES

1. Yu.I.Baukov, A.S.Kostyuk, O.S.Sytina, and I.F.Lutsenko, Zhur.Obshch.Khim., **44**, 955 (1974).
2. P.Ashkenazi, S.Lupan, A.Schwartz, and M.Gais, Tetrahedron Letters, 817 (1969).
3. M.F.Lappert and J.S.Poland, Adv.Organomet.Chem., **9**, 397 (1970).
4. M.Regitz, Angew.Chem., **87**, 259 (1975); Int.Ed.Engl., **14**, 222 (1975).
5. M.Regitz, Synthesis, 351 (1972).
6. M.F.Lappert, J.Lorberth, and J.S.Poland, J.Chem. Soc.A, 2954 (1970).
7. E.Müller and D.Ludsteck, Chem.Ber., **87**, 1887 (1954).
8. E.Müller and W.Rundel, Chem.Ber., **88**, 917 (1955).
9. E.Müller and W.Rundel, Chem.Ber., **90**, 1299 (1957).
10. E.Müller and R.Beutler, Annalen, **719**, 72 (1968).
11. R.Beutler, B.Zeeh, and E.Müller, Chem.Ber., **102**, 2636 (1969).
12. R.L.Kreeger and H.Shechter, Tetrahedron Letters, 2061 (1975).
13. U.Schöllkopf and H.U.Scholz, Synthesis, 271 (1976).
14. D.Seyferth and T.C.Flood, J.Organomet.Chem., **29**, C 25 (1971).
15. E.W.Colvin and B.J.Hamill, J.Chem.Soc., Perkin Trans. I, 869 (1977).
16. U.Schöllkopf and H.Frasnelli, Angew.Chem., 82, 291 (1970); Int.Ed.Engl., **9**, 301 (1970).
17. U.Schöllkopf, B.Banhidai, R.Meyer, H.Beckhaus, and H.Frasnelli, Annalen, 1767 (1974).
18. U.Schöllkopf, H.Frasnelli, B.Banhidai, and R.Meyer, BRD.P.2 245094 (1974); Chem.Abs., **81**, 104 755 (1974).
19. R.Pellicciari and B.Natalini, J.Chem.Soc., Perkin Trans Trans.I, 1822 (1977).
20. E.Wenkert and C.A.McPherson, J.Amer.Chem.Soc., **94**, 8084 (1972).

21. E.Müller and W.Rundel, Chem.Ber., **89**, 1065 (1956).
22. U.Schöllkopf and N.Rieber, Chem.Ber., **102**, 488 (1969).
23. U.Schöllkopf, F.Gerhart, M.Reetz, H.Frasnelli, and H.Schumacher, Annalen, **716**, 204 (1968).
24. U.Schöllkopf and N.Rieber, Angew.Chem., **79**, 238 (1967); Int.Ed.Engl., **6**, 261 (1967).
25. M.Regitz, A.Liedenheger, U.Eckstein, M.Martin, and W.Anschutz, Annalen, **748**, 207 (1971).
26. U.Felcht and M.Regitz, Chem.Ber., **108**, 2040 (1975).
27. D.Seyferth, R.S.Marmor, and P.Hilbert, J.Org.Chem., **36**. 1379 (1971).
28. E.T.Blues, D.Bryce-Smith, J.G.Irvin, and I.W.Lawston, Chem.Comm., 466 (1974).
29. N.Eistert, M.Regitz, G.Heck, and H.Schwall, in "Methoden der organischen Chemie (Houben-Weyl), Aufl.*Bd 10/4*, Verl.Thieme, Stuttgart, 1968, p.473.
30. R.Huisgen, Angew.Chem., **67**, 439 (1955).
31. E.Buchner, Chem.Ber., **28**, 215 (1895).
32. T.Curtius and E.Buchner, J.prakt.Chem., [2], **38**, 411 (1888).
33. T.DoMinh, O.P.Strausz, and H.E.Gunning, Tetrahedron Letters, 5237 (1968).
34. T.DoMinh, H.E.Gunning, and O.P.Strausz, J.Amer. Chem.Soc., **89**, 6785 (1967).
35. P.Yates, F.X.Garneau, and J.P.Lokensgard, Tetrahedron, **31**, 1979 (1975).
36. P.Yates and F.X.Garneau, Tetrahedron Letters, 71 (1967).
37. P.Demaree, M.C.Doria, and J.M.Muchowski, Canad.J. Chem., **55**, 243 (1977).
38. A.A.Fridman, N.A.Kolobov, V.S.Zelesov, and M.P.Sivkova, Zhur.Org.Khim., **10**, 884 (1974).
39. S.J.Valenty and P.S.Skell, J.Org.Chem., **38**, 3937 (1973).
40. J.Lorberth, J.Organomet.Chem., **27**, 303 (1971).
41. A.N.Wright, K.A.W.Kramer, and G.Steel, Nature, **199**, 903 (1963).
42. P.Krommes and J.Lorberth, J.Organomet.Chem., **120**, 131 (1976).
43. P.Krommes and J.Lorberth, J.Organomet.Chem., **93**, 339 (1975).
44. P.Krommes and J.Lorberth, J.Organomet.Chem., **127**, 19 (1976).
45. R.Grüning and J.Lorberth, J.Organomet.Chem., **78**, 221 (1974).
46. P.Krommes and J.Lorberth, J.Organomet.Chem., **110**, 195 (1976).
47. E.Glozbach and J.Lorberth, J.Organomet.Chem., **132**, 359 (1977).
48. J.Lorberth, F.Schmock, and G.Lange, J.Organomet. Chem., **54**, 23 (1973).
49. U.Schöllkopf, B.Banhidai, and H.U.Scholz, Annalen, **761**, 137 (1972).
50. J.Lorberth, J.Organomet.Chem., **15**, 251 (1968).
51. M.F.Lappert and J.Lorberth, Chem.Comm., 836 (1967).
52. A.S.Kostyuk, I.B.Ruderfer, Yu.I.Baukov, and I.F.Lutsenko, Zhur.Obshch.Khim., **45**, 819 (1975).
53. P.S.Skell, S.J.Valenty, and P.W.Humer, J.Amer.Chem. Soc., **95**, 5041 (1973).
54. P.Krommes and J.Lorberth, J.Organomet.Chem., **97**, 59 (1975).
55. U.Schöllkopf, M.Reetz, B.Banhidai, and H.U.Scholz, "The XIIIth International Congress on Pure and Applied Chemistry, Boston", p.11.
56. K.D.Kaufmann and K.Rühlmann, Z.Chem., **8**, 262 (1968).
57. K.D.Kaufmann, "Abstracts of Reports at the IVth International Conference on Organometallic Chemistry, Bristol, 1969", p.D9.
58. U.Schöllkopf and N.Rieber, Angew.Chem., **79**, 906 (1967); Int.Ed.Engl., **6** 884 (1967).
59. U.Schöllkopf, D.Hoppe, N.Rieber, and V.Jacobi, Annalen, **730**, 1 (1969).
60. O.A.Kruglaya, I.B.Fedot'eva, B.V.Fedot'ev, and N.S.Vyazankin, Izv.Akad.Nauk SSSR, Ser.Khim., 2790 (1975).
61. O.A.Kruglaya, I.B.Fedot'eva, B.V.Fedot'ev, and N.S.Vyazankin, Izv.Akad.Nauk SSSR, Ser.Khim., 199 (1975).
62. O.A.Kruglaya, I.B.Fedot'eva, B.V.Fedot'ev, V.V.Keiko, and N.S.Vyazankin, Zhur.Obshch.Khim., **46**. 930 (1976).
63. O.A.Kruglaya, I.B.Fedot'eva, B.V.Fedot'ev, I.D.Kalikhman, E.I.Brodskaya, and N.S.Vyazankin, J.Organomet.Chem., **142**, 155 (1977).
64. D.Seyferth, A.W.Dow, H.Menzel, and T.C.Flood, J.Amer.Chem.Soc., **90**, 1080 (1968).
65. D.Seyferth, H.Menzel, A.W.Dow, and T.C.Flood, J.Organomet.Chem., **44**, 279 (1972).
66. J.M.Crossman, R.N.Haszeldine, and A.E.Tipping, J.Chem.Soc., Dalton Trans., 483 (1973).
67. F.Arndt, in "Organic Syntheses" (Translated into Russian), Inostr.Lit., Moscow, 1949, Vol.2, p.174.
68. V.D.Sheludyakov, G.D.Khatuntsev, and V.F.Mironov, Zhur.Obshch.Khim., **39**, 2785 (1969).
69. J.Mathieu and R.Panico, "Reaction Mechanisms in Organic Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1975, p.218.
70. K.D.Kaufmann, B.Auräth, P.Träger, and K.Rühlman, Tetrahedron Letters, 4973 (1968).
71. A.G.Brook and P.F.Jones, Canad.J.Chem., **47**, 4353 (1969).
72. T.J.Barton, J.A.Kilgour, R.R.Gallucci, A.J.Rothschild, J.Slutsky, A.D.Wolf, and M.Jones, J.Amer. Chem.Soc., **97**, 657 (1975).
73. W.Ando, A.Sekiguchi, A.J.Rothschild, R.R.Gallucci, M.Jones, T.J.Barton, and J.A.Kilgour, J.Amer.Chem. Soc., **99**, 6995 (1977).
74. J.A.Kilgour, Ph.D.Thesis, Iowa State Univ., 1976; Diss.Abs., **B**, **36**, 5054 (1976).
75. N.Wiberg and G.Preiner, Angew.Chem., **89**, 343 (1977).
76. G.Himbert, D.Frank, M.Regitz, Chem.Ber., **107**, 2513 (1974).
77. G.Himbert, D.Frank, and M.Regitz, Chem.Ber., **109**, 370 (1976).
78. D.Frank, G.Himbert, and M.Regitz, Chem.Ber., **111**, 183 (1978).
79. E.W.Colvin and B.J.Hamill, Chem.Comm., 151 (1973).
80. W.Kirmse, Angew.Chem., **88**, 273 (1976).
81. S.Masamune, N.Nakamura, M.Suda, and H.Ona, J.Amer.Chem.Soc., **95**, 8481 (1973).
82. K.Nakasuji, K.Kawamura, T.Ishihara, and I.Murata, Angew.Chem., **88**, 650 (1977).
83. K.Nakasuji, K.Kawamura, T.Ishihara, and I.Murata, Heterocycles, **4**, 1835 (1976).
84. F.Gerhart, U.Schöllkopf, and H.Schumacher, Angew. Chem., **79**, 50 (1967).
85. A.L.Fridman and N.A.Kolobov, Zhur.Org.Khim., **12**, 233 (1976).
86. D.A.Evans, L.K.Truesdale, and K.G.Grimm, J.Org. Chem., **41**, 3335 (1976).
87. R.Huisgen, Angew.Chem., **75**, 742 (1963); Int.Ed. Engl., **2**, 633 (1963).
88. R.Huisgen, Angew.Chem., **75**, 604 (1963); Int.Ed. Engl., **2**, 565 (1963).

89. A.G.Brook and P.F.Jones, Canad.J.Chem., **49**, 1841 (1971).
90. M.F.Lappert and J.S.Poland, Chem.Comm., 156 (1969).
91. M.F.Lappert and J.S.Poland, J.Chem.Soc.C, 3910 (1971).
92. A.R.Bassindale and A.G.Brook, Canad.J.Chem., **52**, 3474 (1974).
93. G.W.Cowell and A.Ledwith, Quart.Rev., **24**, 119 (1970).
94. R.Grüning and J.Lorberth, J.Organomet.Chem., **69**, 213 (1974).
95. R.Grüning and J.Lorberth, J.Organomet.Chem., **129**, 55 (1977).
96. H.Staudinger and G.Luscher, Helv.Chim.Acta, **5**, 75 (1922).
97. H.J.Bestmann, H.Buckschewski, and H.Leube, Chem. Ber., **92**, 1345 (1959).
98. L.E.Gusel'nikov and M.C.Flowers, Chem.Comm., 864 (1967).
99. M.C.Flowers and L.E.Gusel'nikov, J.Chem.Soc.B, 419, 1396 (1968).
100. L.E.Gusel'nikov, N.S.Nametkin, and V.M.Vdovin, Acc.Chem.Res., **8**, 18 (1975).
101. L.E.Gusel'nikov, N.S.Nametkin, and V.M.Vdovin, Uspekhi Khim., **43**, 1317 (1974) [Russ.Chem.Rev., No.7 (1974)].
102. H.Sadurai, Kagaku no Ryoiki, **29**, 50 (1975).
103. W.Ando, A.Sekiguchi, and T.Migita, Chem.Letters, 779 (1976).
104. R.L.Kreeger, Ph.D.Thesis, Ohio State University, 1976; Diss.Abs., Int.B, **37**, 3961 (1977).
105. D.N.Roark and L.H.Sommer, Chem.Comm., 167 (1973).
106. R.D.Bush, C.M.Golino, G.D.Homer, and L.H.Sommer, J.Organomet.Chem., **80**, 37 (1974).
107. W.Ando, A.Sekiguchi, J.Hagiwara, and T.Migita, Chem.Comm., 145 (1975).
108. M.R.Chedekel, M.Skoglund, R.L.Kreeger, and H.Shechter, J.Amer.Chem.Soc., **98**, 7846 (1976).
109. O.L.Chapman, C.C.Chang, J.Kolc, M.E.Jung, J.A.Love, T.J.Barton, and M.L.Tumey, J.Amer.Chem. Soc., **98**, 7844 (1976).
110. H.Tomioka, T.Inagaki, and Y.Izawa, Chem.Comm., 1023 (1976).
111. W.Kirmse, "Carbene Chemistry", Acad.Press, New York, 1971
112. H.Tomioka and Y.Izawa, J.Amer.Chem.Soc., **99**, 6128 (1977).
113. M.Jones and R.A.Moss, "Carbenes", Wiley-Intersci., New York, 1973.
114. R.A.Moss and M.A.Joyce, J.Amer.Chem.Soc., **99**, 1262 (1977).
115. A.M.Trozzolo, Acc.Chem.Res., 1, 329 (1968).
116. M.Regitz, W.Illger, and G.Mass, Chem.Ber., **111**, 705 (1978).
117. G.Maas, M.Regitz, and W.Illger, Chem.Ber., **111**, 726 (1978).
118. M.Regitz, New Synth.Methods, **2**, 145 (1965); Chem. Abs., **86**, 155 721 (1977).
119. W.Ando, A.Sekiguchi, T.Hagiwara, and T.Migita, Chem.Comm., 372 (1974).
120. A.Sekiguchi and W.Ando, Bull.Chem.Soc.Japan, **50**, 3067 (1977).
121. O.A.Kruglaya, B.V.Fedot'ev, I.B.Fedot'eva, and N.S.Vyazankin, "Abstracts of Reports at the VIIIth International Conference on Organometallic Chemistry, Kyoto, Japan, 1977", p.120.
122. O.A.Kruglaya, B.V.Fedot'ev, I.B.Fedot'eva, I.D.Kalikhman, and N.S.Vyazankin, Zhur.Obshch. Khim., **48**, 472 (1978).
123. O.A.Kruglaya, I.B.Fedot'eva, B.V.Fedot'ev, and N.S.Vyazankin, Izv.Akad.Nauk SSSR, Ser.Khim., 2646 (1976).
124. P.Yates and R.J.Crawford, J.Amer.Chem.Soc., **88**, 2646 (1966).
125. H.Maier and K.P.Zeller, Angew.Chem., **87**, 52 (1975).
126. A.P.Marchand and N.MacBrockway, Chem.Rev., **74**, 431 (1974).
127. E.R.Matjeka, Ph.D.Thesis, Iowa State Univ., 1974; Diss.Abs., Int.B, **35**, 5339 (1975).
128. W.Ando, A.Sekiguchi, T.Migita, S.Kammula, M.Green, and J.Jones, J.Amer.Chem.Soc., **97**, 3818 (1975).
129. W.Ando and A.Sekiguchi, see Ref.121, p.124.
130. W.Ando, T.Hagiwara, and T.Migita, J.Amer.Chem.Soc., **95**, 7518 (1973).
131. A.Sekiguchi and W.Ando, J.Synth.Org.Chem.Japan, **35**, 897 (1977).
132. O.P.Strausz, T.DoMinh, and H.E.Gunning, J.Amer. Chem.Soc., **90**, 1660 (1968).
133. T.DoMinh, O.P.Strausz, and H.E.Gunning, J.Amer. Chem.Soc., **91**, 1261 (1969).
134. P.S.Skell and S.J.Valenty, J.Amer.Chem.Soc., **95**, 5042 (1973).
135. M.Weidenbruch, Chem.Ztg, 97, 355 (1973).
136. R.N.Haszeldine, D.L.Scott, and A.E.Tipping, J.Chem. Soc., Perkin Trans.I, 1440 (1974).
137. P.S.Skell and R.C.Woodworth, J.Amer.Chem.Soc., **78**, 4496 (1956).
138. A.J.Ashe, J.Amer.Chem.Soc., **95**, 818 (1973).
139. R.T.Taylor and L.A.Paquette, J.Org.Chem., **43**, 242 (1978).
140. T.V.Mandel'shtam, Symposium, "Sovremannye Problemy Organicheskoi Khimii" (Modern Problems of Organic Chemistry), Leningrad, 1976, p.87.
141. W.Ando, T.Hagiwara, and T.Migita, Tetrahedron Letters, 1425 (1974).
142. C.R.Hauser, S.W.Kantor, and W.R.Brasen, J.Amer. Chem.Soc., **75**, 2660 (1953).
143. W.Ando, Acc.Chem.Res., **10**, 179 (1977).
144. D.Seyferth, R.Damrauer, R.M.Turkel, and L.J.Dodd, J.Organomet.Chem., **17**, 367 (1969).
145. H.Watanabe, T.Nakano, K.I.Araki, H.Matsumoto, and Y.Nagai, J.Organomet.Chem., **69**, 389 (1974).
146. D.Seyferth and J.M.Burlitch, J.Amer.Chem.Soc., **85**, 2667 (1963).
147. O.A.Kruglaya, I.B.Fedot'eva, B.V.Fedot'ev, I.D.Kalikhman, E.I.Brodskaya, and N.S.Vyazankin, Izv.Akad.Nauk SSSR, Ser.Khim., 1887 (1976).
148. L.I.Belousova, O.A.Kruglaya, V.V.Neretin, I.D.Kalikhman, N.A.Ivanova, A.A.Tatarinova, and N.S.Vyazankin, Izv.Akad.Nauk SSSR, Ser.Khim., 2070 (1977).
149. D.Seyferth, R.J.Cross, and B.Prokai, J.Organomet. Chem., **7** P 20 (1967).
150. D.Seyferth, E.M.Hanson, B.Prokai, and R.J.Cross, J.Organomet.Chem., **24**, 33 (1970).
151. E.O.Fischer, Adv.Organomet.Chem., **14**, 1 (1976).
152. O.P.Strausz, G.J.A.Kennepohl, F.X.Garneau, T.DoMinh, B.Kim, S.Valenty, and P.S.Skell, J.Amer. Chem.Soc., **96**, 5723 (1974).
153. T.B.Patrick and T.T.Wu, J.Org.Chem., **43**, 1506 (1978).
154. T.B.Patrick and G.H.Kovith, J.Org.Chem., **40**, 527 (1975).
155. W.A.Herrmann, Angew.Chem., **86**, 895 (1974); Int. Ed.Engl., **13**, 812 (1974).
156. W.A.Herrmann, J.Organomet.Chem., **97**, 1 (1975).

157. C.Glidewell and G.M.Sheldrick, J.Chem.Soc., Dalton Trans., 2409 (1972).
158. A.P.Cox, L.F.Thomas, and J.Sheridan, Nature, **181**, 1000 (1958).
159. R.A.Smith, M.Torres, and O.P.Strausz, Canad.J. Chem., **55**, 2752 (1977).
160. R.A.Smith, M.Torres, and O.P.Strausz, Canad.J. Chem., **55**, 3527 (1977).
161. J.G.Csizmadia, H.E.Gunning, R.K.Gosavi, and O.P.Strausz, J.Amer.Chem.Soc., **95**, 133 (1973).
162. F.Kaplan and G.K.Meloy, J.Amer.Chem.Soc., **88**, 950 (1966).
163. R.Grüning, P.Krommes, and J.Lorberth, J.Organomet. Chem., **128**, 167 (1977).
164. A.Fadini, E.Glozbach, P.Krommes, and J.Lorberth, J.Organomet.Chem., **149**, 297 (1978).
165. Yu.K.Grishin, S.V.Ponomarev, and S.A.Lebedev, Zhur.Org.Khim., **10**, 404 (1974).

Irkutsk Institute of Organic Chemistry,
Siberian Division of the USSR
Academy of Sciences

Translated from *Uspekhi Khimii*, **49**, 706 - 732 (1980) U.D.C. 577.161.2

The Synthesis of Active Metabolites and Analogues of Vitamin D_3

R.I.Yakhimovich

The literature data on the synthesis of the active metabolites and analogues of vitamin D_3 (cholecalciferol), which play an important role in regulating the homeostatis of calcium in the organism, are reviewed.
The bibliography includes 150 references.

CONTENTS

I. Introduction 371
II. The synthesis of cholecalciferol 372
III. The synthesis of 25-hydroxycholecalciferol 373
IV. The synthesis of 1α-hydroxycholecalciferol 376
V. The synthesis of 1α, 25-dihyroxycholecalciferol 378
VI. The synthesis of 3-deoxy-1α-hydroxycholecalciferol 379
VII. The synthesis of 24*R*,25-dihyroxycholecalciferol 380
VIII. The synthesis of 25,26-dihydroxycholecalciferol 381
IX. The synthesis of 1α,24*R*,25-trihydroxycholecalciferol 381

I. INTRODUCTION

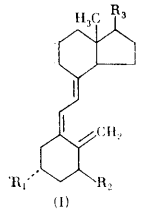
A rigorously defined concentration of calcium in the blood is essential for the normal functioning of the living organism. The factors responsible for maintaining a constant level of calcium are the parathyroid hormone, which mobilises calcium cations from the bones when the calcium concentration falls, as well as calcitonin, which lowers the level of calcium, when its concentration increases, by the calcification of the bone tissue. Both of these hormones maintain a constant level of calcium in the blood by drawing on the internal reserves of the organism[1]. A possible regulator of the homeostasis of calcium entering the organism is vitamin D_3 (cholecalciferol) (Ia), which is a natural and the most active vitamin of the D group.

Vitamins of the D group control the entry of exogenic calcium into the organism by absorbing it from the food in the intestine; in addition, they participate in the mobilisation of calcium from the bones and promote the calcification of the bone tissue and an increase of the concentration of phosphate in the blood. These functions are impaired in rickets, a common disease of a growing organism, and vitamins D are virtually the only radical anti-rickets preparations.

It was believed for a long time that vitamin D_3 acts in the organism without undergoing any changes. The difficulty of studying the mechanism of the action and metabolism of vitamin D_3 is due to the fact that the amounts of the vitamin to which animals respond are vanishingly small and extremely sensitive methods are required for their detection. It was not until the end of the 1960's, after the synthesis of radioactive preparations of vitamin D_3 with a high specific activity, the development of new effective thin-layer and column chromatographic methods, and the application of high-resolution mass spectrometric and NMR methods, that it was possible to investigate the transformations of vitamin D_3 in the organism and to elucidate the mechanism of the action of its metabolites.

In 1966 American investigators[2,3] detected the first metabolite of vitamin D_3, which was isolated and identified as 25-hydroxycholecalciferol (25-OHD_3) (Ib).[4,5] DeLuca and coworkers[6] established that 25-hydroxylation of vitamin D_3 takes place in the liver and that this results in the formation of a metabolite 1.4 times more active than vitamin D_3 in the treatment of rickets and acting three times as fast[7,8].

The synthesis of radioactive 25-OHD_3 made it possible to follow the further transformations of this metabolite in the organism. In 1971 three groups of investigators, headed by Kodicek[9], DeLuca[10,11], and Norman[12], isolated almost simultaneously a new metabolite—1α, 25-dihydroxycholecalciferol [1α, 25-$(OH)_2D_3$] (Ic). It is biosynthesised in the kidneys[13] and is not formed in nephrectomised animals[14]:



(I)

(a) D_3: R_1 = OH; R_2 = H; R_3 =

(b) 25-OHD_3: R_1 = OH; R_2 = H; R_3 =

(c) 1α,25-$(OH)_2D_3$: R_1 = OH; R_2 = OH; R_3 =

(d) 1α-OHD_3: R_1 = OH; R_2 = OH; R_3 =

(e) 3-deoxy-1α-OHD_3: R_1 = H; R_2 = OH; R_3 =

(f) 24*R*, 25-$(OH)_2D_3$: R_1 = OH; R_2 = H; R_3 =

(g) 25, 26-$(OH)_2D_3$: R_1 = OH; R_2 = H; R_3 =

(h) 1α, 24*R*, 25-$(OH)_3D_3$: R_1 = OH; R_2 = OH; R_3 =

The metabolite 1α, 25-$(OH)_2D_3$ is the most active hormonal form of vitamin D_3, being 10–15 times more active than the latter[1,15]. It acts very rapdily on all known systems, which are acted upon by vitamin D_3, stimulating the absorption of calcium in the intestine, the mobilisation of calcium from the bone, and the calcification of the bone tissue; it also increases the concentration of phosphate in blood serum. A very important property of 1α, 25-$(OH)_2D_3$ is that it induces all these processes also in the case of kidney diseases, when neither vitamin D_3 nor its other metabolites have any activity. 1α, 25-$(OH)_2D_3$ has therefore been used successfully

in the treatment of various bone diseases associated with kidney affections, such as osteomalacia, osteoporosis, etc. However, the complexity of the synthesis of 1α, 25-$(OH)_2D_3$ makes it so far relatively unavailable for wide-scale application. The search for a synthetic analogue of 1α, 25-$(OH)_2D_3$ led DeLuca to the synthesis in 1973 [16] of 1α-hydroxycholecalciferol (1α-OHD_3) (Id) which was shown by extensive studies of its biological activity[16-20] to be capable of replacing 1α, 25-$(OH)_2D_3$ in therapeutic practice[21,22].

3-Deoxy-1α-hydroxycholecalciferol (3-deoxy-1α-OHD_3) (Ie), synthesised in 1974 in the laboratories of Norman[23] and DeLuca[24,25], also proved to be an analogue of 1α, 25-$(OH)_2D_3$ with a high biological activity. It stimulates the transport of calcium in the intestine almost as actively as 1α, 25-$(OH)_2D_3$,[23,24,26] but its effect on the bone system is less pronounced. This specific property makes this compound extremely important in the treatment of bone diseases in those cases where it is necessary to stimulate the transport of calcium in the intestine without causing its mobilisation from the bone.

Several other metabolites, in addition to 25-OHD_3, and 1α, 25-$(OH)_2D_3$, were isolated in the study of the metabolism of vitamin D_3. In 1970 DeLuca and coworkers[27,28] isolated 24, 25-dihydroxycholecalciferol [24, 25-$(OH)_2D_3$] (If), which is formed when animals are on a normal or a hypercalcemic diet[29]. The synthesis of two stereoisomers and the study of the biological activity of 24*R*- and 24*S*-25-$(OH)_2D_3$ showed that the 24*R*-isomer is formed in the organism and is almost as active as 25-OHD_3.[30,31]

25,26-Dihydroxycholecalciferol [25,26-$(OH)_2D_3$] (Ig) [32] and 1α, 24,25-trihydroxycholecalciferol [1α, 24,25-$(OH)_3D_3$] (Ih) [33] were isolated from the blood plasma of animals administered radioactive vitamin D_3. These metabolites are active in the transport of calcium in the intestine, but are relatively ineffective in the treatment of rickets and in the mobilisation of calcium from bone[33-37]. However, one cannot rule out the possibility that, on being formed in the organism, these metabolites play an important physiological role †.

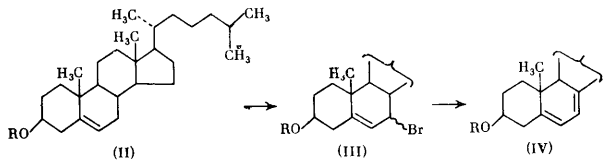
The high activity of vitamin D_3 metabolites not only in the treatment of rickets but also in other severe diseases associated with the breakdown of the homeostasis of calcium in the organism led chemists in many countries to join in the search for a solution to the problem of the chemical synthesis of these compounds. During the last few years, different versions of complex chemical syntheses of active metabolites of vitamin D_3 and some of its active analogues were therefore proposed.

The biochemical synthesis of the metabolites in the organism takes place with the aid of the corresponding enzyme system in the liver or in the kidneys and proceeds in such a way that direct transition from the molecule of vitamin D_3 to that of its hydroxy-derivative is acheived. Chemical syntheses of the active metabolites and analogues of vitamin D_3 involve complex multistage transformations of the entire structure of the steroid molecule of the initial substance and are therefore in most instances mainly of theoretical interest. Practical applications of these important biologically active compounds have unfortunately not been found so far.

† The relation between the structure and biological activity of vitamins D, their metabolites, and synthetic analogues was described in greater detail in a monograph by the author of the present review[38].

II. THE SYNTHESIS OF CHOLECALCIFEROL

The synthesis of vitamin D_3, achieved as early as 1936 by Windaus and coworkers[39,40], includes two main stages: the formation of the provitamin and its photochemical isomerisation. A distinctive feature of provitamins D is the presence of two conjugated double bonds at the ring $C_{(5)}-C_{(6)}-C_{(7)}-C_{(8)}$ atoms of the steroid molecule. 7-Dehydrochloesterol, which is a provitamin of cholecalciferol, is cholesterol (IIa) dehydrogenated at $C_{(7)}-C_{(8)}$. The introduction of an additional double bond into the cholesterol molecule is achieved by different methods: by the oxidisation of a cholesterol ester to the 7-oxo-derivative and then by reduction, benzoylation, and elimination of benzoic acid from 7-hydroxycholesterol 3,7-dibenzoate[41-42]; the formation of the tosylhydrazone from the 7-oxo-derivative by the Bamford–Stevens reaction has been described. It is subsequently converted into the provitamin on interaction with LiH.[43] The method involving the allylic bromination of the cholesterol ester (IIb) with subsequent dehydrobromination of the 7-bromo-derivative (III) and the hydrolysis of the 7-dehydrocholesterol ester (IVb) to 7-dehydrocholesterol (IVa) is most widely used[44]:

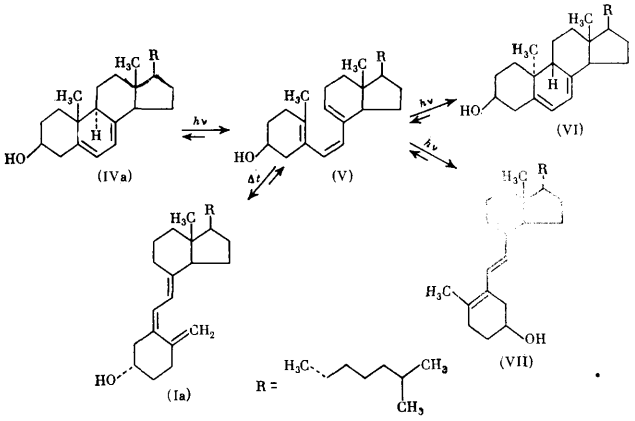


The allylic bromination of cholesterol esters (usually the benzoates) is carried out with 1,3-dibromo-5,5-dimethylhydantoin in a benzene-petroleum ether mixture[45] or in CCl_4 in the presence of radical initiators[46,47]. The yield of compound (III) reaches 92–94%.[47] Depending on the dehydrobrominating agents and the reaction conditions, the dehydrobromination of (III) can lead to the formation, apart from the required $\Delta^{5,7}$-diene (IVb), also of other cholestadienes (the $\Delta^{4,6}$-, $\Delta^{5,8(9)}$-, $\Delta^{6,8(14)}$-, and $\Delta^{8,14}$- derivatives) and cholestatrienes (the $\Delta^{2,4,6}$- and $\Delta^{4,6,8(14)}$- derivatives). The maximum yield of the $\Delta^{5,7}$-diene (up to 60%) was obtained on dehydrobromination in boiling xylene with various organophosphorus compounds (trialkyl phosphites and dioxaphospholans)[45,48-50] as well as $NaHCO_3$ in the presence of catalytic amounts of α-picoline[46,51]. The main side product under these conditions is the $\Delta^{4,6}$-diene.

Provitamins derived from cholecalciferol are usually synthesised in accordance with the above scheme, but in certain cases it is impossible to introduce the double bond at $C_{(7)}-C_{(8)}$ by the methods described or the yield of provitamins is very low[23,52,53]. Certain new methods for the introduction of conjugated double bonds into the B ring, which will be considered directly in connection with the synthesis of hydroxylated cholecalciferols, have therefore been proposed[54-56].

The photochemical isomerisation of provitamins D is accompanied by the dissociation of the $C_{(9)}-C_{(10)}$ bond and the opening of the B ring with the formation of the direct precursor of vitamins D—previtamin D (V). When the previtamin is irradiated with ultraviolet light, two photoisomers are formed—lumisterol (VI) and tachysterol (VII), while thermal isomerisation leads to the formation of vitamins D (I). The mechanism of these reversible transformations, which is nowadays generally accepted, was established by the studies of Velluz and coworkers[57] and Havinga and coworkers[58-60] over a period of many years.

The photochemical isomerisation of provitamins D is usually carried out in solution in ethanol, ether, benzene, and other solvents up to not more than 50% conversion, in order to reduce the accumulation of side products—tachysterol and lumisterol. The yield of the previtamin is a maximum when unfiltered ultraviolet light at $\lambda = 295$ nm [61] or erythemal lamps E-3 phosphor (transmission maximum at 302–305 nm) [62] are used:



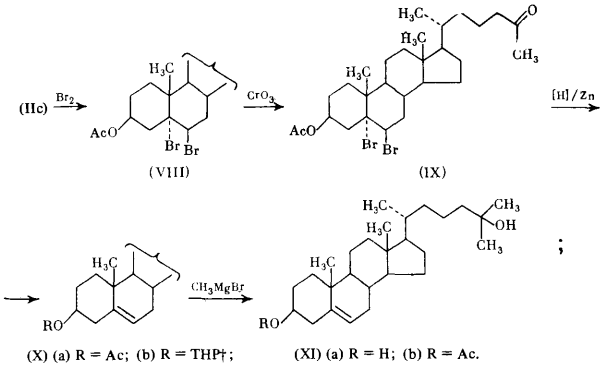
III. THE SYNTHESIS OF 25-HYDROXYCHOLECALCIFEROL

The chemical synthesis of 25-hydroxycholecalciferol was achieved by Blunt and DeLuca[63,64] to confirm the structure of the active vitamin D_3 metabolite isolated from blood plasma, and Haltes and van Vliet[65] obtained for the first time crystalline 25-OHD_3 in the form of the monohydrate.

The main difficulty in the synthesis of 25-OHD_3 is the formation of the key compound—25-hydroxycholesterol. Numerous studies on the synthesis of this compound, differing mainly in the starting material, have therefore been published in recent years. 25-Hydroxycholesterol is converted into 25-OHD_3 as described in Section II.

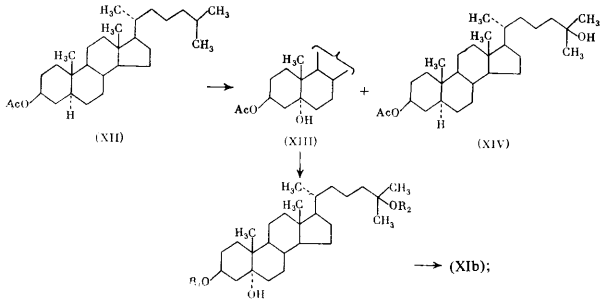
1. Synthesis from Cholesterol and Cholestanol

25-Hydroxycholesterol is formed in a small amount in the autoxidation or photolysis of cholesterol together with other hydroxylated derivatives[66,67]. DeLuca and coworkers[63,64] and Halkes and van Vliet[65] synthesised 25-hydroxycholesterol from cholesterol by the method described as early as 1950.[68–70] The bromination of cholesteryl acetate (IIc), the oxidation of the dibromide (VIII) with CrO_3 in acetic acid to the 27-nor-25-oxo-derivative (IX), and treatment of the latter with zinc dust in acetic acid lead to 25-oxo-27-norcholest-5-en-3β-yl acetate (Xa). The reaction with methylmagnesium bromide yields the 3β-acetate of 25-hydroxycholesterol (XIb). However, the yields of (Xa) and (XIb) are very insignificant.



(X) (a) R = Ac; (b) R = THP†; (XI) (a) R = H; (b) R = Ac.

On irradiating cholestan-3β-yl acetate (XII) ultraviolet light at $\lambda = 300$ nm in acetic acid + hydrogen peroxide solution, Rotman and Mazur[71] obtained 37.5% yield of the 25-hydroxy-derivative (XIV) and a 30% yield of the 5α-hydroxy-derivative (XIII). On further irradiation of compound (XIII), the 3β-acetate of cholestane-3β, 5α, 25-triol (XVa) is formed, giving rise to the 3β-acetate (XIb) after acetylation and treatment of the diacetate (XVb) with a mixture of acetic acid and toluene-*p*-sulphonic acid and hydrolysis:



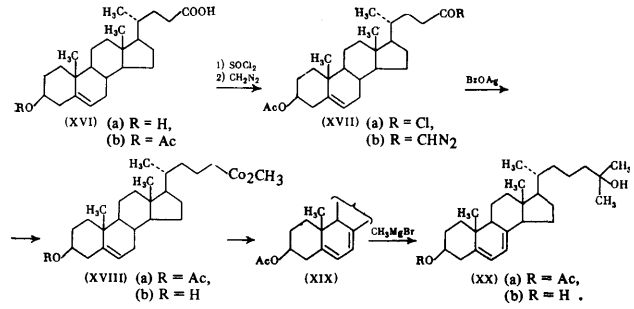
(XV) (a) R_1 = Ac, R_2 = OH; (b) $R_1 = R_2$ = Ac.

2. Synthesis from 3β-Hydroxychol-5-enoic Acid

3β-Hydroxychol-5-enoic acid (XVIa), which is a relatively readily available substance formed on oxidation of the cholesterol side chain, has been used[72,73] to synthesise the provitamin 25-OHD_3. The acid (XVIa) was converted via the 3β-acetate (XVIB) and the acid chloride (XVIIa) into the diazoketone (XVIIb) and then into the 25-homoester (XVIIIa) on interaction with silver benzoate. After these transformations in the side chain, the 5,7-diene (XIX) was obtained by the usual method involving allylic bromination and dehydrobromination. The synthesis of the provitamin–cholesta-5,7-diene-3β, 25-diol (XXb)—is completed by the reaction

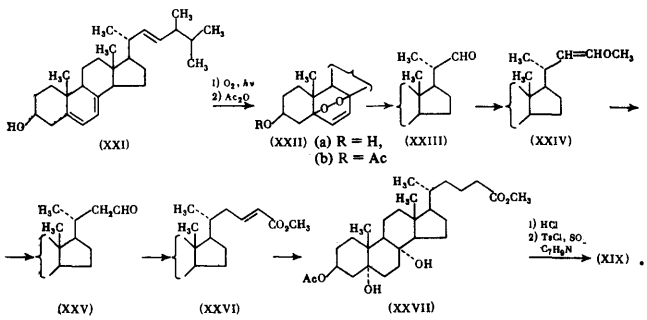
† THP = tetrahydropyranyl ether.

with methylmagnesium bromide and hydrolysis:

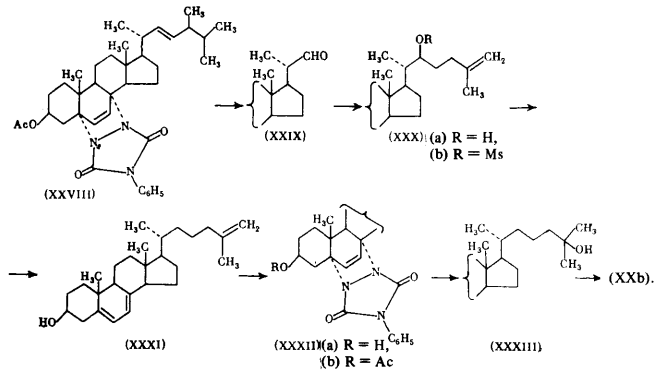


3. Synthesis from Ergosterol

The 5,7-diene (XIX) has been obtained[74-77] by the transformation of the ergosterol side chain. The photosensitised addition of oxygen to ergosterol (XXI) leads to the peroxide (XXIIa), while the cleavage of the double bond in the side chain by the ozonolysis of the acetate (XXIb) yields the aldehyde (XXIII). The growth of the side chain was achieved by condensation with triphenylmethoxymethylenephosphorane to the methyl ether (XXIV), which gives rise to the aldehyde (XXV) after hydrolysis with formic acid. On treatment with triphenylmethoxycarbonylmethylenephosphorane, the aldehyde is converted into a mixture of the *trans*- and *cis*-isomers of the methyl esters of 3β-acetoxy-5,8-epidihydroxyhomochola-6,23-diene-25-ioc acid (XXVI). The methyl ester of the *trans*-acid was hydrogenated in the presence of palladium and the dehydration leading to the formation of compound (XIX) was carried out without isolating the triol acetate (XXVII). The conversion of the ester (XIX) into 25-OHD_3 was described above[72,73]:

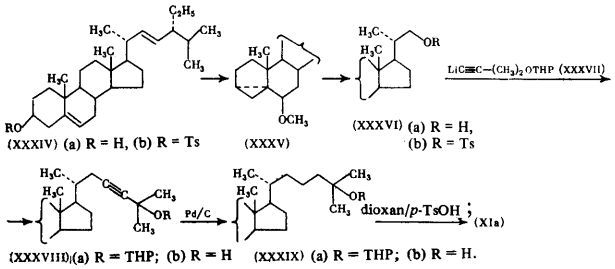


A more convenient pathway from ergosterol to the 25-hydroxy-provitamin (XXb) has been proposed by Eyley and Williams[56,78]. The adduct of the ergosteryl acetate and 4-phenyl-1,2,4-triazoline-3,5-dione (XXVIII) was obtained by the method of Barton et al.[79] and was converted into the aldehyde (XXIX) by ozonolysis. The reaction of compound (XXIX) with the Grignard reagent obtained from 4-chloro-2-methylbut-1-ene in tetrahydrofuran (THF) at 30 °C gave the alcohol (XXXa), which gave rise to the trienol (XXXI) after conversion into the methanesulphonate (XXXb) and reduction with $LiAlH_4$. The 5,7-double bonds were again protected via the adduct (XXXIIa) and the acetylation of the latter, the oxidation of the diene (XXXIIb) with $Hg(OAc)_2$ to the 25-hydroxy-derivative (XXXIII), and reduction with $LiAlH_4$ gave compound (XXb):



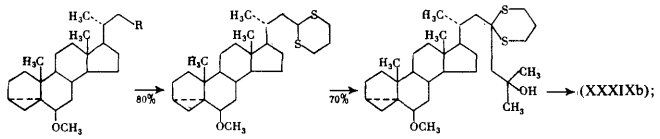
4. Synthesis from Stigmasterol

The synthesis of compound (XIa) from stigmasterol (XXXIVa), which is a fairly readily available plant sterol obtained from soya beans, is also based on the cleavage of the double bond in the side chain. Partridge and coworkers[80,81] achieved this cleavage in the following way. The 5,6-double bonds of stigmasterol were initially protected by the formation of the *i*-methyl ester (XXXV), which is achieved by treating the toluene-*p*-sulphonate (XXXIVb) with methanol and pyridine. The *i*-methyl ester (XXXV) was ozonised at -78 °C and then reduced with sodium bis-(2-methyoxyethoxy)aluminium hydride to the alcohol (XXXVIa), which was converted into the crystalline toluene-*p*-sulphonate (XXXVIb). Alkylation of the latter with lithium acetylide (XXXVII) (obtained from n-butyl-lithium and 3-methyl-1-but-3-ynyl tetrahydropyranyl ether) gave a 90% yield of compound (XXXVIIIa). The acetylenic bond in (XXXVIIIa) was hydrogenated over PtO_2 or Pd/C and compound (XXXIXa) was isolated in quantitative yield. The authors then propose several versions of the synthesis of compound (XIa). One of these involves the conversion of compound (XXXIXa) into the alcohol (XXXIXb), which, on treatment with aqueous dioxan in the presence of catalytic amounts of toluene-*p*-sulphonic acid, gave compound (XIa). The overall yield of compound (XIa) was 30% with respect to stigmasterol.



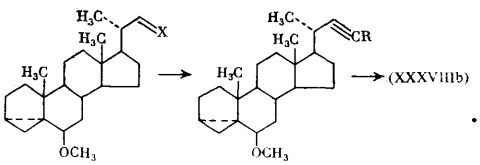
By the reaction of the bromide (XLa) or the iodide (XLb), obtained by Partridge et al.[80] from the alcohol (XXXVIa), with 2-lithiodithian, Salmond and Maisto[82] obtained the dithioacetal (XLI), which gives rise to the alcohol (XLII) after treatment with n-butyl-lithium and subsequent condensation with 1,2-epoxy-2-methylpropanol. When the alcohol (XLII) is refluxed with $LiAlH_4$ + $TiCl_4$ in THF, compound (XXXIXb)

is obtained:



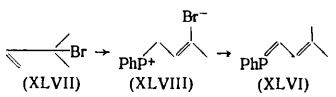
(XL) (a) R = Br; (b) R = I. (XLI) (XLII)

Salmond et al.[83] also used the aldehyde (XLIIIa) [obtained by the ozonolysis of compound (XXXV)], which, on reaction with dibromomethylenetriphenylphosphorane, gives a high yield of 20*R*-dibromovinylpregnane (XLIIIb). Treatment of the dibromo-olefin with n-butyl-lithium at -68 °C leads to the lithio-derivative (XLIV), from which 20*R*-ethynylpregnane (XLV) was obtained by hydrolysis. Its interaction with 1,2-epoxy-2-propanol in the presence of hexamethylphosphoramide results in the formation of the alcohol (XXXVIIIb) in 70% yield. The hydrogenation of the acetylenic bond over PtO_2 results in the formation of the alcohol (XXXIXb):



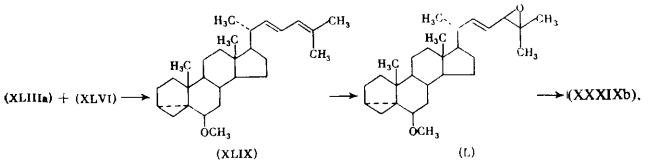
(XLIII) (a) X = O, (XLIV) R = Li
(b) X = CBr_2 (XLV) R = H

Salmond and Sobala[84] recently proposed a still simpler procedure for the formation of compound (XXXIXb) from stigmasterol with an overall yield in excess of 50%. Although the total number of stages was 7, as in the work of Partridge et al.[80], it was necessary to isolate and crystallise the reaction products only three times, which greatly simplifies the synthesis. The first three stages, namely the conversion of stigmasterol into the toluene-*p*-sulphonate (XXXIVb) and the *i*-methyl ester (XXXV) and ozonisation to the aldehyde (XLIIIa), were described above. In order to introduce the side chain, the diene (XLVI) was synthesised from the bromide (XLVII) via the salt (XLVIII):



(XLVII) (XLVIII) (XLVI)

The condensation of the aldehyde (XLIIIa) with (XLVI) yields the diene (XLIX):

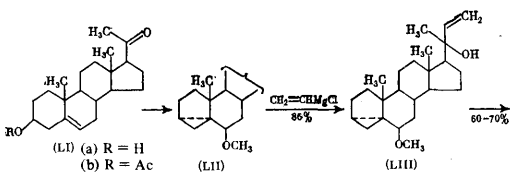


(XLIX) (L)

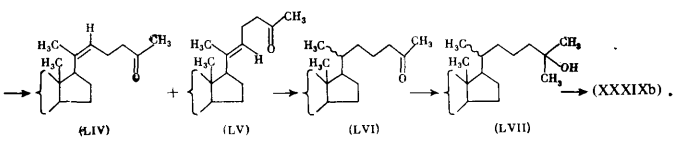
Next the Δ^{24}-double bond was selectively epoxidised with peracetic acid and the epoxide (L) was obtained; it was reduced over Pd/C to compound (XXXIXb) in 56% yield with respect to (XXXIVb). When the *i*-ester (XXXIXb) is refluxed in acetic acid, compound (XIb) is formed in 94% yield.

5. Synthesis from Pregnenolone

Narwid and coworkers[85,86] used a commercial product—pregnenolone (LIa)—and its acetate (LIb) to synthesise 25-hydroxycholesterol. As in the case of stigmasterol, the 5,6-double bonds in compound (LIa) were first protected by conversion into the *i*-steroid (LII), which gives rise to the allyl alcohol (LIII) after reaction with vinylmagnesium chloride. Next the side chain was lengthened to 7 carbon atoms by treating the alcohol (LIII) with an excess of diketen, giving a 1 : 2 mixture of the *cis*- and *trans*-oxo-isomers (LIV) and (LV), which was reduced over PtO_2 to a mixture of saturated ketones (LVI). After treating the latter with CH_3MgI, a mixture of alcohols (LVII) was obtained. The natural 20*R*-isomer (XXXIXb) was separated by crystallisation and obtained in 26% yield, from the alcohol (LIII). The overall yield of 25-hydroxycholesterol with respect to pregnenolone was 17%:

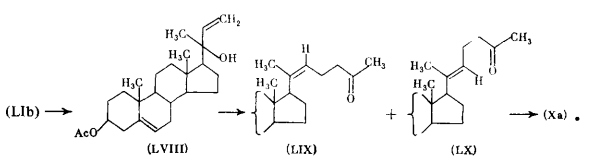


(LI) (a) R = H (LII) (LIII)
(b) R = Ac



(LIV) (LV) (LVI) (LVII)

Compound (XIa) can be synthesised from the acetate of pregnenolone (LIb) without the preliminary protection of the 5,6-double bond. For this purpose, the alcohol (LVIII) was obtained from the acetate (LIb) and vinylmagnesium chloride[85]. The side chain was lengthened by interaction with diketen. A mixture of the *cis*- and *trans*-keto-olefins (LIX) and (LX) was obtained with an overall yield of 72%. Catalytic hydrogenation of this mixture over PtO_2 leads to the 20*R*-ketone (Xa). (Xa) was converted into (XIa) in 88% yield by the Grignard reaction with subsequent hydrolysis of the ester. The overall yield of compound (XI) with respect to compound (LIb) was 25–28%:



(LVIII) (LIX) (LX)

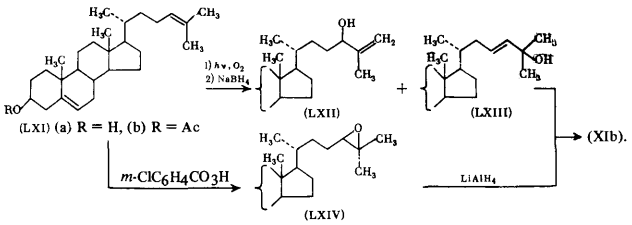
6. Synthesis from 3β-Hydroxyandrost-5-en-17-one

The stereospecific synthesis of 25-hydroxycholecalciferol from 3β-hydroxyandrost-5-en-17-one has been described[87]. Although the overall yield is 42%, the authors carried out more than 10 transformations in order to introduce the cholesterol side chain with the 25-hydroxy-group.

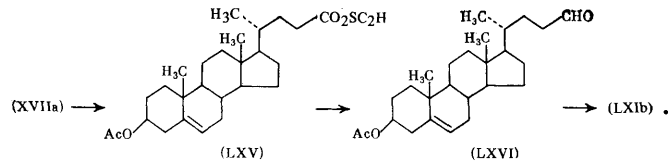
7. Synthesis from Desmosterol

A series of investigations by Japanese workers on the synthesis of active forms of vitamin D was published in 1973[88-92]. Desmosterol (LXIa), the structure of which is very convenient for the introduction of a hydroxy-group at $C_{(25)}$ by various methods, was chosen as the starting material.

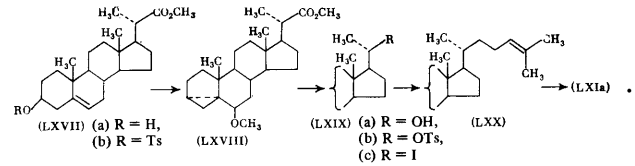
When a solution of desmosteryl acetate (LXIb) [88] was irradiated with sunlight in isopropyl alcohol in the presence of a sensitiser and the unpurified product was reduced with $NaBH_4$, two substances were obtained—the 3β-acetates of cholesta-5, 25-diene-3β,24-diol (LXII) (25%) and cholesta-5,23-diene-3β, 25-diol (LXIII) (35%). The catalytic hydrogenation of the latter over Pd/C gives compound (XIb) in 60% yield. Another way of obtaining compound (XIb) from (LXIb) involves the selective epoxidation of the double bond at $C_{(24)}$–$C_{(25)}$ in *m*-chloroperbenzoic acid with formation of the 24,25-monoepoxide (LXIV), which is then reduced with $LiAlH_4$ to compound (XIb) with an overall yield of 50%. Finally, the third and most convenient method of synthesis of compound (XI) involves the treatment of compound (LXIb) with $Hg(OAc)_2$ or HgBr followed by reduction with $NaBH_4$. After chromatographic purification on silica gel, compound (XIb) is obtained in 85% yield. This is apparently the simplest and most effective method of synthesising 25-hydroxycholesterol among all those described.



Since desmosterol proved to be a very convenient starting material for the synthesis not only of 25-OHD_3 but also of other active vitamin D_3 metabolites, numerous studies have now been carried out on its preparation[94–99]. The Wittig synthesis of desmosterol from the acetate of 3β-hydroxycholest-5-enoic acid (XVIb) has been described[100]. The acid was converted into the chloride (XVIIa), the condensation of which with ethanethiol gave ethyl thiocholenoate (LXV), which was converted into the aldehyde (LXVI) by treatment with Raney nickel, and finally the reaction with the Wittig reagent gave compound (LXIb):

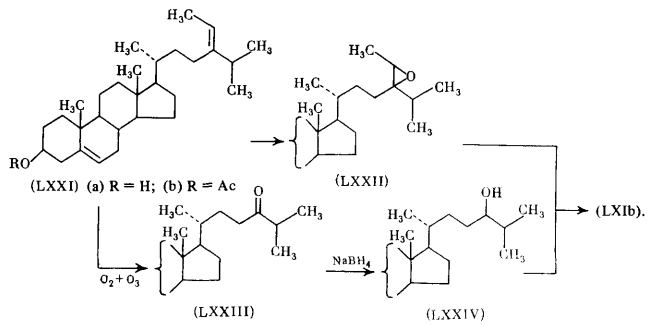


3β-Hydroxybisnorchol-5-enoic and 3β-hydroxynorchol-5-enoic acids can also serve as the starting materials for the synthesis of compound (LXIa).[94] The methyl ester (LXVIIa) was converted into the toluene-*p*-sulphonate (LXVIIb) and then into the *i*-ester (LXVIII), which was reduced with $LiAlH_4$ and converted into the 22-toluene-*p*-sulphonate (LXIXb) without isolating the alcohol (LXIXa). The reaction of the toluene-*p*-sulphonate with NaI gave the corresponding iodide (LXIXc):



Next the iodide was converted by treatment with π-(dimethylallyl)nickel bromide into the desmosterol *i*-ester (LXX), whose treatment with $HClO_4$ gave desmosterol (LXIa) in an overall yield of 20%. Bergmann and Dusza[96] obtained demosterol from 25-oxocholesterol.

Japanese workers[97–99] developed several methods for the preparation of demosterol from fucosterol (LXXIa), the principal sterol in brown algae[101,102]. Fucosteryl acetate (LXXIb) was oxidised with *m*-chloroperbenzoic acid to the 24,28-epoxide (LXXII) and, after treatment of the latter with BF_3. .($SnCl_4$, $AlCl_3$), desmosteryl acetate was obtained in 30% yield. When the 24,28-epoxide was treated with silica gel, a zeolite, and other Lewis acids, the yield of compound (LXIb) was 40%.[99] Fucosteryl acetate was converted into compound (LXIb) via the ketone obtained by the ozonolysis of compound (LXXIb) with a $O_3 + O_2$ mixture in CH_2Cl_2 at -78 °C after its reduction to the alcohol (LXXIV) and dehydration of the latter latter by P_2O_5 in benzene:



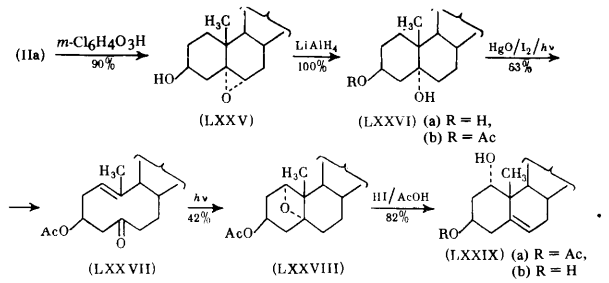
Other methods for the introduction of a hydroxy-group at $C_{(25)}$ are also known[103–105], but unfortunately they all involve many stages and give fairly low yields.

IV. THE SYNTHESIS OF 1α-HYDROXYCHOLECALCIFEROL

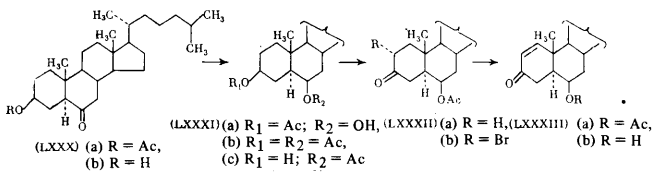
The high biological activity of 1α-hydroxycholecalciferol, comparable to that of 1α, 25-$(OH)_2D_3$,[16–22] and its simpler synthesis, involving the transformation of only the A ring, make this compound the most promising synthetic analogue of 1α, 25-$(OH)_2D_3$—the active hormonal form of vitamin D_3. During the last few years, numerous reports of the synthesis of 1α-OHD_3 have therefore been published.

As in the case of 25-OHD_3, the most complex feature of the synthesis of 1α-OHD_3 is the formation of the 1α-hydroxy-derivative of cholesterol, which is converted into 1α-OHD_3 by the usual methods. 1α-Hydroxycholesterol has been obtained[106] in a study of the photochemical cyclisation of 5,10-seco-steroids together with other products in a fairly low overall yield. At that time the authors' aim was not the development of a 1α-hydroxylation method, which is so necessary for the synthesis of 1α, 25-$(OH)_2D_3$ and 1α-OHD_3. In 1977 Mihailović et al.[107] improved the method of synthesis of 1α-hydroxycholesterol via the seco-derivative and proposed a fairly simple method with an overall yield of approximately 20%. Cholesterol (IIa) was oxidised with *m*-chloroperbenzoic acid to give a 90% yield of the 5α, 6α-epoxide (LXXV), which was reduced quantitatively with $LiAlH_4$ to the 3β, 5α-diol (LXXVIa) and the latter was converted into the 3β-acetate (LXXVIb). Treatment of the acetate with HgO, I_2, and ultraviolet light gave a 63% yield of the 3β-acetate of 5,10-seco-cholest-1(10)-en-5-one (LXXVI), whose photochemical cyclisation gives compound (LXXVIII)(42%). Treatment of compound (LXXVIII) with HI led to an 82% yield of the 3β-acetate of 1α-hydroxy-

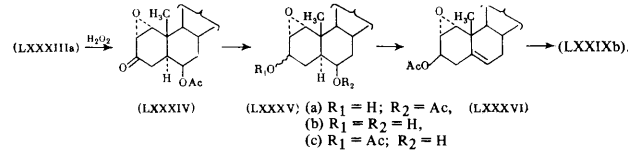
cholesterol (LXXIXa):



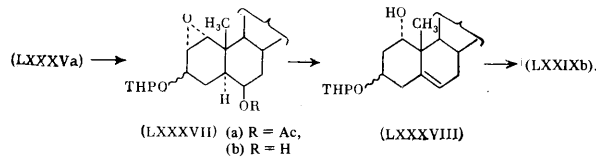
The first study on the specific synthesis of 1α-hydroxycholesterol (LXXIXb) was carried out in 1970 by Pelc and Kodicek[108], who detected, in the study of the metabolism of [1-^{3}H] vitamin D_3, a metabolite with a deficiency of radioactive hydrogen and more polar than 25-OHD_3, probably as a result of the incorporation of an additional oxygen atom at $C_{(1)}$;[109,110] an attempt was therefore made to synthesise the 1α-hydroxy-analogue of vitamin D_3. These workers began with 6-oxo-5α-cholestan-3β-yl acetate (LXXXa), which can be readily obtained from cholesteryl acetate by nitration and subsequent reduction of the nitro-compound and hydrolysis. The 6-oxo-derivative (LXXXa) was reduced with $NaBH_4$ to the 6β-hydroxy-derivative (LXXXIa) in a high yield and the latter was then acylated to the 3β,6β-diacetate (LXXXIb), which was converted by mild aklakine hydrolysis into the 6β-acetate (LXXXIc):



The oxidation of the 3β-hydroxy-group to the carbonyl group with sodium dichromate in acetic acid and then bromination of the ketone (LXXXIIa) with bromine and treatment of the 2α-bromo-derivative (LXXXIIb) with $CaCO_3$ in dimethylformamide (DMF) gave the 6β-acetate (LXXXIIIa). Hydrolysis of the 6β-acetate gave 6β-hydroxy-5α-cholest-1-en-3-one (LXXXIIIb). Pelc and Kodicek were unable to complete the synthesis of 1α-hydroxycholesterol[111], but the ketone (LXXXIIIb) which they synthesised was used by other investigators as the starting material for the preparation of compound (LXXIXb). By oxidising compound (LXXXIIIa) with 35% H_2O_2, Morisaki and coworkers[89,112] obtained in 1973 the 1α, 2α-epoxide (LXXXIV). The reduction of the keto-group with $NaBH_4$ led to a 4 : 1 mixture of the epimeric 3β- and 3α-alcohols (LXXXVa) and, after hydrolysis, a mixture of the epimeric diols (LXXXVb). Chromatographic separation and acetylation with half an equivalent of acetic anhydride led to the isolation of the 3β-acetate (LXXXVc) in an overall yield of 24% with respect to the initial compound (LXXXIIIa). The dehydration of the 3β-acetate (LXXXVc) with $POCl_3$ gives a 75% yield of the Δ^5-olefin (LXXXVI), whose reduction with $LiAlH_4$ leads to the formation of compound (LXXIXb):

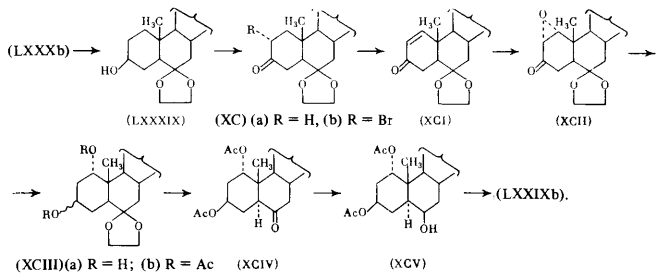


Furst et al.[113] carried out an analogous synthesis of compound (LXXIXb), but the starting material was the ketone (LXXXIIIb), the provitamin and 1α-OHD_3 being obtained in a crystalline form. The conversion of compound (LXXXVa) into (LXXIXb), without the isolation of intermediates and with an overall yield of 30% has been described[89]: compound (LXXXVa) was converted into the tetrahydropyranyl ether (LXXXVIIa), which was hydrolysed to compound (LXXXVIIb). Dehydration with $POCl_3$ and subsequent reduction with $LiAlH_4$ gave a mixture of the 3β- and 3α-tetrahydropyranyl ethers (LXXXVIII), whose hydrolysis led to compound (LXXIXb):



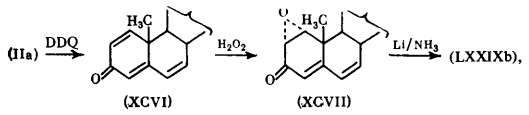
Yet another method of synthesis of 1α-OHD_3 was proposed by Morisaki et al.[114], but the overall yield of the final product was not more than 1%.

The method for the introduction of the 1α-hydroxy-group used by DeLuca and coworkers[16,115,116] in the synthesis of 1α-OHD_3 and 1α, 25-$(OH)_2D_3$ involves a fairly large number of transformations in the A and B rings and consists in the conversion of cholesterol into the 6-oxo-derivative (LXXXb), its treatment with diketen, and the formation of 6-ethylenedioxy-5α-cholestan-3β-ol (LXXXIX). The 3β-hydroxy-group is then oxidised to the carbonyl group [compound (XCa)] by CrO_3 in pyridine and the ketone is brominated with bromine to give the 2α-bromo-derivative (XCb). The dehydrobromination of the latter with *sym*-collidine gives the Δ^1-diene (XCI). The conversion of the diene (XCI) to the epoxide (XCII) and the reduction of the latter with $LiAlH_4$ lead to a mixture of the 3α- and 3β-epimers of the 1α, 3-diol (XCIIIa) and, after acetylation, to a mixture of the 1α, 3-diacetates (XCIIIb). Mild acid hydrolysis yields the ketone (XCIV), whose reduction with $NaBH_4$ gives rise to the 1α, 3-diacetate of the triol (XCV); the dehydration of the latter with $POCl_3$ and hydrolysis lead to 1α-hydroxycholesterol:

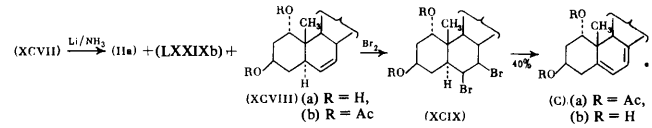


A fairly simple method of synthesis of 1α-OHD_3 has been proposed by Barton and coworkers[17,117]. By dehydrating cholesterol (IIa) with dichlorodicyanobenzoquinone (DDQ),[118] the authors obtained the trienone (XCVI),[119] which was converted by treatment with alkaline hydrogen peroxide[120] into 1α, 2α-epoxycholesta-4,6-diene-3-one (XCVII) with an overall yield of 45%. Treatment of the epoxide (XCVII) with a large excess of metallic lithium in a 1 : 1 NH_3–THF mixture or with sodium in ammonia[121] leads to 1α-hydroxycholesterol in 60% yield. The overall yield with respect to cholesterol is 27%.

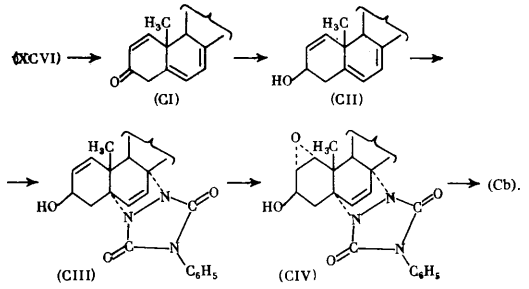
The conversion of 1α-hydroxycholesterol into the provitamin 1α-OHD_3,



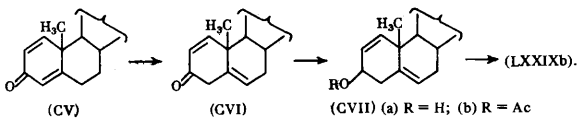
by the usual methods (bromination–dehydrobromination) involves low yields of the $\Delta^{5,7}$-diene. Methods have therefore been developed for the direct synthesis of the provitamin 1α-OHD_3. Mazur and coworkers[54] modified somewhat the method of Barton et al.,[17] in the reduction of the epoxydienone (XCVII) with lithium in liquid ammonia and obtained a mixture of three products: cholesterol (IIa) (15%), 1α-hydroxycholesterol (LXXIXb) (20%), and 5α-cholest-6-ene-1α, 3β-diol (XCVIIIa). The latter was acetylated to the diacetate (XCVIIIb), and brominated with bromine to the diaxial dibromide (XCIX), which was dehydrobrominated to the provitamin (Ca):



The provitamin (Cb) was obtained by Kaneko and coworkers[55,122,123], who used the familiar deconjugation reaction to isomerise the 1,4,6-trienone (XCVI), obtained by the method of Barton et al.[17], to the 1,5,7-trienone (CI) with potassium t-butoxide in dimethyl sulphoxide (DMSO) and then reduced it to the 3β-hydroxy-derivative (CII) with $Ca(BH_4)_2$. After protecting the 5,7-double bonds by forming the cyclic 1,4-adduct (CIII) with 4-phenyl-1,2,4-triazoline-3,5-dione[79], the epoxide (CIV) was obtained by oxidation with *m*-chloroperbenzoic acid. Its reduction with $LiAlH_4$ leads to compound (Cb):



Kaneko et al.[124] used the isomerisation reaction to convert cholesta-1,4-dien-3-one (CV) into the 1,5-dienone (CVI), which was then reduced with $NaBH_4$ or (better) with $Ca(BH_4)_2$ to the 3β-hydroxy-derivative (CVIIa). Hydroboration with B_2H_2 and oxidation with alkaline H_2O_2 give a low yield (10–15%) of compound (LXXIXb). A somewhat higher yield of this compound was obtained by treating the 3β-acetate (CVIIb) with HgO in the presence of trifluoroacetic acid and then reducing with $NaBH_4$:[125,126]

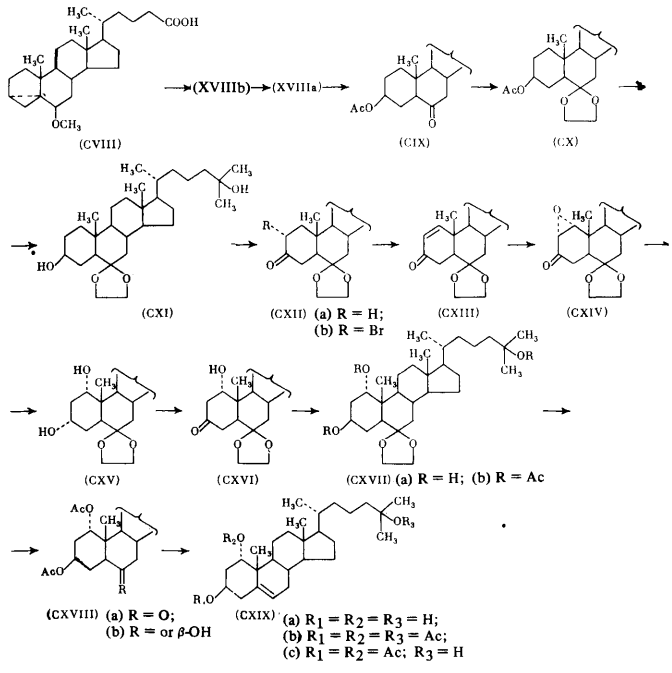


Harrison et al.[127,128] achieved the total synthesis of 1α-OHD_3 in 1973.

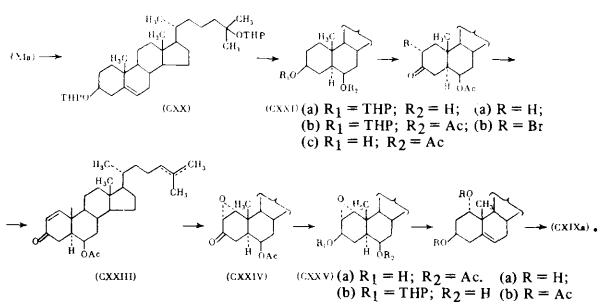
V. THE SYNTHESIS OF 1α,25-DIHYDROXYCHOLECALCIFEROL

The synthesis of 1α, 25-$(OH)_2D_3$, the active hormonal form of vitamin D_3, which involves the introduction of two hydroxy-groups into the molecule of vitamin D_3, still remains fairly complex. All the methods for the introduction of the 1α- and 25-hydroxy-groups described above can be used in the synthesis of 1α, 25-$(OH)_2D_3$. However, the hydroxy-groups are not always introduced consecutively; this usually involves simultaneous transformations in the A and B rings and in the side chain, which leads to the synthesis of new and hitherto unknown intermediates.

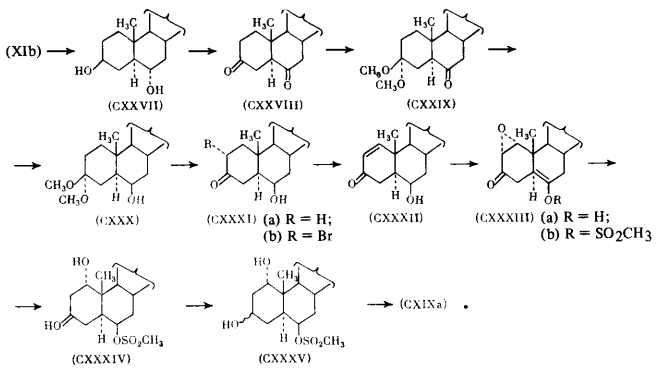
The synthesis of 1α, 25-$(OH)_2D_3$ by DeLuca and coworkers[115], who were the first to obtain this metabolite in 1971, was based on the conversion of the methyl ester of isohomocholanoic acid (CVIII) into a derivative of cholenoic acid (XVIIIb) by esterification with diazomethane and subsequent acid hydrolysis. After nitration, reduction, and acid hydrolysis, the acetate (XVIIIa) was converted into the ketone (CIX) and after the protection of the keto-group, the 25-hydroxy-derivative (CXI) was obtained via the ketal (CX) by the Grignard reaction. The oxidation of the 25-hydroxy-derivative with CrO_3 gives the 3-oxo-derivative (CXIIa), which is converted via the 2α-bromo-derivative (CXIIb) into the Δ^1-compound (CXIII). Its treatment with H_2O_2 leads to the 1α, 2α-epoxide (CXIV), whose reduction with $LiAlH_4$ yields the 1α, 3α-diol (CXV). In order to obtain the required 1α, 3β-diol, compound (CXV) was subjected to selective oxidation with *N*-bromosuccinimide, which gave the 3-oxo-derivative (CXVI), whose reduction with $NaBH_4$ led to the 1α, 3β-isomer (CXVIIa), which was then converted into the triacetate (CXVIIb) and then by mild acid hydrolysis into the 6-oxo-derivative (CXVIIIa). The reduction by $NaBH_4$ to compound (CXVIIIb) and dehydration of the 6-hydroxy-derivative with $POCl_3$ led to the triacetate of 1α, 25-dihydroxycholesterol (CXIXb), which was converted into 1α, 25-$(OH)_2D_3$ in the usual way:



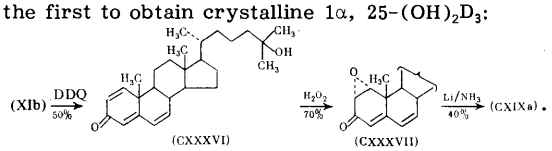
The syntheses of 1α, 25-dihydroxycholesterol described by Japanese workers are similar multistage processes[90,120,130]. One of them consists in the successive treatment of the dihydropyranyl ether (CXX), synthesised from 25-hydroxycholesterol (XIa), with B_2H_6 and H_2O_2 to form the 6-hydroxy-derivative (CXXIa) and then the acetate (CXXIb), whose hydrolysis led to the 3β, 25-diol (CXXIc). Its oxidation with CrO_3 gave the 6β-acetate of 6β, 25-dihydroxy-5α-cholestan-3-one (CXIIa) in an overall yield of 52% with respect to compound (XIa). The 1α-hydroxy group was introduced into compound (CXXIIa) by bromination to the 2α-bromo-derivative (CXXIIb) followed by dehydrobromination to give a mixture of the $\Delta^{1,24(25)}$- and $\Delta^{1,25(26)}$-dienes (CXXIII). The conversion into the 1α-hydroxy-derivative was achieved via the epoxykentone (CXXIV), the alcohol (CXXVa), and the tetrahydropyranyl ether (CXXVb). The dehydration of the latter and alkaline hydrolysis gave the 1α, 3β-diol (CXXVIa). The 25-hydroxy-group was introduced by treating the acetate (CXXVIb) with $Hg(OAc)_2$ and reducing with $NaBH_4$. The hydrolysis of the 1α, 3β-diacetate (CXIXc) gave 1α, 25-dihydroxycholesterol (CXIXa):



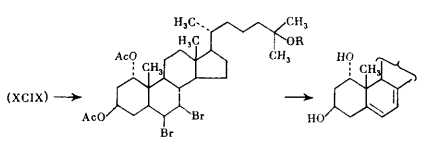
The synthesis of 1α, 25-dihydroxycholesterol from 25-hydroxycholesterol, involving transformations in the A and B rings only to give an 18% yield with respect to 25-hydroxycholesteryl acetate (XIb), has been achieved[131-133]. The hydroboration of (XIb) with diborane followed by treatment with alkaline H_2O_2 gives a mixture of alcohols, among which the main product is the triol (CXXVII). The unpurified mixture of alcohols was oxidised with the Jones reagent ($CrO_3 + H_2SO_4 + H_2O$) to the diketone (CXXVIII) with an overall yield of 74%. In order to convert the 6-oxo-group into the β-hydroxy-group, required for the subsequent introduction of the Δ^5-double bond, the 3-oxo-group in compound (CXXVIII) was converted into the dimethoxy-group in compound (CXXIX) and the latter was then reduced with $NaBH_4$ to the 6β-hydroxy-derivative (CXXX), whose hydrolysis gave the hydroxyketone (CXXXIa). The bromination of the latter to 2α-bromoketone (CXXXIb) followed by dehydrobromination led to the introduction of the Δ^1-double bond. Treatment of compound (CXXXII) with alkaline H_2O_2 gave the epoxyketone (CXXXIIIa). Next the 6β-hydroxy-group was protected by conversion into the methanesulphonate (CXXXIIIb) and the epoxy- compound was cleaved with aluminium amalgam to give the 1α-hydroxyketone (CXXXIV). Its reduction with $NaBH_4$ to a mixture of epimeric 3-hydroxy-derivatives (CXXXV), treatment of the mixture with $LiCO_3$ in DMF, and chromatographic separation of the epimers made it possible to isolate the pure compound (CXIXa):



Using the methods described above for the introduction of the 1α- and 25-hydroxy-groups, Japanese workers[91] achieved the synthesis of 1α, 25-$(OH)_2D_3$ from fucosterol. Fucosterol (LXXI) was converted into desmosterol (LXIb) via the ketone (LXXIII) in 45% yield. After treatment with $Hg(OAc)_2$ and then $NaBH_4$, the 3β-acetate of 25-hydroxycholesterol (XIb) was obtained from desmosterol in 85% yield; the overall yield of compound (XIb) with respect to (LXXI) was 38%. Next the synthesis was continued by the method of Barton and coworkers[17,134]. The dehydrogenation of compound (XIb) with the aid of DDQ leads to 25-hydroxy-1,4,6-trien-3-one (CXXXVI). The synthesis of 1α, 25-dihydroxycholesterol is completed by the conversion of the trienone into the triol (CXIXa) via the epoxide (CXXXVII). The overall yield with respect to fucosterol is not more than 5%. Barton et al.[134] were the first to obtain crystalline 1α, 25-$(OH)_2D_3$:



A relatively simple method of synthesising 1α, 25-$(OH)_2D_3$ has been developed by Mazur and coworkers[105]. The dibromide (XCIX) described above was adsorbed on silica gel and saturated with ozone at -78 °C and the mixture was then slowly heated to room temperature. Chromatographic separation of the mixture gave 51% of compound (CXXXVIIIa) for an 11% conversion of compound (XCIX). The hydroxy-group at $C_{(25)}$ was protected by the formation of the trifuloroacetate (CXXXVIIIb). Compound (CXXXVIIIb) was dehydrobrominated to the provitamin (CXXXIX), as described above[54]. The synthesis of 1α, 25-$(OH)_2D_3$ from cholesterol includes only seven stages:

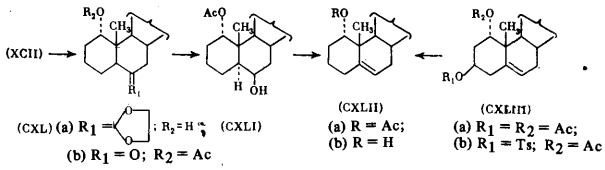


VI. THE SYNTHESIS OF 3-DEOXY-1α-HYDROXYCHOLECALCIFEROL

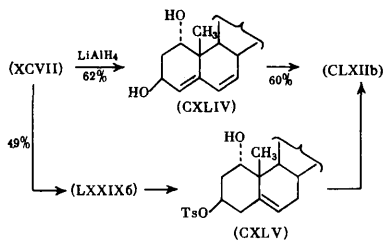
The presence of three hydroxy-groups, at $C_{(1)}$, $C_{(3)}$, and $C_{(25)}$, in the molecule of 1α, 25-$(OH)_2D_3$—the most active metabolite of vitamin D_3—stimulated attempts to elucidate the functional role of each of them. The synthesis of 1α-OHD_3 and the study of its biological activity showed that the absence of the hydroxy-group at $C_{(25)}$ hardly lowers the biological activity. The synthesis of 3-deoxy-1α-OHD_3 (Id) and its

high biological activity made it possible to demonstrate for the first time the exceptionally small role of the 3β-hydroxy-group in the manifestation of biological activity.

3-Deoxy-1α-OHD_3 was synthesised in 1974 by Norman and coworkers[22,135] and by DeLuca and coworkers[24,25]. DeLuca and coworkers synthesised this compound from the epoxy-ketone (XCII) obtained in the synthesis of 1α-OHD_3 [16,25]:



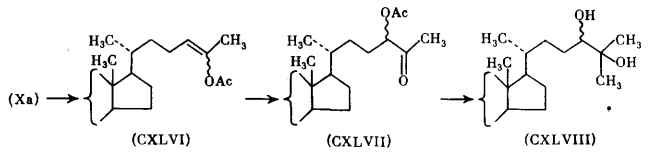
Treatment of the epoxyketone with hydrazine hydrate followed by catalytic hydrogenation led to the formation of the 1α-derivative (CXLa). Hydrolysis of the ketal under mild conditions with subsequent acetylation gave rise to the 6-oxo-derivative (CXLb), which was converted into the 6β-hydroxy-derivative (CXLI) after reduction with $NaBH_4$, while dehydration with $POCl_3$ gave cholest-5-en-1α-yl acetate (CXLIIa). A second method of synthesis of compound (CXLII), based on the diacetate of cholest-5-ene-1α, 3β-diol (CXLIIIa), is possible. Partial hydrolysis of the acetate group at $C_{(3)}$, the formation of the toluene-*p*-sulphonate (CXLIII), and reduction with $LiAlH_4$ lead to compound (CXLIIb). Norman and coworkers[23,135] obtained compound (CXLIIb) from cholesterol via the epoxyketone (XCVII) on reduction of compound (XCVII) with $LiAlH_4$ to the diol (CXLIV) and then with Li/NH_3 to compound (CXLIIb). If compound (XCVII) is reduced initially by the method of Barton et al.[17] to 1α-hydroxycholesterol (LXXIXb) with Li/NH_3, then subsequent treatment of its 3β-toluene-*p*-sulphonate (CXLV) with $LiAlH_4$ leads to the formation of compound (CXLIIb):



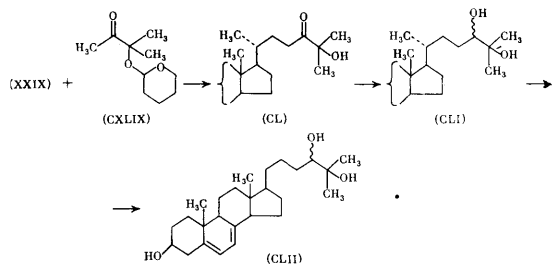
Successive bromination of compound (CXLIIa), dehydrobromination, and photochemical and thermal isomerisation lead to 3-deoxy-1α-OHD_3 with very low yields (8–10%) at each stage.

VII. THE SYNTHESIS OF 24*R*,25-DIHYDROXYCHOLECALCIFEROL

Synthetic 24,25-$(OH)_2D_3$ was obtained by DeLuca and coworkers[136,137] in 1973 from 25-oxo-27-norcholest-5-en-3β-yl acetate (Xa). Refluxing of compound (Xa) with acetic anhydride in the presence of toluene-*p*-sulphonic acid leads to a mixture of the *cis*- and *trans*-acetates of the Δ^{24}-enols (CXLVI). The 24-acetate of the 25-oxo-derivative (CXLVII) was obtained from this mixture via the intermediate bromo- and iodo-derivatives using the method of Moffett and Weisblat[138]. The reaction with a Grignard reagent leads to 24ξ, 25-dihydroxycholesterol (CXLVIII). The triacetate of the latter was converted into the provitamin and then into 24,25-$(OH)_2D_3$ by standard methods:



Eyley and Williams[56] obtained the provitamin 24,25-$(OH)_2D_3$ directly from ergosterol. The aldehyde (XXIX), obtained by the ozonolysis of the adduct of ergosterol with 4-phenyl-1,2,4-triazoline-3,5-dione, undergoes the aldol condensation with the enolate of 3-methyl-3-tetrahydropyranyloxybutan-2-one [which is formed when the ketone (CXLIX) is treated with lithium di-isopropylamide] to give the 24-oxo-derivative (CL):

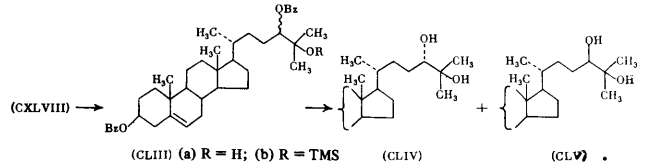


The reduction of this ketone with $NaBH_4$ leads to the adduct of the 3β, 24ξ, 25-triol (CLI). Treatment of the adduct with $LiAlH_4$ yields the provitamin (CLII), the overall yield of which is 38% with respect to the aldehyde (XXIX).

Japanese workers developed a simple method for the synthesis of 24,25-dihydroxycholesterol from desmosterol. Desmosteryl acetate (LXIb) was oxidised with *m*-chloroperbenzoic acid to the 24,25-epoxide (LXIV), whose treatment with H_2SO_4 gave compound (CXLVIII) [92]:

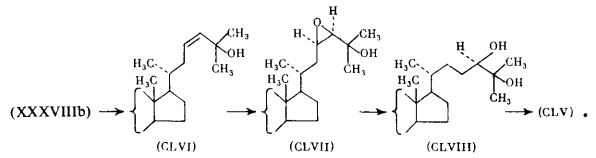
(LXIb) → (LXIV) → (CXLVIII).

An even simpler method of synthesis of compound (CXLVIII) consists in the oxidation of compound (LXIb) with OsO_4 in anhydrous ether[130], the yield being almost quantitative. Kodicek and coworkers[140,141] established that the oxidation of compound (LXIb) with osmic acid in benzene gives rise to a mixture of epimers with respect to $C_{(24)}$ (*R* and *S*). Next the authors obtained a mixture of epimers of 24(*R*,*S*), 25-$(OH)_2D_3$, one of which was the active metabolite isolated by Suda et al.[27] from a living organism. In 1975 Japanese workers[142,143] separated a mixture of 24(*R*,*S*), 25-dihydroxycholesterols into epimers. For this purpose, the mixture (CXLVIII) was converted into the 3β, 24ξ-dibenzoate (CLIIIa), which gave rise to the 25-trimethylsilyl ether (CLIIIb). The latter was resolved on a silica gel column and after hydrolysis two epimers were obtained: 24*S*, 25- and 24*R*, 25-dihydroxycholesterols (CLIV) and (CLV):



Their conversion into 24*S*, 25-$(OH)_2D_3$ and 24*R*, 25-$(OH)_2D_3$ and the study of their biological activity showed that 24*R*, 25-$(OH)_2D_3$ is the natural and active product.

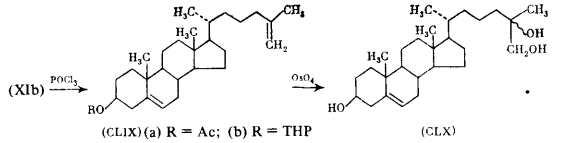
The sterospecific synthesis of 24*R*, 25-dihydroxycholesterol was achieved by Partridge and coworkers[144,145]. The hydrogenation of the unsaturated alcohol (XXXVIIIb) over the Lindlar catalyst gave a 90% yield of the *Z*-allyl alcohol (CLVI). Its oxidation with a peracid or better with t-butyl peroxide gives the 23*R*, 24*R*-epoxyalcohol (CLVII), whose reduction with $LiAlH_4$ results in the formation of the 24*R*, 25-diol (CLVIII). After treating the latter with acid dioxan, 24*R*, 25-dihydroxycholesterol (CLV) was obtained:



VIII. THE SYNTHESIS OF 25,26-DIHYDROXYCHOLECALCIFEROL

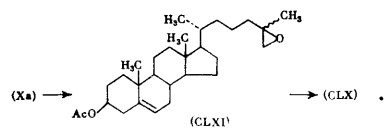
25,26-Dihydroxycholecalciferol was isolated and identified by DeLuca and coworkers in 1970,[32] The same investigators[146] patented a biochemical method of preparing this metabolite from the blood plasma of animals to which labelled vitamin D_3 had been administered. The configuration of the hydroxy-group at $C_{(25)}$ has not so far been established, but biological tests on a synthetic preparation showed that only one of the diastereoisomers with respect to $C_{(25)}$ is biologically active.

25,26-Dihydroxycholesterol was synthesised[92,139] from the acetate of 25-hydroxycholesterol (XIb), whose degradation with $POCl_3$ gave the $\Delta^{5,25}$-diene (CLIXa); the oxidation of the latter with OsO_4 gives a high yield of 25(*R*,*S*), 26-diol (CLX):



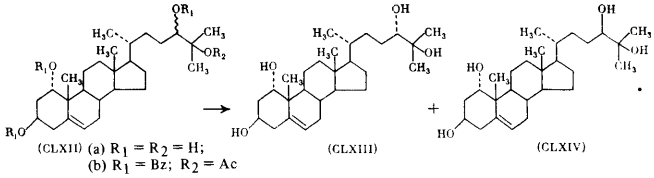
The chemical synthesis of 25,26-$(OH)_2D_3$ was carried out by Kodicek and coworkers[147,148] in 1973. The tetrahydropyranyl ether of 3β-hydroxy-27-norcholest-5-en-25-one (Xb) was converted by the Wittig reaction into the tetrahydropyranyl ether of the $\Delta^{5,25}$-diene (CLIXb). After hydrolysis (with HCl/MeOH) and acetylation, the acetate (CLIXa) was oxidised to compound (CLX) with OsO_4, as described above. The provitamin and 25,26-$(OH)_2D_3$ were obtained by the usual methods.

Lam et al.[34] developed another method for the conversion of compound (Xa) into 25,26-$(OH)_2D_3$. Treatment of compound (Xa) with a mixture of sodium hydride and trimethylsulphonium iodide in DMF yielded the 25,26-epoxide (CLXI), which was converted by treatment with alkali into the crystalline 3β, 25,26-triol (CLX):



IX. THE SYNTHESIS OF 1α, 24*R*, 25-TRIHYDROXYCHOLECALCIFEROL

Ikakawa et al.[149] synthesised the two epimers 24*R*- and 24*S*-1α, 24,25-$(OH)_2D_3$ in order to elucidate the configuration of the natural metabolite. 1α, 24,25-Trihydroxycholesterol was synthesised by the methods described above: 24,25-dihydroxycholesterol was obtained by the method of Seki et al.[92], after which the 1α-hydroxy-grlup was introduced by the method of Barton et al.[17] and a mixture of 1α, 24(*R*,*S*)25-trihydroxycholesterol (CLXIIa) epimers was obtained. They were then esterified and the mixture of tribenzoate acetates (CLXIIb) was separated chromatographically into two epimers. It was established by NMR that the more polar product (CLXIII) is the 24*R*-epimer, while the less polar product (CLXIV) is the 24*R*-epimer:



The conversion of these cholesterol derivatives into 1α, 24*R*, 25-$(OH)_3D_3$ and 1α, 24*R*, 25-$(OH)_3D_3$ [150] and the study of their biological properties showed that the natural metabolite is 1α, 24*R*, 25-$(OH)_3D_3$.

REFERENCES

1. V.K.Bauman, Prikl.Biokhim.Mikrobiol., 12, 805 (1976).
2. J.Lund and H.F.DeLuca, J.Lipid Res., 7, 739 (1966).
3. H.Morii, J.Lund, P.F.Neville, and H.F.DeLuca, Arch.Biochem.Biophys., 120, 508 (1967).
4. J.W.Blunt, H.F.DeLuca, and H.K.Schnoes, Chem. Comm., 801 (1968).
5. J.W.Blunt, H.F.DeLuca, and H.K.Schnoes, Biochemistry, 7, 3317 (1968).
6. G.Ponchon and H.F.DeLuca, J.Nutrition, **99**, 157 (1969).
7. J.W.Blunt, Y.Tanaka, and H.F.DeLuca, Proc.Nat. Acad.Sci.U.S.A., 61, 717 (1968).
8. J.W.Blunt, Y.Tanaka, and H.F.DeLuca, Proc.Nat. Acad.Sci.U.S.A., **61**, 1503 (1968).
9. D.E.M.Lawson, D.R.Fraser, E.Kodicek, H.R.Morris, and D.H.Williams, Nature, **230**, 228 (1971).
10. M.F.Holick, H.K.Schnoes, and H.F.DeLuca, Proc. Nat.Acad.Sci.U.S.A., **68**, 803 (1971).
11. M.F.Holick, H.K.Schnoes, H.F.DeLuca, T.Suda, and R.J.Cousins, Biochemistry, **10**, 2799 (1971).
12. A.W.Norman, J.F.Myrtle, R.J.Midgett, H.G.Nowicki, V.Williams, and G.Popjak, Science, **173**, 51 (1971).
13. D.R.Fraser and E.Kodicek, Nature, **228**, 764 (1970).
14. R.Gray, I.Boyle, and H.F.DeLuca, Science, **172**, 1232 (1971).
15. H.F.DeLuca, Fed.Pro., **33**, 2211 (1974).
16. M.F.Holick, E.I.Semmler, H.K.Schnoes, and H.F.DeLuca, Science, **180**, 190 (1973).
17. D.H.R.Barton, R.H.Hesse, M.M.Pechet, and E.Rizzardo, J.Amer.Chem.Soc., **95**, 2748 (1973).
18. M.R.Haussler, J.E.Zerwekh, R.H.Hesse, E.Rizzardo, and M.M.Pechet, Proc.Nat.Acad.Sci. U.S.A., **70**, 2248 (1973).

19. C.Kaneko, S.Yamada, A.Sugimoto, Y.Eguchi, M.Ishikawa, T.Suda, M.Suzuki, S.Kakuta, and S.Sasaki, Steroids, **23**, 75 (1974).
20. M.F.Holick, P.Kasten-Schraufrogel, T.Tavela, and H.F.DeLuca, Arch.Biochem.Biophys., **166**, 63 (1975).
21. P.Bordier, M.M.Pechet, R.Hesse, P.Marie, and H.Rasmussen, N.Engl.J.Med., **291**, 866 (1974).
22. T.M.Chalmers, M.W.Davie, J.O.Hunter, K.F.Szaz, B.Pelc, and E.Kodicek, Lancet, **2**, 696 (1973).
23. W.H.Okamura, M.N.Mitra, R.M.Wing, and A.W.Norman, Biochem.Biophys.Res.Comm., **60**, 179 (1974).
24. H.Y.Lam, B.L.Onisko, H.K.Schnoes, and H.F.DeLuca, Biochem.Biophys.Res.Comm, **59**, 845 (1974).
25. US P.3 906 014 (1975).
26. A.W.Norman, M.N.Mitra, W.H.Okamura, and R.M.Wing, Science, **188**, 1013 (1975).
27. T.Suda, H.F.DeLuca, H.K.Schnoes, G.Ponchon, Y.Tanaka, and M.F.Holick, Biochemistry, **9**, 2917 (1970).
28. M.F.Holick, H.K.Schnoes, H.F.DeLuca, R.W.Gray, I.T.Boyle, and T.Suda, Biochemistry, 11, 4251 (1972).
29. I.T.Boyle, R.W.Gray, and H.F.DeLuca, Proc.Nat. Acad.Sci.U.S.A., **68**, 2131 (1971).
30. Y.Tanaka, H.F.DeLuca, N.Ikekawa, M.Morisaki, and N.Koizumi, Arch.Biochem.Biophys., **170**, 620 (1975).
31. I.T.Boyle, J.L.Omdahl, R.W.Gray, and H.F.DeLuca, J.Biol.Chem., **248**, 4174 (1973).
32. T.Suda, H.F.DeLuca, H.K.Schnoes, Y.Tanaka, and M.F.Holick, Biochemistry, **9**, 4776 (1970).
33. M.F.Holick, A.Kleiner-Bossaller, H.K.Schnoes, P.M.Kasten, I.T.Boyle, and H.F.DeLuca, J.Biol. Chem., **248**, 6691 (1973).
34. H.Y.Lam, H.K.Schnoes, and H.F.DeLuca, Steroids, **25**, 247 (1975).
35. M.Peacock , G.A.Taylor, and J.Redel, FEBS Letters, **62**, 248 (1976).
36. A.Kleiner-Bossaller and H.F.DeLuca, Biochim. Biophys.Acta, **338**, 489 (1974).
37. D.A.Procsal, H.L.Henry, E.J.Friedlander, A.W.Norman, Arch.Biochem.Biophys., **179**, 229 (1977).
38. R.I.Yakhimovich, "Khimiya Vitaminov D" (The Chemistry of Vitamins D), Izd.Naukova Dumka, Kiev, 1978, p.27.
39. A.Windaus, F.Schnek, and F.Werder, Z.physiol. Chem., **241**, 100 (1936).
40. F.Schenk, Naturwiss., **25**, 159 (1937).
41. A.Windaus, H.Lettre, and F.Schenk, Annalen **520**, 98 (1935).
42. L.F.Fieser and M.Fieser, "Steroids" (Translated into Russian), Izd.Mir, Moscow, 1964, p.158.
43. E.V.Yablonskaya and G.M.Segal', Khim.Prirodn. Soed., 739 (1973).
44. H.B.Henbest, E.R.H.Jones, E.A.Bide, R.W.Peevers, and P.A.Wilkinson, Nature, **158**, 169 (1946).
45. F.Hunziker and F.X.Mullner, Helv.Chim.Acta, **41**, 70 (1958).
46. R.I.Yakhimovich, N.S.Nedashkovskaya, L.K.Kurchenko, and G.G.Girushtin, USSR P., 328 087 (1972); Byul.Izobret., No.6, 63 (1972).
47. R.I.Yakhimovich, E.S.Kotlyar, L.K.Kurchenko, and V.A.Boguslavskii, Khim.Farm.Zhur., **7**, No.6, 33 (1973).
48. Hung.P. 151 690 (1964); Chem.Abs., **62**, 7846 (1965).
49. Hung.P. 148 480 (1961); Chem.Abs., **58**, 8021 (1963).
50. Swiss P. 351 960 (1956); Chem.Abs., **56**,14 376 (1962).
51. R.I.Yakhimovich and L.K.Kurchenko, Khim.Farm. Zhur., **8**, No.9, 22 (1974).
52. R.M.Moriarty, H.Paaren, and J.Gilmore, Chem. Comm., 927 (1974).
53. R.I.Yakhimovich, N.F.Fursaeva, and G.M.Segal', Bioorg.Khim., 2, 1526 (1976).
54. D.Freeman, A.Acher, and Y.Mazuar, Tetrahedron Letters, 261 (1975).
55. C.Kaneko, A.Sugimoto, Y.Eguchi, S.Yamada, M.Ishikawa, S.Sasaki, and T.Suda, Tetrahedron, **30**, 2701 (1974).
56. S.C.Eyley and D.H.Williams, J.Chem.Soc., Perkin Trans I, 727 (1976).
57. L.Velluz, G.Amiard, and B.Goffinet, Bull.Soc. chim.France, 1341 (1955).
58. E.Havinga, Chimia (Switz.), **16**, 145 (1962).
59. G.M.Sanders, J.Pot, and E.Havinga, Fortschr. Chem.Org.Naturst., 27, 131 (1969).
60. E.Havinga, Experientia, **29**, 1181 (1973).
61. T.Kobayashi, Vitamins, **47**, 187 (1973).
62. R.I.Yakhimovich, V.P.Vendt, and V.A.Boguslavskii, Prikl.Biokhim.Mikrobiol., 11, No.2, 254 (1975).
63. J.W.Blunt and H.F.DeLuca, Biochemistry, **8**, 671 (1969).
64. BDR Appl., 1 933 375 (1969); Chem.Abs., 72, 125 058 (1970).
65. S.J.Halkes and N.P.CanVliet, Rec.Trav.chim., **88**, 1080 (1969).
66. J.E.Van Lier, and L.L.Smith, J.Org.Chem., 35, 2627 (1970).
67. G.R.Claude and G.L.Peaumont, Compt.rend., 260, 3204 (1965).
68. L.Ruzicka and W.H.Fischer, Helv.Chim.Acta, 20, 1291 (1937).
69. A.I.Ryer, W.H.Gebert, and N.M.Murrill, J.Amer. Chem.Soc., 72, 4247 (1950).
70. W.G.Dauben and H.L.Brandlow, J.Amer.Chem. Soc., 72, 4248 (1950).
71. A.Rotman and Y.Mazur, Chem.Comm., 15 (1974).
72. J.A.Campbell , D.M.Squires, and J.C.Babcock, Steroids, 13,567 (1969).
73. US P.3 833 622 (1974).
74. Sh.S.Levi, N.A.Bogoslovskii, R.P.Evstigneeva, and G.I.Samokhvalov, Zhur.Obshch.Khim., **44**, 2596 (1974).
75. N.A.Bogoslovskii and Sh.S.Levi, USSR P.341 311 (1974); Ref.Zhur.Khim., 40132 (1975).
76. N.A.Bogoslovskii, Sh.S.Levi, R.P.Evstigneeva, N.P.Lazareva, and E.A.Petrova, Khim.Farm.Zhur., 8, No.6, 44 (1974).
77. N.A.Bogoslovskii, Sh.S.Levi, R.P.Evstigneeva, and G.I.Samokhvalev, Zhur.Obshch.Khim., 45, 925 (1975).
78. S.C.Eyley and D.H.Williams, J.Chem.Soc., Perkin Trans.I, 731 (1976).
79. D.H.R.Barton, T.Shioiri, and D.A.Widdowson, J. Chem.Soc.(C), 1968 (1971).
80. J.J.Partridge, S.Faber, and M.R.Uskokovic, Helv. Chim.Acta, **57**, 764 (1974).
81. US P.3 822 254 (1974).
82. W.F.Salmond and K.D.Maisto, Tetrahedron Letters, 987 (1977).

83. W.G.Salmond, M.C.Sobala, and K.D.Maisto, Tetrahedron Letters, 1237 (1977).
84. W.G.Salmond and M.C.Sobala, Tetrahedron Letters, 1695 (1977).
85. T.A.Narwid, K.E.Cooney, and M.R.Uskokovič, Helv.Chim.Acta, 57, 771 (1974).
86. T.A.Narwid and M.R.Uskokovič, US P. 3 856 780 (1974).
87. J.Wicha and K.Bal, Chem.Comm., 968 (1975).
88. M.Morisaki, J.Rubio-Lightbourn, and N.Ikekawa, Chem.Pharm. Bull.(Tokyo), 21, 457 (1973).
89. M.Morisaki, K.Bannai, and N.Ikekawa, Chem. Pharm. Bull.(Tokyo), 21 1853 (1973).
90. J.Rubio-Lightbourn, M.Morisaki, and N.Ikekawa, Chem.Pharm. Bull.(Tokyo), 21, 1854 (1973).
91. M.Morisaki, J.Rubio-Lightbourn, N.Ikekawa, and T.Takeshita, Chem.Pharm. Bull.(Tokyo), 21, 2568 (1973).
92. M.Seki, J.Rubio-Lightbourn, M.Morisaki, and M.Ikekawa, Chem.Pharm. Bull.(Tokyo), 21, 2783 (1973).
93. N.Ikekawa, M.Morisaki, and J.Rubio-Lightbourn, US P. 3 868 396 (1975).
94. S.K.Dasgupta, D.R.Crump, and M.Gut, J.Org. Chem., 39, 1658 (1974).
95. French P.2 149 796 (1973).
96. W.Bergmann and J.P.Dusza, J.Org.Chem., 23, 459 (1958).
97. N.Ikekawa, M.Morisaki, H.Ohtaka, and Y.Chiyoda, Chem.Comm., 1498 (1971).
98. S.M.L.Chen, K.Nakanishi, N.Awata, M.Morisaki, N.Ikekawa, and Y.Shimizu, J.Amer.Chem.Soc., 97, 5297 (1975).
99. T.Takeshita, S.Ishimoto, and N.Ikekawa, Chem. Pharm.Bull.(Tokyo), 24, 1928 (1976).
100. See Ref.42, p.375.
101. N.Ikekawa, K.Tsuda, and M.Morisaki, Chem.Ind. (London), 1179 (1966).
102. N.Ikekawa, N.Morisaki, K.Tsuda, and T.Yoshida, Steroids, 12, 41 (1968).
103. J.P.Moreau, D.J.Aberhart, and E.Caspi, J.Org. Chem., 39, 2018 (1974).
104. R.K.Varma, M.Koreeda, B.Jagen, K.Nakanishi, and E.Caspi, J.Org.Chem., 40, 3680 (1975).
105. Z.Cohen, E.Keinan, Y.Mazur, and A.Ulman, J.Org.Chem., 41, 2651 (1976).
106. M.Lj.Mihailović, Lj.Lorenc, N.Popov, and J.Kalvoda, Helv.Chim.Acta, 54, 2281 (1971).
107. M.Lj.Mihailović, Lj.Lorenc, V.Pavlovic, and J.Kalvoda, Tetrahedron, 33, 441 (1977).
108. B.Pelc and E.Kodicek, J.Chem.Soc., (C), 1624 (1970).
109. D.E.M.Lawson, P.W.Wilson, and E.Kodicek, Nature, 222, 171 (1969).
110. D.E.M.Lawson, P.W.Wilson, and E.Kodicek, Biochem. J., 115, 269 (1969).
111. B.Pelc and E.Kodicek, J.Chem.Soc.(C), 1568 (1971).
112. N.Ikekawa, M.Morisaki, and K.Bannai, Japan Kokai 75 64263 (1975); Chem.Abs., 83, 114 758 (1975).
113. A.Furst, L.Labler, W.Meier, and K.H.Pfoertner, Helv.Chim.Acta, 56, 1708 (1973).
114. M.Morisaki, A.Saika, K.Bannai, M.Sawamura, J.Rubio-Lightbourn, and N.Ikekawa, Chem.Pharm. Bull. (Tokyo), 23, 3272 (1975).
115. E.J.Semmler, M.F.Holick, H.K.Schnoes, and H.F.DeLuca, Tetrahedron Letters, 4147 (1972).
116. US P.3 741 996 (1973).
117. US P.3 901 928 (1975).
118. A.B.Turner, J.Chem.Soc.(C), 2568 (1968).
119. C.Djerassi, G.Rosenkranz, J.Romo, S.Kaufmann, and J.Pataki, J.Amer.Chem.Soc., 72, 4534 (1950).
120. E.Glotter, M.Weissenberg, and D.Lavie, Tetrahedron, 26, 3857 (1970).
121. BRD.Appl., 2 400 189 (1975).
122. M.Ishikawa, C.Kaneko, S.Sasaki, T.Suda, S.Yamada, Y.Eguchi, and A.Sugimoto, Japan Kokai, 75, 84560 (1975); Chem.Abs., 83, 179 412 (1975).
123. M.Ishikawa, C.Kaneko, S.Sasaki, T.Suda, S.Yamada, Y.Eguchi, and A.Sugimoto, Japan Kokai, 75, 84555 (1975); Chem.Abs., 83, 206 483 (1975).
124. C.Kaneko, S.Yamada, A.Sugimoto, M.Ishikawa, S.Sasaki, and T.Suda, Tetrahedron Letters, 2339 (1973).
125. M.Morisaki, K.Bannai, and N.Ikekawa, Chem.Pharm. Bull. (Tokyo), 24, 1948 (1976).
126. N.Ikekawa, M.Morisaki, and K.Bannai, Japanese P.75 69059 (1975); Chem.Abs., 83, 114 757 (1975).
127. R.G.Harrison, B.Lythgoe, and P.W.Wright, Tetrahedron Letters, 3649 (1973).
128. R.G.Harrison, B.Lythgoe, and P.W.Wright, J.Chem. Soc., Perkin Trans I, 2654 (1974).
129. N.Ikekawa, M.Morisaki, F.Rubio, Japanese P. 7 564 264 (1975); Chem.Abs., 83, 114 759 (1975).
130. I.Matusnaga, K.Ochi, H.Nagano, and M.Shindo et al., Japanese P.7 610 056 (1976); Chem.Abs., 86, 90143 (1977).
131. T.A.Narwid, J.F.Blount, J.A.Iacobelli, and M.R.Uskoković, Helv.Chim.Acta, 57, 781 (1974).
132. US P. 3 887 545 (1976).
133. US P. 3 993 675 (1976).
134. D.H.R.Barton, R.H.Hesse, M.M.Pechet, and E.Rizzardo, Chem.Comm., 203 (1974).
135. M.N.Mitra, A.W.Norman, and W.H.Okamura, J. Org.Chem., 39, 2931 (1974).
136. H.Y.Lam, H.K.Schnoes, H.F.DeLuca, and T.C.Chen, Biochemistry, 12, 4851 (1973).
137. US P. 3 715 374 (1973).
138. R.B.Moffett and D.I.Weisblat, J.Amer.Chem.Soc., 74, 2183 (1952).
139. BRD Appl., 2 409 971 (1974); Chem.Abs., 82, 4480 (1975).
140. J.Redel, P.Bell, F.Delbarre, and E.Kodicek, Compt. rend. D, 278,529 (1974).
141. J.Redel, N.Bazely, Y.Calando, F.Delbarre, P.A.Bell, and E.Kodicek, J.Steroid Biochem., 6, 117 (1975).
142. N.Koizumi, M.Morisaki, N.Ikekawa, A.Suzuki, and T.Takeshita, Tetrahedron Letters, 2203 (1975).
143. M.Seki, N.Koizumi, M.Morisaki, and N.Ikekawa, Tetrehedron Letters, 15 (1975).
144. J.J.Partridge, V.Toome, and M.R.Uskoković, J. Amer.Chem.Soc., 98, 3739 (1976).
145. US P. 3 994 878 (1976).
146. US P. 3 739 001 (1973).
147. J.Redel, P.Bell, F.Delbarre, and E.Kodicek, Compt. rend. D, 276, 2907 (1973).
148. J.Redel, P.A.Bell, N.Bazely, Y.Calando, F.Delbarre, and E.Kodicek, Steriods, 24, 463 (1974).
149. N.Ikekawa, M.Morisaki, N.Koizumi, Y.Kato, and T.Takeshita, Chem.Pharm.Bull. (Tokyo), 23, 695 (1975).
150. Y.Kato et al., Japanese P.76 108 046, 108 047, 108 048, 108 049; Chem.Abs., 86,73009–73012 (1977).

Institute of Biochemistry,
Academy of Sciences of
Ukrainian SSR, Kiev

RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

May 1980

Translated from *Uspekhi Khimii*, 49, 737-770 (1980)

U.D.C. 577.150.3+577.150.4+577.156+541.182.644

The Stabilisation of Enzymes—a Key Factor in the Practical Application of Biocatalysis

K.Martinek and I.B.Berezin

The present state of the problem of the practical application of biocatalysis is examined and physicochemical approaches whereby the denaturation of enzymes under the influence of elevated temperatures, extreme pH values, and organic solvents can be suppressed are analysed. The general principles of the stabilisation of enzymes are formulated.
The bibliography includes 225 references.

CONTENTS

I.	Introduction	385
II.	The stability and stabilisation of enzymes; definitions and general remarks	387
III.	The stabilisation of enzymes in relation to thermal inactivation (in relation to the uncoiling of the protein globule)	388
IV.	The stabilisation of enzymes in relation to inactivation under the influence of extreme pH values	395
V.	Enzymic reactions in organic solvents with a low content of water (or in its absence)	396
VI.	Conclusion	396

I. INTRODUCTION

1. Practical Application of Biocatalysis

Enzymes as biocatalysts differ from the usual chemical catalysts by their exceptionally high catalytic activity under mild conditions and their unique substrate specificity[1,2]. This leads to wide prospects for their use as catalytic and regulating elements in various branches of science and engineering. A number of factors have interfered hitherto with the realisation of these possibilities: the low availability (and hence relatively high cost) of enzymes, high lability, and the difficulty of their separation from the reaction products.

However, in recent years the situation has altered radically. Firstly, the development of methods for the preparation of enzymes from micro-organisms has virtually solved completely the first problem[3-5], and one can claim confidently that, after a further improvement of microbiological technology, the cost of enzymes will decrease. Secondly, a new field, involving the preparation and study of immobilised enzymes[5-9], has been established at the junction between a number of chemical and biological disciplines[6]. As a result of immobilisation (for example the covalent binding of enzymes to water-insoluble particles, the inclusion of enzymes in a gel or hollow fibres, and the adsorption of enzymes on various carriers), the first benefit has been the possibility to separate the heterogeneous catalyst thus obtained from soluble

products and the ability to use it again. In many instances the stability of the enzymes has also been significantly increased. Because of this, the practical applications of enzymes have increased sharply. We shall indicate certain examples.

(1) The use of enzymes has been firmly included among the methods of analytical chemistry[9-11] and medicine[9,11].

(2) Particularly notable advances have been achieved in the fine organic synthesis of medicinal preparations and important biochemical compounds. Certain enzymic processes of this kind have already been carried out on the laboratory scale. As an example, one may mention the separation of the racemates of synthetic aminoacids[12,13], the synthesis of aminoacids[13-15] and antibiotics[15-17], the transformation of steroids[18,19], the synthesis of *N*-oxides of medicinal preparations[20,21], the synthesis of pyrrole porphobilinogen[9,22], the synthesis of hydroxynitriles[23], the preparation of pharmaceutically pure labelled aminoacids[24], the synthesis of important biochemical substances such as ATP,[25] NAD,[26] and others[27], and the synthesis of homopolynucleotides[28,29]. There is no doubt that the application of enzymes in preparative organic synthesis will develop vigorously also in the future[9,30,31].

(3) The use of enzymes has served as a powerful stimulus in the development of new large-scale technologies, such as the preparation of glucose by the hydrolysis of starch[32] and the isomerisation of glucose to fructose[33], the synthesis of L-DOPA and L-methionine[34], and reduction of the lactose content in milk[35,36]. Research into the possibilities of the industrial preparation of glucose from cellulose with the aid of cellulase is being vigorously prosecuted[37].

(4) Approaches to the preparation of enzymic light-sensitive[38] and sound-sensitive[39] materials, which can serve as chemical amplifiers of weak signals (particularly for the creation of new photographic and sonographic processes), have been developed.

(5) Methods for the solution of energy problems of the future with the aid of enzymes have been outlined[5,7,40].

The above list of problems which have been already solved or merely formulated cannot be regarded as complete and it can be extended (see, for example, Refs.5–9 and 41); however, we shall concentrate attention on the discussion of the causes which for fundamental reasons still limit the application of enzymes as catalysts of chemical reactions of practical importance, namely the inactivation of enzymes under technological conditions.

2. The Causes of the Inactivation of Enzymes

The loss of observed catalytic activity by the system as a whole can be due, for example, to the elution of the immobilised enzyme from within the carrier or from its surface or the partial breakdown (or deformation) of the carrier itself by both mechanical and microbiological means[42,43]. These and similar technological aspects[43] are of only partial interest, because the observed inactivation of this kind can be readily prevented by choosing another carrier or by altering the method for the immobilisation of the enzyme.

The following inactivation processes, in which the enzyme itself (its active centre) is "destroyed" are more important.

A. The enzyme can be "poisoned" by inhibitors such as heavy metal cations: in order to avoid this, one can add a metal-chelating agent of the type of EDTA [44] either in a free form (this appears more promising) or in an immobilised form[45].

B. The catalytic activity can decrease as a result of the oxidation of the functional groups of the protein. In this case protective agents must be introduced into the system. In principle, one can employ for this purpose antioxidants [(inhibitors of free radical reactions, which have already proved useful in the solution of other applied problems in biochemistry and medicine (see, for example Emanuel'[46])]. Sulphydryl compounds are used to protect the SH groups[47]. The oxidative degradation of enzymes can be eliminated by employing anaerobic conditions (in principle, a very low oxygen concentration can be maintained in the system by absorbing oxygen via auxiliary autocatalytic oxidative processes or even with the aid of enzymic oxidative processes coupled with the main reaction.

C. The "eating" of the protein catalyst by micro-organisms (they are almost always present in the system as an impurity) can be avoided by immobilisation if the enzyme is incorporated in a carrier (for example a microporous carrier) which protects it as a result of steric hindrance[5,42,43].

D. Covalent immobilisation also prevents various kinds of polymolecular inactivating processes of the type of enzyme–enzyme interaction, such as aggregation[48] or autolysis in the case of proteolytic enzymes[5,7].

E. When used in flow reactors, the enzyme can be inactivated as a result of the elimination of the cofactor from the system. However, recently this problem has been solved in principle. There exist three most promising (from our point of view) approaches: (a) a membrane reactor is used and the cofactor is attached to a water soluble polymer[49]; (b) the enzyme (enzymes) and the cofactor are jointly subjected to covalent immobilisation[49]; (c) more complex enzyme systems are created in which the cofactor is regenerated[25,49,50].

F. Inactivation of enzymes caused by the denaturing activity of the external medium. Since methods for the suppression of inactivation via mechanisms (A)–(E), developed to a greater or smaller extent, already exist, in the present review we shall deal only with mechanism (F). There is naturally no special point in considering the problems of preventing the denaturation of enzymes under the influence of the carrier[51]—it is simplest to use another carrier. We shall have in mind primarily the following denaturing factors: increased temperature, unfavourable pH values, and the addition of organic solvents.

3. The Necessity to "Suppress" the Denaturation of Enzymes

The prevention of the denaturation of enzymes is an essential step towards their wide-scale practical application. We shall demonstrate this on the following examples.

1. When enzymes are extracted from their natural environment (*in vivo*), they become as a rule labile and in many instances their "lifetime" is measured in minutes[52-54]. For example, the stability of immobilised aspartase proved to be unsatisfactory for its use in industry[55].

2. It is desirable to carry out many processes at an elevated temperature. This is associated, in the first place, with the fact that the rates of the majority of chemical reactions, including enzymic reactions, increase with increasing temperature (in accordance with the Arrhenius equation). It is therefore natural that at elevated temperatures the specified degree of conversion of the substrate in the chemical reactor is attained after a shorter period or even in the presence of smaller amounts of the immobilised enzyme, and in many industrial processes the cost of the enzyme is an important economic factor, for example, in the case of glucoamylase[32]. In the second place, an increase of temperature ensures bactericidal conditions[43], which are very important, for example, for processes in the food industry[35, 56,57]. However, we may note that at elevated temperatures the denaturation of biocatalysts intensifies[52-54].

3. The equilibrium position in many processes of practical importance is such that the required products can be obtained when the reaction is carried out in a mixture of water and an organic solvent with a high content of the latter. On the other hand, enzymes as a rule lose their catalytic activity or specificity under these conditions[53,58] (see also the references in the paper of Klibanov et al.[59]).

4. In certain cases the pH optimum of the reaction and the pH range corresponding to the stability of the enzyme catalysing it are not the same. A typical example is in the synthesis of penicillin antiobiotics under the influence of penicillin amidase: the equilibrium position in the synthesis is displaced towards products in an acid medium, where the enzyme is fairly unstable[60].

5. Evidently in the practical employment of enzyme preparations their direct application takes place long (sometimes very long) after their preparation. This gives rise to the problem of the stabilisation of enzymes in relation to their inactivation on prolonged storage[61].

4. Methods for the Solution of the Problem of Undesirable Inactivation

In order to solve the problem of the undesirable inactivation of enzymes, a number of approaches have been proposed. Firstly, one can use whole (or only partly degraded) cells as the catalyst without extracting the enzyme from its natural environment[4-9]. For example, owing to the low stability of free aspartase, immobilised cells of *Escherichia coli* had to be used for the continuous synthesis of L-aspartic acid[55]. Partly degraded cells retain their catalytic properties even in organic solvents[62]. Secondly, the enzyme can be isolated from specially stable, for example, thermophilic, strains[54,63].

However both these approaches have their disadvantages. The use of whole cells creates the problem of the diffusion of the substrates or products through cell walls; furthermore, the choice of the method of immobilisation is in this case evidently limited. The use of enzymes from thermophilic microorganisms is limited by the fact that the search for strains suitable in the required catalytic reaction constitutes in each case a special (individual) problem, which is by no means simple.

In the present review, we shall therefore consider the third possible solution—the stabilisation of an enzyme molecule (globule) in relation to denaturing influences by artificial means.

The stabilisation of enzymes could not be achieved "at a stroke" by their immobilisation: the stability of enzymes in relation to inactivating influences in some cases increases on immobilisation, in others it decreases, while in instances of a third kind, it remains virtually unaltered[6]. Certain advances in the formation of enzyme preparations with an increased stability have therefore come to be regarded[7,42] as an exception rather than a rule. Furthermore a large text published in 1976 and devoted to immobilised enzymes[9] altogether failed to provide a genuine treatment of this problem.

II. THE STABILITY AND STABILISATION OF ENZYMES; DEFINITIONS AND GENERAL REMARKS

The stability of an enzyme *E* will be understood as its ability to retain its intrinsic catalytic activity under conditions where the inactivating mechanisms (A)–(E) are absent. The effective first-order rate constant, characterising the unimolecular inactivating process

$$k_{inact} = (d[E]/dt)/[E],$$

where [E] is the relative specific catalytic activity, will serve as a quantitative criterion of the stability of the given enzyme under the given conditions.

The decrease of k_{inact}, observed as a result of a particular treatment of the enzyme (modification, immobilisation, etc.), will serve as a measure of stabilisation.

In certain systems, an apparent stabilisation of the immobilised enzyme in relation to its native precursor is observed, being caused, for example, by diffusion-dependent obstacles to the enzymic reaction, which arise under the influence of the carrier[64]. We shall consider only studies where complications of this kind have been excluded; we shall make use of the kinetic criteria formulated by Berezin et al.[65] (see also Goldstein[66]).

The problem of the stabilisation of enzymes in relation to denaturing influences does not have only practical aspects of the kind discussed above. It is important also for the study of the mechanisms of the denaturation of enzymes. Furthermore, certain stabilised enzyme systems serve as models of systems functioning *in vivo*. All these aspects will be considered in the present review.

Below we shall analyse methods (mechanisms) of stabilisation, which, being to some extent general, in the first place do not reduce unduly the initial level of the catalytic activity of enzymes extracted from their natural environment (as a rule, not more than by a factor of 2–3) and, in the second place, ensure the continuing functioning of the enzyme under unfavourable conditions in the surrounding medium. We shall consider separately the preparation of water-insoluble (truly immobilised) heterogeneous catalysts with an increased stability and, on the other hand, stabilised water-soluble enzyme preparations. The need for soluble enzymes has been continuously increasing in recent years[5,67], primarily in medicine[5,9,11,68] and in chemical engineering, in processes involving the use of water-insoluble substrates[69]; the cellulase cleavage of cellulose to glucose is particularly promising in this connection[37].

However, we shall in no way endeavour to compile fully all the studies in which the enzyme stabilisation effect has been observed (a continuously increasing number of such studies apparently precludes this within the framework of a single article). We shall concentrate attention only on those investigations where the observed effects have been subjected to an experimentally tested physicochemical treatment; the number of such studies is relatively small. The main aim of this review is to formulate (and to illustrate by the most striking examples) the physicochemical principles of the solution of the problem of the stabilisation of enzymes. We shall begin with the fact that enzymes are inactivated via identical mechanisms (see above) under both technological conditions and on storage. We may note that the stability of enzymes is usually considered separately in the two cases; this is justified in view of the fact that, under particular conditions, the contribution of each inactivating mechanism can be signifcantly different. For example, at an elevated temperature (in technological processes) mechanisms involving the denaturation uncoiling of the protein or its oxidation largely operate, whereas during storage (usually at a reduced temperatue) one may expect mainly the degradation of the enzymes under the influence of micro-organisms and proteases (particularly in a moist state). For attempts to stabilise the enzyme to be well-founded, it was therefore necessary to begin in the first place with the causes of the inactivation; it is even better (although not essential) to know the mechanism of the inactivation.

III. THE STABILISATION OF ENZYMES IN RELATION TO THERMAL INACTIVATION (IN RELATION TO THE UNCOILING OF THE PROTEIN GLOBULE)

As a result of the modification of enzymes by chemical reagents (including water-soluble synthetic reagents or biopolymers) or their attachment to a water-soluble carrier, their thermal stability is frequently altered (both decreased and increased). This is usually explained (see, for example Refs.5–7, 42, and 70) by the following causes: (1) the change in the conformation of the enzyme molecule compared with its native structure on the assumption that the thermal stability of the protein globule depends on its conformational state; (2) the change in the microenvironment of the enzyme molecule, assuming that it influences the intramolecular links (factors) which maintain its native structure.

These views, however valid they may be, cannot serve as a basis for the development of general methods for the stabilisation of enzymes. The point is that we do not know in what way the stability of the enzyme is related to its conformation and microenvironment; furthermore, even if this relation actually exists†, it ought to be, in all probability, specific to each enzyme.

The fact that the overall fundamental mechanisms of the inactivation of enzymes still remain unelucidated[52] although vigorous research in this field has continued for many decades also hinders the development of rational ways of increasing enzyme stability. It is extremely likely that a single general mechanism of the denaturation of proteins does not exist al all[77]. However, there is no doubt that the inactivation of enzymes under the influence of, for example, heat or denaturing agents is accompanied by considerable conformational changes in protein molecules, i.e. their uncoiling[52–54,77]. It therefore appears evident that an increase of the thermal stability of enzymes can be achieved by yet another procedure, namely if (3) the native conformation of the protein globule is made more rigid (is fixed).

In fact, if it is recognised that a necessary stage in the inactivation of the enzyme is the uncoiling of its molecule, then, the more rigidly (firmly) is the protein globule of the enzyme fixed, the greatly the difficulty of uncoiling it and hence of inactivating its active centre. One should note that this approach (involving a variation of the rigidity of proteins) is widely used in nature in the adaptation of organisms to the conditions in the environment[54].

The fixation of the enzyme globule to prevent its uncoiling can be achieved in several ways: by the introduction of cross links (1), by covalent (2) or non-covalent (3) attachment to a carrier, and by mechanical inclusion (4) in the narrow pores of a carrier. We shall consider each of these approaches in greater detail.

1. Intramolecular Cross Links and Their Influence on the Thermal Stability of Enzymes

There is extensive information in the literature about methods for the chemical modification of enzymes and the properties of the resulting preparations. However, one can hardly predict in a single instance how the thermal stability of the enzyme will alter as a result of its chemical modification. This is associated with the exceptional complexity of the molecular structure of biocatalysts (which, in addition, are still unknown for many enzymes). As an example of the extremely complex dependence of the thermal stability of an enzyme on the degree of modification of its surface layer, we shall indicate the behaviour of α-chymotrypsin alkylated via its NH_2 groups[105]. The enzyme was modified by treating it with acroleine with subsequent reduction of the Schiff bases by sodium tetrahydroborate (using the methods indicated by Feeney et al.[106]); this entailed hardly any loss of catalytic activity by the enzyme. Fig.1 shows that the alkylation of the NH_2 groups, which are the first to be modified, also hardly affects the thermal stability of α-chymotrypsin. The modification of the least reactive NH_2 groups (apparently relatively inaccessible groups deep in the globule) plays a decisive role: the thermal stability of the enzyme increases sharply in the concluding state of its modification (by two orders of magnitude); on further alkylation, the thermal stability of the enzyme preparation falls (as a result of the complete modification of all the NH_2 groups titratable by trinitrobenzenesulphonic acid). Fig.1 shows that the observed effect (a sharp increase of thermal stability with a subsequent sharp fall) is manifested to the maximum extent when only two-thirds of the NH_2 groups, the total number of which is 17, are modified.

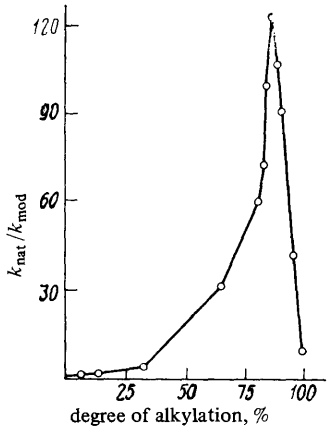


Figure 1. Dependence of the pseudo-first-order rate constant (k_{mod}) for the unimolecular thermal inactivation of α-chymotrypsin on the degree (based on titration data) of alkylation of the NH_2 groups by acroleine (with reduction of the Schiff bases by sodium tetrahydroborate); the value of k_{nat} obtained for the native (unmodified) enzyme was adopted by convention as unity. Conditions: 50 °C, pH 8 (5×10^{-3} M tris.HCl + 0.1 M KCl).[105]

The situation is different when bifunctional reagents, capable of cross-linking covalently the protein globule, are used: here one may expect an increase of the conformational stability of the protein molecule[78]. This approach therefore leads to wide prospects for the preparation of water-soluble stabilised enzyme preparations, which may find practical applications (see Section I).

Intramolecular cross links in nature. Nature makes an extensive use of intramolecular cross links for increasing the rigidity (and hence the stabilisation) of protein molecules[54].

† Thus it has been shown in recent studies by direct physical methods that the attachment of proteins to carriers does not lead to any significant conformational changes in their macromolecules[71–76].

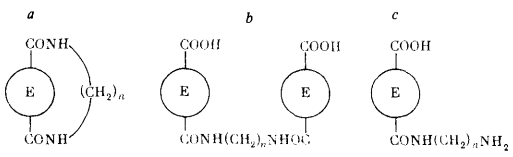
These cross links can be both covalent bonds (disulphide bonds[79-81]) and weaker linkages ("salt bridges"[82], or, for example, Ca^{2+} ions incorporated into the protein molecules[83], etc.).

The artificial introduction of cross links ("clamps") into protein molecules can be achieved by treating them with bifunctional reagents[11,84,85]. Dialdehydes, diimidoesters, diisocyanates, bisdiazonium salts, etc. are usually employed as reagents of this kind. Analysis of literature data[67,78,86-94] shows that in most cases the stabilisation effects are extremely small and sometimes are apparently in fact caused not by the cross links but by simple (single-point) chemical modification of the enzyme[67] as shown recently for glutaric dialdehyde[92]. In other cases the stabilisation effect proved to be more appreciable[78,91], an increase of stability being correlated with the increase of the rigidity of the protein molecule[78].

In all probability the success or failure of the attempt to increase the stability of the enzyme by treating it with bifunctional reagents, depends mainly on the extent to which the length of the bifunctional reagent corresponds to the distance between the possible centres of cross links in the protein globule. Evidently, for each given protein there is an optimum size of the intramolecular cross-linking agent. Studies directed to the selection of the optimum size of the bifunctional reagent are therefore of greatest interest.

Variation of the length of the intramolecular cross link. Studies of this kind are rarely performed, probably because the bifunctional reagents used directly to introduce cross links are commercially unavailable and their chemical synthesis is extremely laborious. It is therefore a very attractive propostion to employ bifunctional reagents which cannot be used directly to cross-link the enzymes intramolecularly but become suitable if the enzyme is subjected to an appropriate preliminary modification. A number of aliphatic diamines, which are commercially available, have a carbon chain comprising between 0 and 12 methylene groups, and are fairly cheap, proved useful for this purpose[95]; both factors are particularly important for possible practical applications. The diamines can be used to cross-link the carboxy-groups of enzymes (which are usually fairly numerous in proteins) provided that they are first activated with carbodiimide. This results in the formation of a strong amide linkage between the amino-group of the modifying agent (the diamine) and the carboxy-group of the protein[96]:

Scheme 1



Under conditions where there are no intermolecular cross links between the protein molecules (leading to the formation of enzyme oligomers—see Scheme 1*b*), it has been found that[95] there is a significant increase of the thermal stability of α-chymotrypsin intramolecularly cross-linked by this method (relative to the native preparation, the thermal inactivation rate constant decreases by a factor greater than 40). The observed stabilisation effect cannot be explained by simple (single-point) chemical modification of the enzyme (Scheme 1*c*), because the modification of chymotrypsin by a monoamine (provided the enzyme is subjected to preliminary activation with carbodiimide), namely 1-amino-3-propanol, actually reduces its thermal stability. The stabilisation effect depends on the number of methylene groups n in the molecule of the modifying agent $H_2N-(CH_2)_n-NH_2$. Fig. 2*a* shows that the dependence of the first-order reaction rate constant (observed for the thermal inactivation of chymotrypsins "cross-linked" by various diamines) has a minimum at $n = 4$, although the stabilisation of the enzyme is also observed for $n = 2$, 5, and 6.

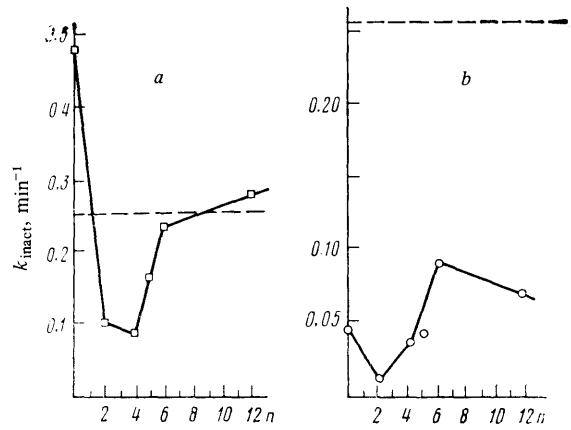


Figure 2. Dependence of the first-order rate constant (k_{inact}) for the unimolecular thermal inactivation of α-chymotrypsin (*a*) and succinylated α-chymotrypsin (*b*) cross-linked intramolecularly by diamines on the number of methylene groups in the molecule of the modifying agent $NH_2(CH_2)_nNH_2$.[95] The dashed line represents the level of the thermal stability of the native and succinylated enzymes. Conditions: pH 7 (0.02 M phosphate), 50 °C.

The fact that treatment with tetramethylenediamine leads to the maximum stabilisation of chymotrypsin is apparently due to the optimum correspondence between the length of the above cross-linking agent and the distance between the carboxy-groups of the protein molecule; this leads to the formation of a greater number of intramolecular cross links than for other diamines.

The grafting onto the enzyme of ability to interact with bifunctional (polyfunctional) reagents. Presumably the greater the number of clamps (cross links) applied to the protein molecule, the greater its stability in relation to uncoiling and hence inactivation. The possible number of cross links is determined in its turn by the number and relative positions of functional groups on the surfaces of the protein interacting with the cross-linking agent. Clearly their number (and hence the number of possible cross links) can be increased by the appropriate modification of the protein.

Reiner et al.[97] suggested that SH groups be introduced into the enzyme molecule for this purpose (by means of *N*-acetylhomocysteine thiolactone or other compounds)[98-100] with subsequent employment of the bisiodoacetamides derived from various aliphatic diamines as bifunctional reagents. For the system described above (Fig. 2*a*), it proved useful to subject the enzyme to a preliminary modification with succinic anhydride in order to increase the content of carboxy-groups in its surface layer[101]. The succinylated chymotrypsin was then treated (by the same method as the native

enzyme) with diamines of different lengths. Fig.2*b* illustrates the relation obtained under these conditions[95]. Evidently, firstly the maximum enzyme stabilisation effect has increased; secondly the maximum stabilising influence is shown by the shorter bifunctional reagent ethylenediamine and not tetramethylenediamine (cf. Fig.2*a*). The latter finding indicates a denser "population" of the surface of the succinylchymotrypsin globule (containing native chymotrypsin) by carboxy-groups.

The use of intramolecular cross links in fundamental biochemical research. Studies designed to select the optimum size of the cross-linking agent are not only important from the practical point of view (in order to obtain stabilised enzyme preparations) but can also yield new information about the tertiary structure (conformation) of proteins in solution[84] (for example, the distance between the functional groups in the surface layer of the protein globule can be estimated[102]), about the topography of the active centre (see the reference in the paper of Kennedy[85]), about the symmetry of the distribution of subunits in oligomeric proteins[85,102], about cooperative and allosteric effects[104], etc.

2. Multipoint Covalent Attachment of the Enzyme to the Complementary Surface of the Carrier

The methods for the covalent attachment of enzyme molecules to different carriers have been described fairly completely in numerous reviews (see, for example, Refs.5–9 and 11). This immobilisation procedure can promote, in principle, an increase of the conformational stability of the protein molecule and hence can prevent its uncoiling and inactivation. Thus the study of the conformational mobility of immobilised proteins (using various physical methods) showed that the attachment of the protein to the carrier makes the molecular structure of the former more rigid (it becomes "frozen")[71,72,74]. The same conclusion can be arrived at on the basis of many indirect data (obtained by both physical methods and by measuring the enzyme activity)[72,74,107–109]: after such proteins have been grafted to the carrier, the conformation transitions in them are greatly hindered. At the same time, Gabel showed in his pioneer investigation[110] that the greater the number of linkages attaching trypsin to Sephadex, the greater its resistance to inactivation by urea (under the influence of which the protein is known to become uncoiled[111]).

Thus the above findings suggest that the general principle governing the stabilisation of enzymes involves *multipoint* attachment of the catalyst molecule to the carrier. Such grafting should make the conformation of the catalyst molecule more rigid (incidentally it may not be otherwise altered in this process) and hence more resistant to uncoiling and inactivation. However, this principle is extremely difficult to apply methodologically because of steric factors: both the surface of the carrier and the surface of the protein have their individual reliefs which, generally speaking, are not complementary. Furthermore, it is evident that even in the case of multipoint interaction, when the enzyme is connected to the carrier solely by a small section of the surface, it is difficult to expect a significant increase of the rigidity of the entire molecule. Presumably this is why many attempts to stabilise enzymes failed[71,112,113]. The problem in fact reduces to creating a carrier surface which is rigorously complementary to the surface of the enzyme molecules. Only then is it possible to create a multipoint interaction between the protein and the carrier favourable for stabilisation.

The creation of a polymeric carrier complementary to the molecule of the immobilised enzyme. The essential feature of the approach permitting a solution of this problem[114–116] is as follows. The enzyme is modified by an analogue of the monomer and the resulting preparation is then copolymerised with the monomer itself (and in certain cases also with the cross-linking agent). Ultimately one obtains an enzyme which is chemically built into the three-dimensional network of the polymeric gel, the centres of the preliminary modification of the enzyme molecule serving as the points of attachment of the enzyme to the carrier. Evidently, by virtue of the very principle of the proposed method, the microsurface of the gel near the protein molecule built into it will be complementary to the surface of the protein.

A method for the preparation of enzymes immobilised by copolymerisation has been developed by Jaworek et al.[117], who endeavoured to prevent the elution of immobilised enzymes from gel carriers. The authors of the present review[114–116] developed this method independently in order to stabilise enzymes. It is very convenient to employ as monomer analogues acylating and alkylating agents containing a double bond capable of copolymerisation, for example, acryloyl chloride (which acylates the NH_2 and OH groups of the protein) or acroleine[114] (which interacts with the NH_2 groups; when the Schiff bases formed are reduced with sodium tetrahydroborate, the protein is found to be alkylated); a method has also been developed for the vinylation of the carboxyl-groups of the protein[118]. Acrylamide, sodium methacrylate, and ethylene methacrylate, which are frequently used to synthesise gels, can be used as the monomers and the cross-linking agent can be *N,N'*-methylenebisacrylamide. All these reagents are commercially available and cheap.

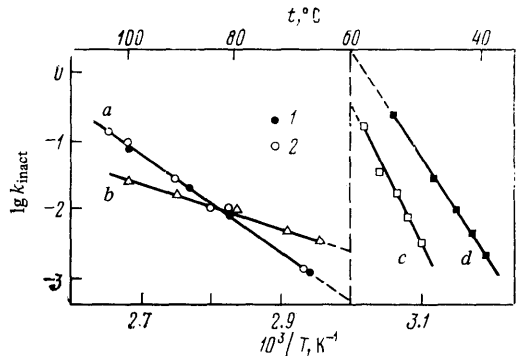


Figure 3. Temperature variation of the pseudo-first-order rate constant (k_{inact}, min^{-1}) for the unimolecular thermal inactivation of acryloylchymotrypsin incorporated in polymethacrylate (*a*) and polyacrylamide (*b*) gels [1) water-insoluble enzyme; 2) water-soluble enzyme], native α-chymotrypsin (*c*) and α-chymotrypsin modified by acryloyl chloride (*d*). Conditions: pH 8 (0.005 M tris.HCl+3 M KCl).[114]

The magnitude of the stabilisation effect. Fig.3 presents, as a striking example, data, expressed in terms of the Arrhenius coordinates, for the rate of thermal inactivation of α-chymotrypsin built into polymethacrylate and polyacrylamide gels (straight lines *a* and *b*)[114]. The resistance of the

immobilised enzyme preparations to heating is so much greater than that of the native enzyme (line *c*) that a direct, i.e. at the same temperature, experimental comparison is impossible. It is therefore necessary to compare the thermal inactivation rate constants determined by extrapolation, for example, at 60 °C (the vertical dashed line in Fig.3). At 60 °C acryloylchymotrypsin built into polymethacrylate (line *a*) and polyacrylamide (line *b*) gels is respectively 1000 and 200 times more stable than the native enzyme (line *c*). Compared with free acryloylchymotrypsin (line *d*), an even more striking difference is observed.

Fig.3 shows that the activation energies for the thermal inactivation of acryloylchymotrypsin built into both polymethacrylate and polyacrylamide gels are much lower (35 and 15 kcal mol^{-1} respectively) than for the native enzyme (110 kcal mol^{-1}). From this it follows that, with increase of temperature, the degree of stabilisation of the immobilised chymotrypsin will increase compared with the native enzyme. Thus extrapolation of straight line *c* in Fig.3 shows that at 102 °C the enzyme built into the gels is more stable than the native enzyme by a factor greater than 10^8.

Dependence of the stabilisation effect on the number of links between the immobilised enzyme and the carrier. It is noteworthy that the stabilisation effect in systems discussed above (Fig.3) is independent of both the initial density of the gel carrier (i.e. of the polymer concentration or more correctly of the monomer concentration) in the polymerisation mixture in the range from 10–15 to 50 wt.% and of the degree of its swelling (which depends on the amount of cross-linking agent, namely *N,N'*-methylenebisacrylamide). Furthermore, if the acrylic derivatives of the enzyme are copolymerised with the comonomers altogether in the absence of a cross-linking agent, the resulting gel-like polymer can be fully dissolved in water and, what is most important, the enzyme preparation obtained has the same high thermal stability as the enzyme immobilised in an insoluble gel (Fig.3*a*)[114]. This phenomenon is apparently due to the fact that the polymeric structure of the gel in the vicinity of the enzyme molecule, being complementary to its surface, is specified by the number of cross links with the protein.

The degree of covalent binding of the copolymerised enzyme to the carrier exerts in its turn a decisive influence on the thermal stability of the enzyme, namely, with increase of the number of cross links between the immobilised enzyme and the carrier, there is an increase in the thermal stability of the catalytic activity in the system. Thus Fig.4 shows that the effective rate constant for the thermal inactivation of α-chymotrypsin (at 60 °C) falls by a factor greater than 1000 when the degree of binding of the enzyme to the polymethacrylate carrier increases (the number of residual free NH_2 groups after acryloylation was determined experimentally by titration)[114].

The stabilisation mechanism. The observed enzyme stabilisation effect cannot be explained by the possible change in the thermal stability of the enzyme as a result of chemical modification, because free acryloylchymotrypsin is thermally even less stable than the native enzyme (Fig.3). Nor can stabilisation be explained by the influence of the micromedium in the gel on the enzyme, because the thermal stability of chymotrypsin physically incorporated in the polymethacrylate gel at the same concentration is virtually the same as that of the free enzyme[119,120] (Fig.5). The nature of the gel is also not a decisive factor for the stabilisation of the enzyme—analogous effects have been obtained for both polyelectrolyte (polymethacrylate) and electrostatically neutral (polyacrylamide) gels (Fig.3). The stabilisation effect occurs when different methods are used for the preliminary modification of the enzyme: alkylation of the NH_2 groups by acroleine or acylation of the protein by acryloyl chloride (Fig.3)[114] or vinylation of the carboxy-groups[118]. Finally, stabilisation has been achieved for different enzymes: α-chymotrypsin, trypsin[114], and penicillin amidase[121]. Consequently the very fact that the enzyme molecule is built into the three-dimensional network of the gel and not the method of preliminary modification or the nature of the gel is of decisive importance. Evidently the stabilisation mechanism depends on the fact that the uncoiling of the globule on heating is difficult in a fixed state of the protein. Here one must emphasise that the native (catalytically active) conformation of the active centre can be preserved only if the enzyme is bound to the carrier via numerous points of attachment (Fig.4).

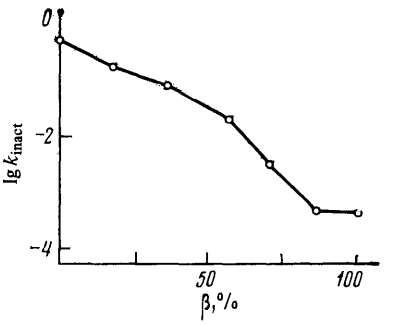
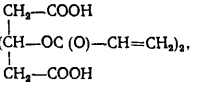


Figure 4. Dependence of the pseudo-first-order rate constant (k_{inact}) characterising the unimolecular thermal inactivation of α-chymotrypsin incorporated in a polymethacrylate gel on β (the degree of covalent binding of the enzyme to the carrier). Conditions: pH 8 (0.005 M tris.HCl + 3 M KCl), 60 °C.[114]

Further prospects. There is no doubt that the thermal stability of the copolymerised enzyme must depend (for the specified number of cross links between the protein and the carrier) on the rigidity (flexibility) of the polymer chains linked covalently to the protein globule and maintaining the native structure of the latter: for more rigid (less flexible) polymers (we have in mind this property at the molecular level), one should expect a greater stabilisation effect[115]. This principle must be tested experimentally in the future. Protein modifying agents and comonomers containing in their molecule at least two polymerisation centres and hence ensuring the formation of branched (completely cross-linked) polymeric gel structure may prove to be useful for this purpose. In order to ensure an adequate solubility, these compounds must be electrolytes, for example, the compound



which must be synthesised by acylating tartaric acid by acryloyl chloride. Furthermore, the polyelectrolyte nature of the resulting polymer might ensure an additional increase of the rigidity of its chains[122].

Gels suffer from a number of disadvantages as carriers[123], which include, in particular, low mechanical strength and a tendency of the gel grains to deteriorate on storage. However, these disadvantages can be avoided if the polymerisation is carried out within the pores of fairly stable carriers, for example, inorganic carriers, which have proved to be very useful[32,124,125]. The covalent attachment of the enzyme to elastic carriers (including gel-like carriers) leads to the possibility of regulating the catalytic activity by mechanical means[126]. In the case of polyelectrolyte carriers the catalytic activity of the immobilised enzyme can also be regulated by altering the ionic strength of the solution[127]. These aspects of the regulation can prove to be useful when enzymes are employed in organic synthesis (in chemical engineering).

The use of covalently immobilised enzymes in fundamental research has been very fully described by Mosbach[9].

3. The Multipoint Non-Covalent Interaction between the Enzyme and the Carrier

The multipoint interaction between the enzyme and the carrier can ensure, in principle, the stabilisation of the biocatalyst even when physical immobilisation methods are used. Physical immobilisation methods (for example, mechanical inclusion in gels[123], microencapsulation[128], adsorption on carriers[129,130], etc.) have been developed in fair detail[5,9,11], but the thermodynamic causes (mechanism) of the thermal stabilisation of enzymes in such systems have been discussed only recently and recommendations have been made for the formation of stabilised enzyme preparations[119,120]. As an example, we shall consider in greater detail the thermal stability of α-chymotrypsin incorporated mechanically in a polymethacrylate gel. In principle, the enzyme can form weak electrostatic or hydrogen bonds with this polyelectrolyte matrix.

The magnitude of the stabilisation effect. Fig.5 presents the variation of the logarithm of the effective rate constant for the thermal inactivation of α-chymotrypsin with the concentration of the polymethacrylate gel (up to the limit of the solubility of the monomer in water). Evidently, when the gel concentration is varied from 0 to 30 wt.%, the rate of thermal inactivation (at 60 °C) of the enzyme is almost constant, but, on further increase of the gel concentration, it falls very rapidly: in 50% gel the stabilisation effect reaches 10^5. Furthermore, extrapolation of the linear relation between $\lg k_{inact}$ against $1/T$ showed[119] that the lifetime of the enzyme immobilised in a polymethacrylate (45 wt.%) gel can amount to millions of years at room temperature.

The stabilisation mechanism depends on the interaction between the enzyme molecules and the polymer matrix. In principle, protein molecules can form electrostatic and hydrogen bonds with the carboxy-groups of the carrier, i.e. with polymethacrylic acid. However, these bonds are relatively weak; this is probably why they are hardly formed in a polymer solution or in dilute gels, where the formation of such a complex would entail considerable entropy losses in the "quenching" of the translational as well as rotational movements of the enzyme molecules.

The situation should be different in concentrated gels, where one may expect that the translational (possibly rotational) movement of protein molecules is significantly retarded (regardless of the formation of the complex) by virtue of steric hindrance introduced by the dense three-dimensional polymer network. Consequently in a concentrated gel the formation of a protein–matrix complex should be thermodynamically much more favourable, because there is no expenditure of free energy (or it is significantly reduced) caused by the loss of translational and rotational entropy by the enzyme globule when it is sorbed on the polymer matrix. One cannot rule out the possibility that in a concentrated gel the mobility of the polymer chains themselves is somewhat limited, so that the entropic losses of free energy, necessary for the local "freezing" of the matrix on formation of its complex with the enzyme, are therefore also significantly reduced compared with dilute gels (or a polymer solution).

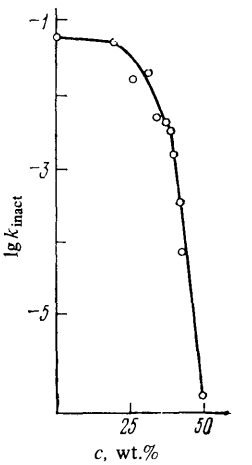


Figure 5. Dependence of the pseudo-first-order rate constant (k_{inact}, s^{-1}), characterising the unimolecular thermal inactivation of α-chymotrypsin incorporated mechanically in a polymethacrylate gel, on the concentration c of the polymethacrylate in the gel. Conditions: pH 8, 60 °C.[119]

Finally, under the conditions of a concentrated gel one may expect that the interaction of the enzyme with the matrix should be of the multipoint type for purely steric reasons, because polymer chains will approach the enzyme globule from all sides. Such multipoint interaction can lead to a sharp increase of the thermal stability of the immobilised enzyme (as already shown above for the covalent enzyme–carrier interaction).

All these postulates have been proved[119] as a result of a study of the thermal stability and the translational and rotational mobilities of enzyme molecules as a function of the gel concentration.

The proposed mechanism[120] operates also in other systems investigated previously. The specific protein–carrier interaction can also be of a type other than in the case discussed above, where electrostatic and hydrogen bonds are formed. We shall consider data[131,132] for the thermal stability of acetylcholinesterase, glucose oxidase, and peroxidase incorporated mechanically in the hydrophobic organosilicon gel silastic. While the thermal stability of the first enzyme increased sharply after incorporation in this gel, those of the remaining enzymes remained virtually unchanged when the enzymes were immobilised. In principle, all three enzymes could be stabilised in relation to uncoiling and hence thermal inactivation by forming multipoint hydrophobic contacts with the carrier. However, the enzyme–matrix interaction can be thermodynamically favourable, as shown by the examination of the above mechanism, only subject to the condition that the molecular mobility of the protein molecules

incorporated mechanically in the gel is reduced even in the initial stage. In the gel silastic at a given concentration the inhibition of translational diffusion (and hence stabilisation) is apparently achieved only for very large acetylcholinesterase molecules but not for the relatively small glucose oxidase and peroxidase molecules.

Further prospects. One can hardly give preference to any particular physical immobilisation method without knowing the purpose of the resulting enzyme preparation. If, however, one endeavours merely to increase the thermal stability of the enzyme as a result of immobilisation, then we believe that mechanical incorporation of the enzyme in a gel capable of specific interaction with the protein is most attractive. The advances achieved in this field (see above) can be enhanced still further if an attempt is made to optimise the gel structure using more than one monomer (not counting the cross-linking agent) and thus introducing various functional groups into the carrier[123,133].

On the other hand, one should recall that the stabilisation effect in such systems depends radically on the concentration (density) of the gel (Fig.5) and that only a concentrated gel exerts a stabilising influence (if such an influence occurs at all). Consequently the swelling of gel particles (grains) in water results in the reversible disappearance of the stabilisation effect[119]. It would seem that this limits the applicability of such systems in the formation of stabilised enzyme preparations. However, the swelling of the gel in water can be prevented (and the thermal stabilisation effect can thus be retained) by employing gels which are sufficently cross-linked (by carrying out the cross-linking either directly during polymerisation using comonomers of the type *N,N'*-methylenebisacrylamide or by an additional treatment of the gel particles—grains several microns in size—with bifunctional cross-linking agents)[134]

Thermally stabilised enzyme preparations based on gels have found applications also in the catalysis of reactions in organic solvents. However in this case the organic solvent should be immiscible with water and the gel will hardly swell (after a suitable choice of polymer); consequently the thermal stabilisation effect (of the kind illustrated in Fig.5) should be preserved; the enzymic reactions in water–organic solvent systems will be described in greater detail below.

Biological aspects (model of biological membranes). The mechanism of the stabilisation of enzymes incorporated mechanically in concentrated polymeric matrices (i.e. the forced arrest of the translational movement of the enzyme molecule followed by multipoint interaction between the protein and the relatively immobile matrix), proposed by Martinek et al.[119], can function *in vivo* in membrane enzyme systems[135,136], where, firstly, an extremely low mobility of the molecules in the membrane is observed (the translational and rotational movements are inhibited)[137] and, secondly, the enzyme molecules can interact with the constituent phospholipids and structural proteins in the membrane, forming a set of relatively weak bonds—hydrophobic, electrostatic, hydrogen, etc.[138] Furthermore, such formal similarity makes it possible to understand certain aspects of the functioning of biological membranes. Thus it is known that, in the adaptation of organisms to changes in the temperature of the environment, the thermal stability of membrane enzymes also changes[54]. The molecular mechanism of such regulation may consist in an alteration of the fraction of unsaturated lipids in membranes[54], which should influence the viscosity of the membrane phase and hence the molecular mobility of the enzyme molecules incorporated in it. The molecular mobility and the thermal stability of the enzymes incorporated mechanically in the matrix are in their turn interrelated; this has been shown[119] by the model system "α-chymotrypsin in a polymethacrylate gel" (see above).

4. Mechanical Incorporation of Enzymes in the "Narrow" Pores of the Carrier

The uncoiling of the protein globule on denaturation can also be prevented by accommodating the native enzyme molecule in a cell which does not react with it via either chemical or sorption mechanisms but is so "narrow" that the uncoiled conformation cannot be formed for steric reasons. In this case the native conformation of the protein globule can be maintained by purely mechanical means. This mechanism has been frequently proposed in the literature as a hypothesis (frequently in a very implicit form)[139–142], but experimental evidence has been obtained only recently[134,143,144] in studies of the properties of α-chymotrypsin and trypsin in a polyacrylamide gel or in (on) polysaccharide carriers.

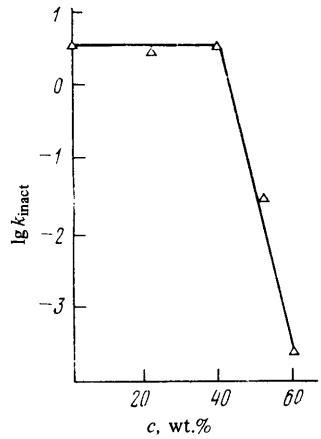


Figure 6. Dependence of the pseudo-first-order rate constant (k_{inact}, min^{-1}), characterising the unimolecular thermal inactivation of α-chymotrypsin incorporated mechanically in a polyacrylamide gel, on the concentration *c* of polyacrylamide in the gel. Conditions: pH 8, (0.02 M tris.HCl + 0.1 M KCl), 60 °C.[134,143]

The polyacrylamide gel is an extremely suitable carrier for research of this kind: firstly, this gel is chemically inert[145], secondly, the size of its pores can be readily varied by altering the monomer concentration[146], and, thirdly, at fairly high gel concentrations the size of its pores is comparable to the size of enzyme globules[147,148].

Two methods have been used for the mechanical incorporation of the enzyme in the gel: acrylamide at the required concentration is polymerised directly in the enzyme solution (as described by Martinek and coworkers[114,119]) or the gel particles (obtained in the absence of the enzyme and carefully washed free of low-molecular-weight impurities) are impregnated with the enzyme solution and are then lyophilised to give the required concentration of polyacrylamide[143,144]. The thermal stability of the enzyme is the same in both cases (Fig.6): whereas at a not unduly high gel concentration (less than 45 wt.%) there is no appreciable stabilisation of the enzyme in relation to irreversible unimolecular thermal

inactivation, in a denser carrier (more than 50 wt.% of polyacrylamide) the thermal stability of the enzyme increases sharply.

The magnitude of the stabilisation effect. The thermal stability of the enzyme incorporated mechanically in a very concentrated polyacrylamide gel (lyophilised powder) is so much higher than the thermal stability of the enzyme in solution that the two quantities cannot be measured at the same temperature. It is necessary to investigate the temperature variation of the rate of unimolecular thermal inactivation: linear extrapolation of the data presented in Fig.7 to the centre of the temperature range (120 °C, vertical dashed line) shows that the stabilisation effect in a fully dried gel reaches a value corresponding to an increase by a factor of 10^{13}. For less concentrated gels, the stabilisation effect is naturally smaller.

The stabilisation mechanism is not associated with the influence of the non-polymerised acrylamide[149] because it was completely washed out of the comminuted gel[143,144]. Nor can stabilisation be explained by the chemical grafting of the enzyme to the gel, because both chymotrypsin and trypsin could be completely eluted from the swollen gel[143,144]. The enzyme hardly interacts with the matrix via a sorption mechanism, because the protein globule retains a high rotational mobility up to a gel concentration of 50 wt.% (where appreciable thermal stabilisation is already observed)[119,143,144]. Consequently the pore size presumably diminishes with increasing gel concentration and ultimately the enzyme globule is "clamped" and cannot uncoil (be denatured) as a result of the "cage effect".

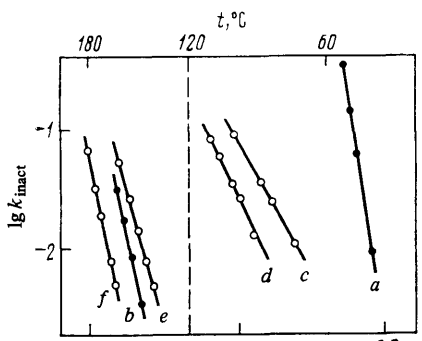


Figure 7. Temperature variation of the pseudo-first-order rate constant (k_{inact}, min^{-1}) characterising the unimolecular thermal inactivation of α-chymotrypsin: *a*) solution of native enzyme (pH 5–8); *b*) lyophilised enzyme; *c*)–*f*) enzyme incorporated mechanically in 48, 60, 80, and 100 wt.% polyacrylamide gel respectively (the polymer concentrations indicated are those in 60 μm gel grains washed after lyophilisation)[134,143].

It might have been supposed that a different stabilisation mechanism operates, namely that the dehydration of the protein can lead to a decrease of the mobility of the polypeptide chains, which would hinder the uncoiling of the globule. A choice between these alternative mechanisms cannot be made in a study of the thermal stability of a lyophilised preparation of the free enzyme. In this state the protein molecules are in all probability involved in a very close packing, where each globule can be incorporated (as in immobilisation in a gel) in a "narrow pore" formed by similar globules. The exceptionally high thermal stability of dry (lyophilised) enzyme preparations[139,141,142] (particularly that of chymotrypsin, see Fig.7), observed experimentally, can be caused both by the "dehydration of the polypeptide chains" and by the "cage effect". This problem was resolved, i.e. an unambiguous choice was made between these two mechanisms, by employing polysaccharide carriers.

Polysaccharide carriers are inert and hardly interact with proteins. This is indicated by the following fact: although the translational diffusion of protein molecules (lactoglobulins, ribonuclease, etc.) virtually disappears in a 40% dextran solution, their rotational diffusion is not significantly inhibited (compared with an aqueous solution without a polysaccharide)[150].

Pseudo-first-order rate constants (min^{-1}) for the irreversible unimolecular thermal inactivation (60 °C) of native and immobilised α-chymotrypsin[134,144].

Preparation	Free enzyme	Enzyme attached to the surface of cellulose	Enzyme incorporated in the pores of Sephadex
Solution or suspension at pH 8 (2×10^{-2} M tris-HCl + 0.1 M KCl)	3	0.1	0.08
Lyophilised state	*	0.05	*

*Thermal inactivation was not observed for 30 min even at a higher temperature (100 °C).

In order to obtain an answer to the above question, a study was made of the thermal stability of chymotrypsin attached covalently to two polysaccharide carriers—cryptocrystalline cellulose and Sephadex. Although these carriers are very similar in their chemical compositions, they are structurally fundamentally different: in contrast to cellulose, Sephadex has a porous structure. Consequently, whereas in the case of cellulose the enzyme is attached to the surface, in Sephadex the attached protein molecule is incorporated within a carrier pore. On lyophilising the carrier, the "cage effect" can therefore obtain in the latter case (and only in the latter case). The Table shows that covalent immobilisation has only a slight influence on the thermal stability of chymotrypsin on both polysaccharide carriers (in relation to the free enzyme). The additional lyophilisation of the enzyme attached to the surface of cryptocrystalline cellulose also does not alter significantly the thermal stability of the enzyme preparation. On the other hand, thermal inactivation of the enzyme attached to Sephadex G-150 could be observed neither under comparable conditions (see Table) nor even at 100 °C (incubation time 30 min).

Since the only significant difference between these two polysaccharide carriers is that in the Sephadex the enzyme was located in a narrow pore after drying, while in cellulose it remained on the surface of the particle, one may reach the following conclusion: the very high increase of the thermal stability of enzymes in concentrated porous carriers (Sephadex and polyacrylamide) is caused by the "cage effect" and not the dehydration of the protein.

Further prospects. Preparations with such high thermal stability can be used in practice if the swelling of the carrier in water is prevented. This can be achieved by employing sufficiently cross-linked polymeric materials or by carrying out enzymic reactions in organic solvents immiscible with water (for further details, see below).

The method involving the immobilisation of protein globules in the narrow pores of an inert carrier leads to new possibilities for the stabilisation (as a result of the "cage effect") of even extremely labile enzymes, which are usually inactivated as a result of immobilisation on interaction with carriers.

In nature a similar mechanism (based on the "cage effect") can stabilise proteins in spores in relation to unfavourable conditions in the environment.

5. Approaches Based on the pH Dependence of the Rate of Thermal Inactivation

The rate of thermal inactivation sometimes depends significantly on the pH (see, for example, Goldstein and coworkers[6,101]). In this case the denaturation of the enzymes can be suppressed by procedures based on the physicochemical principles described below in Sections IV.2 and IV.3.

IV. THE STABILISATION OF ENZYMES IN RELATION TO INACTIVATION UNDER THE INFLUENCE OF EXTREME pH VALUES

Many enzymes lose their catalytic activity rapidly and irreversibly under the influence of what for them are extreme pH values (i.e. at pH values of the medium remote from the natural pH range of their activity)[52]. The "alkaline" inactivation of pig pepsin (which begins already at pH 5) and the "acid" inactivation of chicken lactate dehydrogenase (which takes place effectively at pH 4) can be pointed out as thoroughly investigated examples.

In principle, when an enzyme is immobilised, its pH stability can change (as well as its thermal stability—see the previous Section). Indeed this phenomenon has been observed experimentally[5,6,42,151] for many enzymes. In order to account for it, one usually points (see, for example, Goldstein and coworkers[6]) to the change in the microenvironment of the enzyme when it is immobilised; another possible effective factor may be a change in the enzyme conformation on immobilisation (induced, for example, by its chemical modification or interaction with the carrier).

However, as in the consideration of the thermal stability of enzymes, we are forced to conclude that, despite the probable validity of these causes, they cannot be used in the development of general principles for increasing the pH stability of enzymes, since it is not known in what way the stability is related to the microenvironment of enzymes and their conformations. On the other hand, one can now already formulate several general principles (unrelated to those discussed above), which increase the pH stability of enzymes as a result of their immobilisation.

1. Prevention of the Uncoiling of Enzyme Molecules

The pH inactivation of enzymes, like thermal inactivation, apparently includes as a significant stage the uncoiling of protein molecules[53] caused by the change in the balance of electrostatic and hydrogen bonds when the ionised state of ionogenic protein groups is altered by the change of pH. In this case all the recommendations made in the discussion of the stabilisation of enzymes in relation to thermal inactivation are applicable (see above).

2. Immobilisation of the Enzyme on a Carrier with Buffer Properties

Suppose that the enzyme is immobilised on a carrier with ionogenic groups exhibiting buffer properties with a considerable capacity. It is then evident that, following a change in the pH of the solution, the change in "micro-pH" in the carrier (i.e. the pH values around the enzyme) will always be considerably smaller. This increases the observed pH stability of the immobilised enzyme compared with its native state.

A brilliant illustration of this postulate is apparently provided by the work of Kaplan and coworkers[152], who investigated the acid inactivation of native lactate dehydrogenase and the enzyme attached covalently to glass. Whereas the native enzyme is almost completely inactivated after 1 h at pH 3.2 (25 °C), the immobilised enzyme retains virtually 100% activity under these conditions even after incubation for 35 days (Fig.8). The buffer properties of the carrier surface are in this case confirmed by the fact that, in contrast to the native lactate dehydrogenase, the catalytic activity of the enzyme attached to glass is almost independent of the pH of the medium[152].

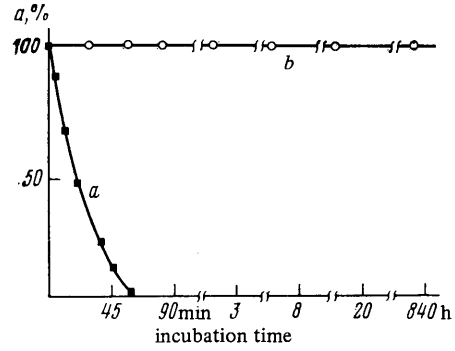


Figure 8. The pH stability of native lactate dehydrogenase (*a*) and the enzyme bound covalently to porous glass (*b*) (25 °C, pH 3.2).[152]

3. The Shift of the pH Profile for the pH Inactivation of the Enzyme

After the studies by Katchalski and coworkers[153,154], which have become classical, the shift of the pH profile of the catalytic activity of enzymes when they are attached to polyelectrolytes appears quite natural[65]. When enzymes are immobilised on polyanions, the pH profile of their activity shifts to the alkaline region (in consequence of the higher proton concentration in the carrier phase compared with the solution), and when they are immobilised on polycations there is a shift to the acid region (in consequence of the lower proton concentration in the carrier phase compared with the solution); see, for example, Fig.9*a*. The shift of the pH

profile of the catalytic activity of enzymes on immobilisation should also be observed, generally speaking, in the case of a non-electrolyte carrier owing to a specific distribution of protons between the latter and the medium[65].

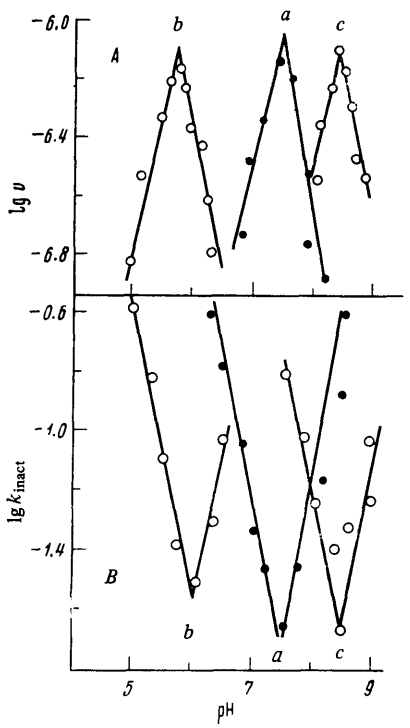


Figure 9. The pH variation of the maximum rate V (arb. units) of hydrolysis of benzylpenicillin catalysed by penicillin amidase (A) and of rate constant (min^{-1}) for the inactivation (at 50 °C) of penicillin amidase (B): a) native enzyme; b) enzyme–polycation complex; c) enzyme–polyanion complex[155].

Evidently analogous effect should obtain also in the pH inactivation of enzymes—the difference between the pH values of the solution and the carrier phase should lead to a shift of the observed pH profile for the pH inactivation process. Indeed, a series of studies by Katchalski and coworkers (see the references in a paper of Goldman et al.[6]) showed that, as was to be expected, the attachment of enzymes to a polyanionic carrier increases their stability at alkaline pH, while attachment to a polycationic carrier makes them more stable in acid solutions. This phenomenon is illustrated by the results of a study[155] (Fig. 9) in which the activity and stability of penicillin amidase immobilised on different carriers were investgiated. Evidently (Fig. 9*B*) the pH profiles of the rate constant for the pH-inactivation of the enzyme are displaced depending on the nature of the carrier, in full agreement with this theory.

V. ENZYMIC REACTIONS IN ORGANIC SOLVENTS WITH A LOW CONTENT OF WATER (OR IN ITS ABSENCE)

Many enzymes have been adapted by nature to function effectively primarily in aqueous solutions. This fact limits, in principle, the activation of enzymes as catalysts of reactions employed in practice. The point is that many chemical reactions are thermodynamically favourable only in specific organic solvents, which is due to specific solvation effects, the solubility of individual reactants, and the fact that, apart from the required product, water is sometimes formed, so that the equilibrium is strongly displaced towards the initial substances when the reactions are carried out in aqueous solutions. The last cause inhibits the use of biocatalysis in important processes such as the synthesis of esters or amides, the polymerisation of aminoacids or sugars, dehydation reactions, etc.

Evidently this difficulty can be overcome by replacing water as the reaction medium by a non-aqueous solvent. There have been fairly numerous studies in which attempts were made to carry out enzymic reactions in organic solvents or aqueous organic media with a high concentration of the non-aqueous component[58,156–181]. However, all valid studies of this kind, led to the conclusion that on passing from water to the organic solvent, the catalytic activity of the enzymes falls sharply and their substrate specificity disappears.

A partial solution to this problem can be found by selecting an organic component which denatures the enzyme to the smallest extent[181]. However, two other approaches are more promising: the use of two-phase aqueous organic systems (mixtures of water and organic solvents with which it is immiscible)[59,182] or inclusion of enzymes in "inverted" micelles of surfactants[183]. We shall consider in greater detail the physicochemical principles of these three approaches.

1. Criteria for the Selection of the Optimum Organic Solvent

In order to carry out enzymic processes in non-aqueous or aqueous organic media with a high content of the non-aqueous component, one uses as a rule organic solvents such as dimethyl sulphoxide[158–165], formamide[163,166], dimethylformamide[163,167–169], dioxan[170–174], ethylene glycol[172,175], glycerol[175,176], monohydric alcohols[165,172,177–180], and acetone[165,174]. The choice of a particular solvent is in most cases random and lacks theoretical foundations.

The criterion for the selection of the optimum solvent (from the standpoint of its influence on the enzyme) can be based on the general ideas of the relative role of the forces maintaining the native structure of protein molecules in aqueous solutions: hydrophobic interactions play a dominant role[79]. Consequently a non-aqueous solvent which is "satisfactory" for the protein should not disrupt such interactions.

In order to obtain an answer to the question which solvents have this property, we shall turn to data for the model process involving the formation of surfactant micelle in various solvents. Ray[184] concluded that hydrophobic interactions constitute merely a special case of solvophobic interactions. All solvents can be divided into three classes in terms of their ability to undergo solvophobic interactions: the first class includes water, glycerol, ethylene glycol, aminoethanol, formamide, and certain others; the second includes methyl, and dimethyl-formamides, and the third includes methanol, ethanol, and toluene. Solvophobic interactions occur to the greatest extents in solvents of the first class (thus it has been found that[184] detergent micelles are formed only in such solvents); they take place to a much lesser extent in solvents

of the second class and are virtually absent in solvents of the third class.

According to Ray[184], this difference is due to the fact that the molecules of solvents of the first class contain at least two or three fragments capable of forming hydrogen bonds. As a result of intermolecular interactions, hydrogen bonds form rigid (thermodynamically unfavourable) skeletal solvent structures around the solvophobic solute molecules. This leads to solvophobic (or in the special case hydrophobic interactions). In the series of solvents of the first class solvophobic interactions occur most effectively in water and glycerol (estimated from critical concentrations for micelle formation); in the remaining solvents this ability is significantly smaller.

The above data made it possible to formulate[181] a criterion for the choice of the optimum solvent. The criterion is extremely universal, because the efficiency of solvophobic (as well as hydrophobic[185]) interactions is determined primarily by the nature of the solvent and not the nature of the interacting molecules. Consequently if it is assumed that hydrophobic interactions play the main role in maintaining the structure of protein molecules[79], one must recognise that the best solvents for enzymic reactions should be those of the first class, including water (which is employed in nature) and glycerol.

We may note that the authors of the majority of studies used solvents belonging to the second or even third group (see above), i.e. the least successful solvents. However, in some investigations it was nevertheless found experimentally[172,180,186,187] that solvents belonging to the first class (particularly glycerol and to a lesser extent ethylene glycol) denature proteins much less than others. These empirical findings can be given a physicochemical explanation in the light of studies by Martinek and coworkers[181,184].

2. Enzymic Reactions in Two-Phase Systems Comprising Water and an Organic Solvent Immiscible with It

Following the development of research into immobilised enzymes, studies began to appear whose authors attempted to make enzymes function in organic solvents and aqueous organic media with a high concentration of the organic component having increased their stability in relation to the denaturing influence of the non-aqueous medium by attaching them to a carrier (see, for example, Refs.165, 168, 169, 173, 174, 176, 179, 180, and 189–191). However, even in the most successful systems, when the concentrations of the organic component are above 90%, the immobilised enzyme is nevertheless inactivated. Thus, from the standpoint of preparative enzymic synthesis, the problem formulated remains unsolved. It is extremely likely that in this form it is insoluble, in principle, because, on passing from water to a non-aqueous medium, there is bound to be a significant change in the conformation of enzymes[58,192] and a consequent sharp impairment of their catalytic function.

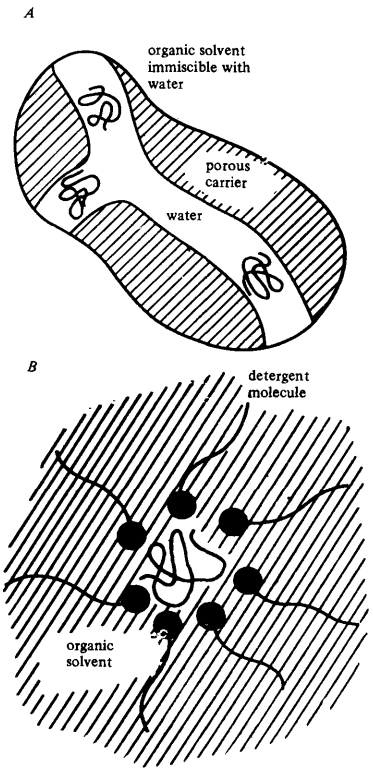
We found a fundamentally new solution[59,182]. In all the studies with which we are familiar, where the behaviour of enzymes was investigated in aqueous organic or organic media, solvents such as acetone, acetonitrile, dioxan, dimethyl sulphoxide, dimethylformamide, methanol, ethanol, and others (see above) were used as the non-aqueous component. A common feature of these solvents is that they are infinitely miscible with water. This is in fact why one has to solve the problem of the stabilisation of enzymes in relation to inactivation by the organic component.

The basic idea of our approach[59,182] is that the organic solvents added to the enzyme-containing aqueous phase should be virtually immiscible with water (for example, chloroform, ether, aliphatic alcohols, hydrocarbons, etc.). In this case the resulting system will consist of two phases—aqueous and organic. The enzyme will be contained solely in the aqueous phase, because, firstly, it can be immobilised there, and, secondly, even if immobilisation is impossible, proteins, which are satisfactorily soluble in water, are usually virtually insoluble in hydrophobic solvents[58]. The substrates, being soluble in the organic phase, can in their turn diffuse freely[193,194] from the latter to water, where they undergo a chemical transformation under the influence of the enzyme; the products diffuse from water back to the organic phase. Thus the thermodynamic equilibrium in the given chemical reaction is established throughout the aqueous organic system via water (with the aid of the enzyme catalyst present in water).

Such a two-phase system has a number of fundamentally important properties: (1) since the enzyme is not in contact with the non-aqueous component of the reaction medium, there is no need to solve the problem of its stabilisation[59,192]; (2) the volume fraction of the organic phase can be in principle as close to unity as required, so that equilibrium conditions in a two-phase system of this kind can be made as close to equilibrium in the pure organic medium as one wishes (see the theoretical aspects below[59,182]); (3) a high content of the non-aqueous component of the medium can ensure also a solubility of hydrophobic reactants, for example, steroids, sufficient for preparative synthesis[195,196].

Methodological aspects. The enzyme system comprising water and an organic solvent immiscible with it can be prepared as an emulsion of an aqueous solution of the enzyme in the organic medium or as a suspension in the organic medium of porous particles (for example, a porous glass or ceramic, a hydrophilic gel, etc.) impregnated by the aqueous enzyme solution[59,182] (see Scheme 2, *A*), the latter procedure being much more convenient both methodogically and tecnologically.

Scheme 2



The aqueous enzyme solution can also be enclosed in microcapsules or hollow fibres[9,11] or even in the microcracks of a polymeric carrier by mechanical deformation of the latter[197]. The enzyme can be used in both free and immobilised states.

It would seem that preparative enzymic synthesis in a two-phase system is inapplicable to reactions in which the reactants (and in the first place products) are ions, because ions cannot pass from water to the organic phase. However this difficulty can be overcome[182] by selecting hydrophobic counterions for ionic reactants (as suggested in the chemistry of nucleotides[198] and used widely in phase transfer catalysis—see, for example, Dehmlow[199]).

Examples. (a) The idea of carrying out enzymic organic synthesis in a two-phase aqueous organic medium with a high content of the non-aqueous component was tested[59,182] in relation to the chymotrypsin-catalysed synthesis of the methyl ester of *N*-acetyl-L-tryptophan from ethanol and *N*-acetyl-L-tryptophan. Since water is formed together with the ester in the synthesis, the equilibrium was strongly displaced towards the initial reactants when the reaction was carried out in water (see the references in the papers by Martinek et al.[200] and Carpenter[201]). Furthermore, at neutral pH (at which the enzyme employed is active) there is an additional shift of the equilibrium unfavourable for the synthesis of the ester and caused by the thermodynamically favourable ionisation of one of the initial components—the acid. Ultimately the yield of the ester is negligible, amounting to less than 0.01% even at a relatively high ethanol concentration (~10 M). In the "chloroform + 1 vol.% of water" two-phase system the equilibrium was completely displaced towards the ester[59,182] and the yield was virtually 100%.

The enzymic synthesis was carried out as follows. The porous glass was simply soaked in an aqueous buffer solution (1 M KH_2PO_4, pH 7) of chymotrypsin (5×10^{-4} M) and then 0.3 g of the resulting preparation was transferred to 30 ml of chloroform containing the substrates, i.e. 10^{-2} M *N*-acetyl-L-tryptophan and 1 M ethanol, and the system was stirred overnight. Analysis of the resulting mixtures showed that the entire *N*-acetyl-L-tryptophan was converted into the corresponding ethyl ester. The identity of the product with the commercial ethyl ester of *N*-acetyl-L-tryptophan was demonstrated by gas–liquid chromatography—the retention times agreed. In order to isolate the product, it was sufficient to separate the aqueous phase and to evaporate the chloroform on a rotating evaporator.

(b) The equilibrium could be shifted analogously in the synthesis of glycerophosphate from glycerol and inorganic phosphate catalysed by alkaline phosphatase[182]. In order to ensure the solubility of the ionic phosphate reactants in the two-phase "chloroform + 1 vol.% of water" system, tetrabutylammonium was used as the counterion. Whereas the yield of the ester in water[188] was neglibile (less than 0.1%), in the two-phase system it amounted to 30%.

Theoretical aspects and prospects. The observed shift of the equilibrium is common to chemical reactions. In order to demonstrate this, consider the reaction

$$A + B \overset{K}{\rightleftarrows} C + D, \qquad (1)$$

where K is the equilibrium constant. Suppose that the aim of the synthesis is, for example, the formation of product C. Its yield is evidently defined by the expression

$$[C] = K[A][B]/[D]. \qquad (2)$$

It is seen that there are two causes of the shift of the equilibrium (and of the increase of the yield of product C) on passing from water as the reaction medium to the two-phase aqueous organic system described. Firstly, if the product D of the reaction is water, a decrease of its concentration in the system leads to an increase of the yield of products in accordance with Eqn.(2). Thus in the syntheses described above a change from 100% water to an approximately 1% aqueous system resulted in an approximately 100-fold increase of the yield of the ester.

Secondly, the shift of the equilibrium in reaction (1) can occur due to a change in the effective equilibrium constant on passing from water to the two-phase system. Suppose that the equilibrium constant for reaction (1) in water is K_w. Then the effective equilibrium constant in the two-phase system K is defined (by analogy with the study of Martinek et al.[202]) by the expression

$$K = K_w \frac{(1+\alpha P_C)(1+\alpha P_D)}{(1+\alpha P_A)(1+\alpha P_B)}, \qquad (3)$$

where α is the ratio of the voumes of the non-aqueous and aqueous phases and P_A, P_B, P_C, and P_D are the partition coefficients of the reactants between the non-aqueous and aqueous phases. We shall assume that the initial reactants A and B are sparingly soluble in the organic phase, but are effectively soluble in water, i.e. have low partition coefficients—for example, $P_A \cong P_B \cong 10^{-2}$. In this case, even if only one of the products is sparingly soluble in water but effectively soluble in the organic phase, i.e. has a high partition coefficient, for example, $P_C \cong 100$, then it follows from Eqn.(3) that $K > 2500\ K_w$ for $\alpha = 100$.

Evidently the effective equilibrium constant in the two-phase system can in principle exceed that in water by many orders of magnitude. This constitutes an additional (in some cases the main one) cause of the shift of equilibrium (1).

In principle, by varying the nature of the non-aqueous phase (and hence by varying the partition coefficients of the reactants), it is possible to alter K as required and hence also the yield of the product. The partition coefficients of ionic reactants can be altered (and hence the reaction equilibrium can be displaced in the required direction) by selecting hydrophobic counterions (see the methodological aspects described above).

3. Catalysis by Water-Soluble Enzymes Incorporated in "Inverted" Surfactant Micelles in Organic Solvents

The molecules of many surfactants form in organic solvents associated species of the type of "inverted" micelles in which the polar (ionic) groups of the surfactant molecule constitute the nucleus of the associated species, while the hydrocarbon fragments make up the outer layer[203–205]. Such micelles are known to be capable of solubilising ions, polar organic substances, as well as considerable amounts of water (several tens of H_2O molecules per surfactant molecule). It has been shown recently[183] that relatively high concentrations of biopolymers (enzymes) can also be solubilised by micelle-forming surfactants in organic solvents, up to 1 mg ml^{-1}, which corresponds to $\geqslant 10^{-5}$ M active centres (for a molecular weight of the enzyme not more than 100 000) and greatly exceeds the required level of "catalytic concentrations" of the majority of enzymes[1,2]. The enzyme then retains almost completely its catalytic activity and substrate specificity.

When it is enclosed in the inverted micelle (see Scheme 2, *B*), the enzyme molecule is apparently protected against denaturation (against the uncoiling of its structure) by the fact that the "interface" between the protein globule (or its surface layer of water) and the organic solvent is stabilised by the surfactant molecules. Ultimately the biocatalyst may not in fact come into direct contact with the organic solvent unfavourable for it, being located in a kind of microreactor

containing only several hundredths of H_2O molecules per enzyme molecule (this corresponds to a total water content in the organic solvent–surfactant system less than 1 vol.%). Thus the relative catalytic activity of α-chymotrypsin solubilised in octane is retained for months at room temperature[183].

The systems investigated. All these postulates have been demonstrated[183] in relation to the proteolytic enzyme chymotrypsin (in the hydrolysis of the *p*-nitroanilide of *N*-glutaryl-L-phenylalanine) as well as peroxidase [in the oxidation of hexacyanoferrate(II) ions and pyrogallol]. The reactions of these enzymes with their specific substrates have been investigated in extremely hydrophobic (hydrocarbon) solvents, namely octane and benzene, using as the surfactant a product manufactured on a large scale—the di-(2-ethyl) ester of the sodium salt of sulphosuccinic acid (Aerosol OT), which was kindly supplied to us by Prof.Menger (USA). Data for the formation and properties of the micelles of this surfactant in organic solvents have been reviewed[206]. A typical experiment was as follows: 2 ml of 0.1 M solution of the surfactant in the hydrocarbon was treated with $\leqslant$0.01 ml of a concentrated (10^{-3} M or less) solution of the enzyme in an aqueous buffer, $\leqslant$0.01 ml of the substrate solution in water or acetonitrile was introduced, and the rate of enzymic reaction was measured spectrophotometrically in the resulting homogeneous (optically transparent) system.

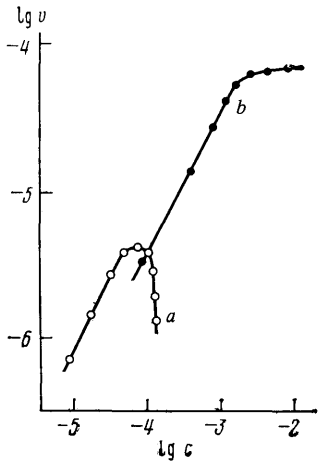


Figure 10. Dependence of the initial rate of the peroxidase oxidation of pyrogallol in water (*a*) and octane (*b*) on the molar pyrogallol concentration. Conditions: pH 7, 26 °C, 2.5×10^{-3} M H_2O_2, 3×10^{-9} M peroxidase, in octane containing 2 vol.% of water and 0.01 M Aerosol OT.[183]

As an example, Fig.10 presents data[183] for the peroxidase oxidation of pyrogallol. Evidently, when the reaction is transferred from water to a medium containing inverted micelles in octane, the kinetic mechanism of the catalysis changes. This is associated with the fact that in the latter case there is no substrate inhibition characteristic of the reaction in water.

Use in fundamental biochemical research. Enzymes solubilised by the method of Martinek et al.[183] in organic solvents (to which a surfactant forming inverted micelles has been added) will undoubtedly find applications as models of enzymes functioning *in vivo* in biological membranes and also in the study of the role of water in the structure of proteins and of the mechanisms of enzyme catalysis (particularly the catalysis of processes where water is a chemical reactant). The point is that the amount of water solubilised in the system and hence the amount surrounding the enzyme in the inverted surfactant micelle can be strictly controlled.

VI. CONCLUSION

1. Stabilisation of Enzymes under the Influence of Water-Soluble Additives

We endeavoured to describe as fully as possible the problem of the stabilisation of enzymes, but we deliberately disregarded an enzyme stabilisation phenomenon which is widespread and is frequently discussed in the literature; it takes place under the influence of effectors such as bivalent metal ions (in the first place Ca^{2+}, Mg^{2+}, Sr^{2+}, Zn^{2+}, Co^{2+}, and Mn^{2+} [207–210]) ammonium sulphate[211], various anions (in the first place phosphate and sulphate[212–215]), serum albumin[216,217], polyols (in the first place glycerol as well as ethylene glycol, sucrose, etc.)[218–220], detergents[221], and organic solvents[222,223].

In the present review we did not consider this type of stabilisation of enzymes for the following reasons. Firstly, the above effects are not general: the same effector can stabilise one enzyme and reduce the stability of another[211,224]. At the same time a given enzyme can be stabilised by one of the above effectors and labilised by others[225]. Secondly, in most cases the physicochemical mechanism of the stabilisation of enzymes by the effectors is obscure and in others is trivial—for example, sometimes when serum albumin is added as a stabilising additive. This protein is either effectively adsorbed on the interface (for example on the water/air interface) and thus prevents the surface inactivation of the enzyme itself, or it sorbs heavy metal cations and other admixtures which "poison" the enzyme. At the same time, one must emphasise the practical and theoretical importance of studies in this field, particularly those with the correct quantitative profile.

2. Two General Principles of the Stabilisation of Enzymes

In the present review we considered fairly extensively only the general physicochemical approaches, which are also of technological importance and which protect the enzyme from denaturing factors in the medium (elevated temperature, extreme pH values, and the addition of organic solvents). The entire wide variety of approaches discussed (see Sections III–V) can be divided into only two groups, corresponding to the following two general principles.

(1) An increase of the rigidity of the protein globule which prevents its uncoiling on denaturation and hence inactivation; this can be achieved both by cross-linking the protein (with formation of a water-soluble preparation) and as a result of the multipoint interaction of the protein (both covalent and physical) with a complementary carrier surface (for the preparation of an insoluble heterogeneous catalyst).

(2) The spatial separation of the enzyme and those factors in the medium which do not favour the retention of catalytic activity and specificity. The application of this principle depends on the nature of the inactivating influence. Thus, in order to prevent the pH inactivation, one can immobilise the enzyme on a carrier either having buffer properties or

ensuring a local shift of the pH in its surface layer. The influence of the organic solvent can also be avoided in two ways: either by carrying out the enzymic reaction in a two-phase system comprising water and an organic solvent immiscible with it or by enclosing the enzyme in the "inverted" micelles of a surfactant.

3. Stabilisation of Enzymes as a Problem with Optimum Solution

The methods for the stabilisation of enzymes developed at the present time (in relation to inactivation as a result of the uncoiling of protein globules) can lead in many instances to undesirable secondary effects, which hinders somewhat the practical application of biocatalysis.

Thus, firstly, when attempts are made to stabilise the enzyme, the increase in the rigidity of the protein globule should not be too extreme: otherwise a loss of catalytic activity may ensue. The point is that the functioning of the active centre presupposes as a rule the concerted action of several functional groups of the protein and therefore requires a definite mobility of the polypeptide chains[1,2]. Incidentally, the relation between the stability and catalytic activity of enzymes apparently plays an important role in the adaptation of the organism to changes in the environment (temperature, salt content in sea water)[54].

Secondly, when the enzyme is included in a carrier (particularly in a gel), there may be an increase of steric hindrance to the interaction of the enzyme with macromolecular substrates (see the references in the reviews by Berezin et al.[5,65]).

Thirdly, and finally, in unduly dense carriers, which ensure a high thermal stability of the immobilised enzyme, there may arise in their turn significant diffusion-dependent obstacles to the exchange of reactants between the catalyst and the medium (see the references in Refs.5 and 64–66).

Consequently, in many instances enzyme stabilisation involves a problem with an optimum solution, i.e. it is necessary to optimise the enzyme immobilisation process in such a way that the gain in thermal stability is achieved at the expense of only a slight loss of catalytic activity.

Naturally, approaches based on the principle of the spatial separation of the enzyme and those factors in the region which do not favour its functioning are largely or completely free from these disadvantages.

REFERENCES

1. K.J.Laidler and P.S.Bunting, "The Chemical Kinetics of Enzyme Action", Clarendon Press, Oxford, 1973.
2. I.V.Berezin and K.Martinek, "Osnovy Fizicheskoi Khimii Fermentativnogo Kataliza" (Fundamentals of the Physical Chemistry of Enzyme Catalysis), Izd.Vysshaya Shkola, Moscow, 1977.
3. L.B.Wingard, in "Advances in Biochemical Engineering" (Edited by T.K.Chose, A.Fiechter, and N.Blakebrough), Springer-Verlag, Berlin–Heidelberg–New York, 1972, Vol.2, p.1.
4. D.L.Cooney, A.L.Demain, P.Dunnill, A.E.Humphrey, M.D.Lilly, and D.I.C.Wang, "Fermentation and Enzyme Technology", Wiley, New York, 1977.
5. I.V.Berezin, V.K.Antonov, and K.Martinek (Editors), Symposium, "Immobilizovannye Fermenty" (Immobilised Enzymes), Izd.Moskov.Gos.Univ., Moscow, 1976.
6. R.Goldman, L.Goldstein, and E.Katchalski, in "Biochemical Aspects of Reactions on Solid Supports" (Edited by G.R.Stark), Acad.Press, New York, 1971, p.1.
7. O.R.Zaborsky, "Immobilized Enzymes", CRC Press, Cleveland, 1973.
8. H.H.Weetall and S.Suzuki (Editors), "Immobilized Enzyme Technology", Plenum Press, New York–London, 1975.
9. K.Mosbach (Editor), "Methods in Enzymology", Acad. Press, New York, 1976, Vol.44.
10. I.V.Berezin and A.A.Klesov, Uspekhi Khim., **45**, 180 (1976) [Russ.Chem.Rev., No.2 (1976)].
11. T.Chang (Editor), "Biomedical Applications of Immobilized Enzymes and Proteins", Plenum Press, New York, 1977.
12. I.Chibata, T.Tesa, T.Sate, and T.Mori, Methods in Enzymology, **44**, 746 (1976).
13. H.H.Weetall and G.Baum, Biotechnol.Bioeng., **12**, 399 (1970).
14. J.R.Wykes, P.Dunnill, and M.D.Lilly, Nature New Biol., **230**, 187 (1971).
15. W.Marconi, S.Gulinelli, and F.Morisi, Chimica e Industria, **56**, 417 (1974).
16. D.A.Self, G.Kay, and M.D.Lilly, Biotechnol.Bioeng., 11, 337 (1969).
17. B.K.Hamilton, J.P.Montgomery, and D.I.Wang, in "Enzyme Engineering" (Edited by E.K.Pye and L.B.Wingard), Plenum Press, New York–London, 1974, Vol.2, p.153.
18. K.Mosbach and P.-O.Larson, Biotechnol.Bioeng., **12**, 19 (1970).
19. M.J.Grove, G.W.Strandberg, and K.L.Smiley, Biotechnol.Bioeng., **13**, 709 (1971).
20. S.S.Sofer, D.M.Ziegler, and R.P.Popovich, Biochem. Biophys.Res.Comm., **57**, 183 (1974).
21. I.Parikh, D.W.McGlashan, and C.Fenselau, J.Medicin. Chem., **19**, 296 (1976).
22. D.Gurne and D.Shemin, Science, **180**, 1188 (1973).
23. W.Becker and E.Pfeil, J.Amer.Chem.Soc., **88**, 4299 (1966).
24. M.B.Cohen, L.Spolter, C.C.Chang, N.S.MacDonald, J.Takahashi, and D.D.Bobinet, J.Nuclear Med., **15**, 1192 (1974).
25. D.L.Marshall, Biotechnol.Bioeng., **15**, 447 (1973).
26. A.Traub, E.Kaufmann, and Y.Teitz, Anal.Biochem., **28**, 469 (1969).
27. H.D.Brown, A.B.Patel, and S.K.Chattopadhyay, J.Chromatog., **35**, 103 (1968).
28. C.H.Hoffman, E.Harris, S.Choadroff, S.Michelson, J.W.Rothrock, E.Peterson, and W.Reuter, Biochem. Biophys.Res.Comm., **41**, 710 (1970).
29. M.N.Tchang, M.Graffe, and M.Grunberg-Manage, Biochem.Biophys.Res.Comm., **31**, 1 (1968).
30. V.H.Edwards, in "Enzyme Engineering" (Edited by L.B.Wingard), Wiley, New York, 1972, p.343.
31. J.B.Jones, C.J.Sik, and D.Perlman (Editors), "Applications of Biochemical Systems in Organic Chemistry", Wiley, New York, 1976.
32. H.H.Weetall, W.P.Vann, W.H.Pitcher, D.D.Lee, Y.Y.Lee, and G.T.Tsao, Methods in Enzymology, **44**, 776 (1976).
33. W.R.Vieth and K.Venkatasubramanian, Methods in Enzymology, **44**, 768 (1976).
34. I.Chibata, T.Tosa, T.Sato, T.Mori, and Y.Matsuo, in "Fermentation Technology Today" (Edited by G.Terul), Society of Fermentation, Technology, Japan, 1972, p.383.

35. M.Pastore, F.Morisi, and D.Zaccardelli, Methods in Enzymology, **44**, 822 (1976).
36. W.H.Pitcher, J.R.Ford, and H.H.Weetall, Methods in Enzymology, **44**, 792 (1976).
37. R.K.Andren, M.Mandels, and J.E.Modeiros, Process. Biochem., **11**, 2 (1976).
38. I.V.Berezin and K.Martinek, Uspekhi Khim., **48**, 1921 (1979) [Russ.Chem.Rev., No.11 (1979)].
39. I.V.Berezin, A.M.Klibanov, G.P.Samokhin, V.S.Goldmacher, and K.Martinek, in "Biomedical Applications of Immobilized Enzymes and Proteins" (Edited by T.Chang), Plenum Press, New York, 1977, p.237.
40. J.R.Benemann, J.A.Berenson, N.O.Kaplan, and M.D.Kamen, Proc.Nat.Acad.Sci.USA, **70**, 2317 (1973).
41. K.Mosbach, FEBS Letters, **62**, E80 (1976).
42. W.R.Vieth and K.Venkatasubramanian, Chem. Technol., **4**, 309 (1974).
43. M.D.Lilly and P.Dunnill, Methods in Enzymology, **44**, 717 (1976).
44. A.K.Sharp, G.Kay, and M.D.Lilly, Biotechnol. Bioeng., **11**, 363 (1969).
45. C.F.Meares, D.A.Goddwin, C.S.-H.Leung, A.Y.Girgis, D.J.Silvester, A.D.Nunn, and P.J.Levander, Proc. Nat.Acad.Sci.USA, **73**, 3803 (1976).
46. N.M.Emanuel', "Kinetika Eksperimental'nykh Opukholevykh Protsessov" (Kinetics of Experimental Tumour Processes), Izd.Nauka, Moscow, 1977.
47. Yu.M.Torchinskii, "Sera v Belkakh" (Sulphur in Proteins), Izd.Nauka, Moscow, 1977.
48. K.Tanizawa and M.L.Bender, J.Biol.Chem., **249**, 2130 (1974).
49. K.Mosbach, P.-O.Larsson, and Ch.Lowe, Methods in Enzymology, **44**, 859 (1976).
50. G.M.Whitesides, A.Lamotte, O.Adalsteinsson, and C.K.Colton, Methods in Enzymology, **44**, 887 (1976).
51. I.V.Berezin, B.M.Kershengol'ts, and N.N.Ugarova, Dokl.Akad.Nauk SSSR, **223**, 1256 (1975).
52. V.P.Kushner, "Konformatsionnaya Ustoichivost' i Denaturatsiya Biopolimerov" (Conformational Stability and Denaturation of Biopolymers), Izd.Nauka, Leningrad, 1977.
53. C.Tanford, Adv.Protein Chem., **23**, 121 (1968).
54. V.Ya.Aleksandrov, "Kletki, Makromolekuly i Temperatura" (Cells, Macromolecules, and Temperature), Izd.Nauka, Leningrad, 1975.
55. I.Chibata, T.Tosa, and T.Sato, Methods in Enzymology, **44**, 739 (1976).
56. H.H.Weetall, "Sovetsko-Amerikanskii Seminar po Immobilizovannym Fermentam" (Soviet-American Seminar on Immobilised Enzymes), Izd.Moskov.Gos. Univ., Moscow, 1975.
57. J.Woodward and A.Wiseman, J.Appl.Chem.Biotechnol., **26**, 580 (1976).
58. S.J.Singer, Adv.Protein Chem., **17**, 1 (1962).
59. A.M.Klibanov, G.P.Samokhin, K.Martinek, and I.V.Berezin, Biotechnol.Bioeng., **19**, 1351 (1977).
60. I.V.Berezin, A.A.Klesov, A.L.Margolin, P.S.Nys, E.M.Savitskaya, and V. Svedas, Antibiotiki, **21**, 519 (1976).
61. H.H.Weetall, Biochim.Biophys.Acta, **212**, 1 (1970).
62. G.Bell, J.A.Blain, J.D.E.Patterson, and R.Todd, J.Appl.Chem.Biotechnol., **26**, 582 (1976).
63. T.I.Vilai, "Termostabil'nye Fermenty Gribov" (Thermostable Fungal Enzymes), Izd.Naukova, Dumka, Kiev, 1979.
64. D.F.Ollis, Biotechnol.Bioeng., **14**, 871 (1972).
65. I.V.Berezin, A.M.Klibanov, and K.Martinek, Uspekhi Khim., **44**, 17 (1975) [Russ.Chem.Rev., No.1 (1975)].
66. L.Goldstein, Methods in Enzymology, **44**, 397 (1976).
67. O.R.Zaborsky, in "Enzyme Engineering" (Edited by L.B.Wingard), Wiley, New York, 1972, Vol.1, p.21.
68. V.P.Torchilin, E.G.Tischenko, V.N.Smirnov, and E.I.Chazov, J.Biomed.Mater.Res., **11**, 223 (1977).
69. A.D.McLaren and L.Packer, Adv.Enzymol., **33**, 245 (1970).
70. G.J.H.Melrose, Rev.Pure Appl.Chem., **21**, 83 (1971).
71. D.Gabel, I.Z.Steinberg, and E.Katchalski, Biochemistry, **10**, 4661 (1971).
72. G.M.Giacometti, A.Colosimo, S.Stefanini, M.Brunori, and E.Antonini, Biochim,Biophys.Acta, **285**, 320 (1972).
73. L.J.Berliner, S.T.Miller, R.Uy, and G.P.Royer, Biochim.Biophys.Acta, **315**, 195 (1973).
74. T.A.Moore and C.Greenwood, Biochem.J., **149**, 169 (1975).
75. J.Lasch, Acta Biol.Med.Germ, **34**, 549 (1975).
76. A.O.Barel and J.-P.Prieels, Europ.J.Biochem., **50**, 463 (1975).
77. L.A.Blyumenfel'd, "Problemy Biofiziki" (Problems of Biophysics), Izd.Nauka, Moscow, 1974, Chapter 5.
78. O.R.Zaborsky, in "Enzyme Engineering" (Edited by E.K.Pye and L.B.Wingard), Plenum Press, New York–London, 1974, Vol.2, p.115.
79. W.Kauzmann, Adv.Protein Chem., **14**, 1 (1959).
80. W.F.Harrington and M.Sela, Biochim.Biophys.Acta, **31**, 427 (1959).
81. C.Tanford, K.Kawahara, and S.Lapenje, J.Amer.Chem. Soc., 89, 729 (1967).
82. G.P.Hess, in "The Enzymes" (Edited by P.O.Boyer), Acad.Press, New York, 1971, Vol.3, p.213.
83. A.Hasegawa and K.Imahori, J.Biochem., **79**, 469 (1976).
84. F.Wold, Methods in Enzymology, **25**, 623 (1972).
85. J.H.Kennedy, L.J.Kricka, and P.Wilding, Clinica Chim. Acta, **70**, 1 (1976).
86. L.J.Saidel, S.Leitzes, and W.H.Elfring, Biochem. Biophys.Res.Comm., **15**, 409 (1964).
87. D.J.Herzig, A.W.Rees, and R.A.Day, Biopolymers, **2**, 349 (1964).
88. J.H.Wang and J.Tu, Biochemistry, **8**, 4403 (1964).
89. R.Josephs, H.Eizenberg, and E.Reisler, Biochemistry, **12**, 4060 (1973).
90. G.H.Beaven and W.B.Gratzer, Int.J.Peptide Protein Res., **5**, 215 (1973).
91. P.D.Snyder, J.F.Wold, R.W.Bernlehr, C.Dullum, R.J.Desnich, W.Krivit, and R.M.Condie, Biochem. Biophys.Acta, **350**, 432 (1974).
92. A.V.Maksimenko, V.P.Torchilin, A.M.Klibanov, and K.Martinek, Vestnik Moskov.Gos.Univ., Khim., **19**, 590 (1978).
93. R.Reiner, H.-U.Siebeneick, I.Christensen, and H.Döring, J.Mol.Catal., **2**, 119 (1977).
94. J.Woodward and A.Wiseman, J.Appl.Chem.Biotechnol., **26**, 580 (1976).
95. V.P.Torchilin, A.V.Maksimenko, V.N.Smirnov, I.V.Berezin, A.M.Klibanov, and K.Martinek, Biochim. Biophys.Acta, **522**, 277 (1978).
96. H.G.Khorana, Chem.Rev., **53**, 145 (1953).
97. R.Reiner, H.-V.Siebeneick, I.Christensen, and H.Lukas, J.Mol.Catal., 1, 3 (1975).
98. N.R.Perham and J.O.Thomas, J.Mol.Biol., **62**, 415 (1971).
99. J.Carlsson, R.Axen, and T.Unge, Europ.J.Biochem., **59**, 567 (1975).
100. F.H.White and A.Sandoval, Biochemistry, **1**, 938 (1962).
101. L.Goldstein, Biochemistry, **11**, 40 (1972).
102. H.Fasold, J.Klappenberger, C.Mayer, and H.Remold, Angew.Chem., **83**, 875 (1971).

103. B.A.Baird and G.G.Hammes, J.Biol.Chem., **252**, 4743 (1977).
104. M.Kapoor and M.D.O'Brien, Canad.J.Biochem., **55**, 43 (1977).
105. V.P.Torchilin, A.V.Maksimenko, V.N.Smirnov, I.V.Berezin, A.M.Klibanov, and K.Martinek, Biochim. Biophys.Acta, **56**, 71 (1979).
106. R.E.Feeney, G.Blankenborn, and H.B.F.Dixon, Adv. Protein Chem., **29**, 135 (1975).
107. C.K.Glassmeyer and J.Ogle, Biochemistry, **10**, 786 (1971).
108. G.P.Royer and R.Uy, J.Biol.Chem., **248**, 2627 (1973).
109. A.M.Klibanov, G.P.Samokhin, K.Martinek, and I.V.Berezin, Biochim.Biophys.Acta, **438**, 1 (1976).
110. D.Gabel, Europ.J.Biochem., **33**, 348 (1973).
111. M.Delaage and M.Lazdunski, Europ.J.Biochem., **4**, 378 (1968).
112. D.Gabel and V.Kasche, Biochem.Biophys.Res.Comm., **48**, 1011 (1972).
113. K.Mosbach and S.Gestrelius, FEBS Letters, **42**, 200 (1974).
114. K.Martinek, A.M.Klibanov, V.S.Goldmacher, and I.V.Berezin, Biochim.Biophys.Acta, **485**, 1 (1977).
115. K.Martinek, A.M.Klibanov, and I.V.Berezin, "Sovetsko-Amerikanskii Seminar po Immobilizovannym Fermentam" (Soviet-American Seminar on Immobilised Enzymes), Moscow, 1975, p.100.
116. K.Martinek, V.S.Gol'dmakher, A.M.Klibanov, V.P.Torchilin, V.N.Smirnov, and I.V.Berezin, Dokl. Akad.Nauk SSSR, **228**, 1468 (1976).
117. D.Jaworek, H.Botsch, and J.Maier, Methods in Enzymology, **44**, 195 (1976).
118. V.S.Gol'dmakher, A.M.Klibanov, and K.Martinek, Vestnik Moskov.Gos.Univ., Khim., **19**, 429 (1978).
119. K.Martinek, A.M.Klibanov, A.V.Tchernysheva, V.Mozhaev, I.V.Berezin, and B.O.Glotov, Biochim. Biophys.Acta, **485**, 13 (1977).
120. K.Martinek, A.V.Chernysheva, A.M.Klibanov, and I.V.Berezin, Dokl.Akad.Nauk SSSR, **223**, 233 (1975).
121. A.A.Klesov and V.Yu.-K.Shvyadas, in "Immobilizovannye Fermenty i Bioorganicheskikh Kataliz (Seriya Itogi Nauki i Tekhniki)" [Immobilised Enzymes and Bioorganic Catalysis (Advances in Science and Engineering Series)] (Edited by V.L.Kretovich and I.V.Berezin), Izd.VINITI, Moscow, 1978, Vol.12.
122. H.Morawetz, "Macromolecules in Solution", Interscience, New York, 1965.
123. K.F.O'Driscoll, Adv.Biochem.Eng., **4**, 155 (1976).
124. R.A.Messing, Process Biochem., **9**, 26 (1974).
125. A.M.Filbert and W.P.Pitcher, Process Biochem., 11, 3 (1976).
126. I.V.Berezin, A.M.Klibanov, G.P.Samokhin, V.S.Goldmacher, and K.Martinek, Methods in Enzymology, **44**, 558 (1976).
127. V.P.Torchilin, V.S.Gol'dmakher, A.M.Klibanov, K.Martinek, and I.V.Berezin, "Sovetsko-Amerikanskii Simpozium po Khimii i Fizike Belkov, Sbornik Dokladov" (The Soviet-American Symposium on the Chemistry and Physics of Proteins. Collected Reports), Riga, 1976, p.116.
128. T.M.S.Chang, "Artificial Cells", Thomas Publ., Springfield, Illinois, 1972.
129. R.A.Messing, Methods in Enzymology, **44**, 148 (1976).
130. O.M.Poltorak and E.S.Chukhrai, "Fiziko-Khimicheskie Osnovy Fermentativnogo Kataliza" (Physicochemical Principles of Enzyme Catalysis), Izd.Vysshaya Shkola, Moscow, 1974, Chapter 14.
131. S.N.Pennington, H.D.Brown, A.B.Patel, and C.O.Knowles, Biochim.Biophys.Acta, **167**, 479 (1968).
132. S.N.Pennington, H.D.Brown, A.B.Patel, and S.K.Chattopadhyay, J.Biomed.Mater.Res., **2**, 443 (1968).
133. K.F.O'Driscoll, Methods in Enzymology, **44**, 169 (1976).
134. V.S.Gol'dmakher, Candidate's Thesis, Moscow State University, 1977.
135. T.W.Goodwin and O.Cinberg (Editors), "Biological Structure and Function", Acad.Press, London–New York, 1961, Vol.2.
136. A.L.Lehninger, "Biochemistry", Worth Publishers, New York, 1972, Chapter 18.
137. M.Edidin, Ann.Rev.Biophys.Bioeng., **3**, 179 (1974).
138. D.Wallach, J.Gen.Physiol., **54**, 3 (1969).
139. E.W.Chapelle, E.Rich, and N.H.MacLeod, Science, **155**, 1287 (1967).
140. T.Morigome, H.Kasai, and T.Okuyama, J.Biochem., **75**, 299 (1974).
141. Z.Schneider, A.Stroinski, and J.Pawelkiewicz, Bull. Acad.Polon.Sci., Ser.Sci.Biol., **16**, 203 (1968).
142. D.R.Norris and I.Pawelkiewicz, Phytochemistry, **14**, 1701 (1975).
143. V.S.Gol'dmakher, A.M.Klibanov, A.A.Mishin, V.V.Mozhaev, and K.Martinek, Vestnik Moskov.Gos. Univ., Khim., **19**, 358 (1978).
144. K.Martinek, V.S.Gol'dmakher, A.A.Mishin, V.P.Torchilin, V.N.Smirnov, and I.V.Berezin, Dokl.Akad. Nauk SSSR, **239**, 277 (1978).
145. R.C.Allen and H.R.Maurer (Editors), "Electrophoresis and Isoelectric Focussing in Polyacrylamide Gel", DeGruyter, Berlin–New York, 1974.
146. M.L.White, J.Phys.Chem., **64**, 1563 (1960).
147. J.Gressel and A.W.Robards, J.Chromatog., **144**, 455 (1975).
148. I.V.Berezin, A.M.Klibanov, V.S.Goldmacher, and K.Martinek, Methods in Enzymology, **44**, 571 (1976).
149. K.Martinek, V.S.Goldmacher, A.M.Klibanov, and I.V.Berezin, FEBS Letters, **51**, 152 (1975).
150. B.Obrink and T.C.Laurent, J.Biochem., **41**, 83 (1974).
151. J.Gryszkiewicz, Folia Biol., **19**, 119 (1971).
152. J.E.Dixon, F.E.Stolzenbach, J.A.Berenson, and N.O.Kaplan, Biochem.Biophys.Res.Comm., **52**, 905 (1973).
153. Y.Levin, M.Pecht, L.Goldstein, and E.Katchalski, Biochemistry, **3**, 1905 (1964).
154. L.Goldstein, Y.Levin, and E.Katchalski, Biochemistry, **3**, 1913 (1964).
155. A.Strel'tsova, V.Yu.-K.Shvyadas, A.V.Maksimenko, A.A.Klesov, E.E.Braudo, V.B.Tolstoguzov, and I.V.Berezin, Bioorg.Khim., 1, 1464 (1975).
156. M.L.Barnard and K.J.Laidler, Arch.Biochem.Biophys., **44**, 338 (1953).
157. Yu.I.Khurgin, V.Ya.Roslyakov, Yu.M.Azizov, and E.D.Kaverzneva, Izv.Akad.Nauk SSSR, Ser.Khim., 2840 (1968).
158. F.A.Bettelheim and A.Lukton, Nature, **198**, 357 (1963).
159. F.A.Bettelheim and P.Senatore, J.chim.phys.et phys.-chim.biol., **61**, 105 (1964).
160. D.H.Rammler, in "Dimethyl Sulfoxide" (Edited by S.W.Jacob, E.E.Rosenbaum, and D.C.Wood), Marcel Dekker, New York, 1971, Vol.1, p.189.
161. Yu.M.Azizov, I.V.Zverinskaya, A.N.Nikitina, V.Ya.Roslyakov, and Yu.I.Khurgin, Izv.Akad.Nauk SSSR, Ser.Khim., 2843 (1968).
162. A.A.Klyosov, N.V.Viet, and I.V.Berezin, Europ.J. Biochem., **59**, 3 (1960).
163. J.P.Hutton and J.G.Wetmur, Biochem.Biophys.Res. Comm., **66**, 942 (1975).

164. L.B.Lachman and R.E.Handschumacher, Biochem. Biophys.Res.Comm., **73**, 1094 (1974).
165. H.H.Weetall and W.P.Vann, Biotechnol.Bioeng., **18**, 105 (1976).
166. S.I.Case and R.F.Baker, Anal.Biochem., **64**, 477 (1975).
167. P.Elödi, Acta Physiol.Acad.Sci.Hung., **20**, 311 (1961).
168. T.Barth, K.Jošt, and I.Rychlik, Coll.Czech.Chem. Comm., **38**, 2011 (1973).
169. C.Horvath, Biochim.Biophys.Acta, **358**, 164 (1974).
170. T.Inagami and J.M.Strutevant, Biochim.Biophys.Acta, **38**, 64 (1960).
171. V.V.Mosolov, P.V.Afanas'ev, M.S.Dolgikh, and E.V.Lushnikova, Biokhimiya, **33**, 1030 (1968).
172. K.H.Tan and R.Lovrien, J.Biol.Chem., **247**, 3278 (1972).
173. K.Tanizawa and M.L.Bender, J.Biol.Chem., **249**, 2130 (1974).
174. H.Wan and C.Horvath, Biochim.Biophys.Acta, **410**, 135 (1975).
175. J.S.Myers and W.B.Jakoby, Biochem.Biophys.Res. Comm., **51**, 631 (1973).
176. G.Z.Hussain and T.F.Newcomb, Proc.Soc.Exp.Biol. Med., **115**, 301 (1963).
177. M.Castaneda-Agullo and L.M.DelCastillo, J.Gen. Physiol., **42**, 617 (1959).
178. B.H.J.Bielski and S.Freed, Biochim.Biophys.Acta, **89**, 314 (1964).
179. T.Tosa, T.Mori, and I.Chibata, Enzymologia, **40**, 49 (1971).
180. R.G.Ingalis, R.G.Squires, and L.G.Butler, Biotechnol. Bioeng., **17**, 1627 (1975).
181. A.M.Klibanov, A.N.Semenov, G.P.Samokhin, and K.Martinek, Bioorg.Khim., **4**, 82 (1978).
182. K.Martinek, A.M.Klibanov, G.P.Samokhin, A.N.Semenov, and I.V.Berezin, Bioorg.Khim., **3**, 696 (1977).
183. K.Martinek, A.V.Levashov, N.L.Klyachko, and I.V.Berezin, Dokl.Akad.Nauk SSSR, **236**, 920 (1977).
184. A.Ray, Nature, **231**, 313 (1971).
185. C.Tanford, "The Hydrophobic Effect", Wiley, New York, 1973.
186. C.Tanford, C.E.Buckley, P.K.De, and E.P.Lively, J.Biol.Chem., **237**, 1168 (1962).
187. T.T.Herskovits, B.Gadegbeku, and H.Jaillet, J.Biol. Chem., **245**, 2588 (1970).
188. L.M.Ginodman, Biokhimiya, **19**, 666 (1954).
189. L.Butler and R.Squires, Enzyme Technol.Digest, 4, 108 (1975).
190. C.Schwabe, Biochemistry, **8**, 795 (1969).
191. S.J.Kelly, L.G.Butler, and R.G.Squires, Enzyme Technol.Digest, **5**, 107 (1976).
192. J.F.Brandts, in "Structure and Stability of Biological Macromolecules" (Edited by S.H.Timasheff and G.D.Fasman), M.Dekker, New York, 1969, p.213.
193. J.T.Davies and E.K.Rideal, "Interfacial Phenomena", Acad.Press, New York, 1961.
194. J.R.Scholtens and B.H.Bijsterbosch, FEBS Letters, **62**, 233 (1976).
195. F.Cremonesi, G.Carrea, L.Ferrara, and E.Antonini, Biotechnol.Bioeng., **17**, 1101 (1975).
196. B.C.Buckland, P.Dunnill, and M.D.Lilly, Biotechnol. Bioeng., **17**, 815 (1975).
197. A.M.Klibanov, G.P.Samokhin, K.Martinek, and I.V.Berezin, Biotechnol.Bioeng., **19**, 211 (1977).
198. V.Z.Raj Bhandary, R.J.Young, and H.G.Khorana, J.Biol.Chem., **239**, 3875 (1964).
199. E.V.Dehmlow, Angew.Chem., Int.Ed., **13**, 170 (1974).
200. K.Martinek, A.A.Klyosov, and I.V.Berezin, Int.J. Chem.Kin., **6**, 801 (1974).
201. F.H.Carpenter, J.Amer.Chem.Soc., **82**, 1111 (1960).
202. K.Martinek, A.K.Yatsimirski, A.P.Osipov, and I.V.Berezin, Tetrahedron, **29**, 963 (1973); **31**, 709 (1975).
203. K.Shinoda, T.Nakagawa, B.I.Tamamushi, and T.Isemura, "Colloidal Surfactants", Acad.Press, New York–London, 1963.
204. J.H.Fendler and E.J.Fendler, "Catalysis in Micellar and Macromolecular Systems", Acad.Press, New York, 1975.
205. K.Mittal (Editor), "Micellization, Solubilization, and Microemulsions", Plenum Press, New York, 1977.
206. A.V.Levashov, V.Pantin, and K.Martinek, Kolloid. Zhur., **41**, 453 (1979).
207. M.R.Pollock, The Bacteria, **4**, 158 (1962).
208. S.M.Snaith, G.A.Levy, and A.J.Hay, Biochem.J., **117**, 129 (1970).
209. K.Shimada and Y.Sugino, Biochim.Biophys.Acta, **185**, 367 (1969).
210. J.C.Luday and J.N.Aronson, Biochim.Biophys.Acta, **191**, 397 (1969).
211. H.Neurath, J.P.Greenstein, F.W.Putnam, and J.O.Frickson, Chem.Rev., **34**, 157 (1944).
212. M.Yeshine, J.Biochem., **68**, 321 (1970).
213. M.Shimizu, T.Suzuki, K.Kamed, and Y.Abiko, Biochim. Biophys.Acta, **191**, 550 (1969).
214. J.H.Fox and W.N.Kelley, J.Biol.Chem., **246**, 5739 (1971).
215. M.R.Deutscher, J.Biol.Chem., **247**, 450 (1972).
216. M.B.Lee, C.D.Bolger, and C.M.Bridges, Biochem. Biophys.Acta, **242**, 226 (1971).
217. K.Ogasahara, A.Imanishi, and T.Isemura, J.Biochem., **67**, 83 (1970).
218. S.Y.Gerlsma, J.Biochem., **14**, 150 (1970).
219. J.Kyte, J.Biol.Chem., **246**, 4157 (1971).
220. A.Fernandez-Sorensen and D.M.Carlson, J.Biol.Chem., **246**, 3485 (1971).
221. Y.Takeda and S.Hizukuri, Biochim.Biophys.Acta, **268**, 175 (1972).
222. H.George, J.McMahan, J.Bowler, and M.Elliott, Biochim.Biophys.Acta, **191**, 719 (1969).
223. K.Ono, M.Nozaki, and O.Hayashi, Biochim.Biophys. Acta, **220**, 224 (1970).
224. H.Dutler, M.J.Coon, A.Kull, H.Vogel, G.Waldvogel, and V.Prelog, Europ.J.Biochem., **22**, 203 (1971).
225. P.H.Von Hippel and K.-Y.Wong, Science, **145**, 577 (1964).

Faculty of Chemistry,
Lomonosov Moscow State University

Translated from *Uspekhi Khimii*, 49, 771-788 (1980) U.D.C. 541.128

Problems in the Study of Supported Metal Catalysts

A.A.Slinkin

Our current understanding of catalysis on supported metals is reviewed, and the three most important problems still outstanding in this area of catalysts are discussed: 1) the sintering mechanism of the supported metals, 2) the structure and catalytic properties of small metallic crystals, and 3) catalysis by metal clusters. 96 references.

CONTENTS

I. Introduction 404
II. Sintering mechanism of supported metal catalysts 404
III. Structure and catalytic properties of small metallic crystals 406
IV. Catalysis by metal clusters 409

I. INTRODUCTION

Among the various problems encountered in the study of the structure and catalytic properties of supported metals the following appear to be the most important:

1) the sintering mechanism of supported metal catalysts

2) the structure of small metal crystals, and their catalytic properties

3) catalysis by metal clusters.

Without attempting a comprehensive treatment of these complex problems, we shall formulate the basic concepts and approaches which have been developed for their solution.

II. SINTERING MECHANISM OF SUPPORTED METAL CATALYSTS

The scope of theoretical and experimental studies of the sintering of supported metal catalysts has increased in recent years because of the great practical importance of this problem in the development of stable catalysts, and also because many of the theoretical problems to be solved are relevant to catalysis as a whole, i.e.: 1) the interaction and diffusion of metal atoms on the metal surface, 2) the interaction of metal microcrystals and atoms with the carrier, 3) the effect of various gases on the sintering process, 4) the effect of impurities in the metal and in the carrier on the sintering mechanism.

We shall briefly review the basic theoretical considerations and some of the most important experimental results in this field of research.

1. Model of Particle Growth Through the Migration, Collision, and Coalescence of Crystals

A phenomenological description of these processes was recently developed by Ruckenstein and Pulvermacher[1,2] (the RP model) and analysed by Wynblatt and Ahn[3]. Sintering is described in terms of binary collisions on a plane surface, and rate limitation is associated either with the migration or with the coalescence of the particles. In either case we can write

$$\left[\frac{S_0}{S}\right]^n = 1 + (\text{const})\,t \qquad (1)$$

or

$$\frac{dS}{dt} = -kS^n, \quad n = 3+m,$$

where n and m are integers, and m is related to the diffusion coefficient (D) and to the radius of the particle (R) by the expression

$$D = c(1/R)^m;$$

S_0 is the initial value of S (the aggregate surface area of particles per unit area of carrier surface).

This model can be used to calculate the distribution of particles for either migration or coalescence as the rate-limiting step of the growth process. However for $n = 3$ the model predicts a diffusion coefficient independent of particle size, which is difficult to accept. The formalism of the RP model was extended by Wynblatt and Jostein[3], who calculated the coalescence times (τ_C) and the migration times (τ_p) of the particles on the surface (see Table).

Calculated coalescence and migration times of particles on the surface*.

$2R$, Å	τ_c, s	D_p, $cm^2 s^{-1}$	τ_p, s
25	$3.5 \cdot 10^{-4}$	$1.3 \cdot 10^{-13}$	12
100	$8.9 \cdot 10^{-2}$	$5.0 \cdot 10^{-16}$	$3 \cdot 10^4$
250	3,5	$1.3 \cdot 10^{-17}$	$1.2 \cdot 10^7$
2500	$3.5 \cdot 10^4$	$1.3 \cdot 10^{-21}$	$1.2 \cdot 10^{13}$

* $T = 700$ °C; the migration path is $10 \times 2R$.

The coalescence time is seen to be much shorter than the time for migration of the particle over a significant distance, and therefore the rate-limiting step of the sintering process is migration rather than coalescence. From the tabulated results and their associated calculations we conclude that the growth of particles can be limited by migration only for particle sizes below 50 Å. The RP model has been criticised[4,5] on the following grounds:

1) it ignores the energetic and morphological non-uniformity of the surface;

2) it fails to explain the observed increase in the dispersion of the metal at high temperatures in an O_2 atmosphere;

3) there is no independent demonstration that the motion of the particles is sufficient to account for sintering.

2. Model of Particle Growth Through the Migration of Atoms or of Sub-atomic Molecular Units

This model, which was developed by various workers[6-8], is illustrated in Fig. 1. Particles grow as a result of matter transport by two mechanisms: diffusion through the gas phase and diffusion on the carrier surface.

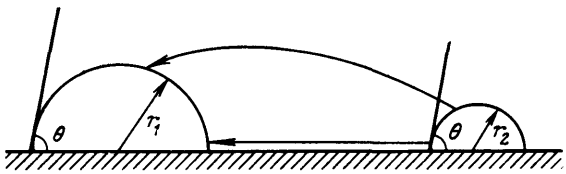


Figure 1. Transfer of matter between two particles on a plane surface[6].

The angle θ is given by the formula

$$\gamma_s = \gamma_{ms} + \gamma_m \cos\theta,$$

where γ_S and γ_m are the surface tensions of the carrier and of the particle respectively, and γ_{mS} is the interfacial tension. The chemical potential μ of the particle depends on the particle radius r according to the Gibbs–Thomson equation

$$\mu = \mu_0 + 2\gamma_m \Omega / r,$$

where Ω is the atomic volume.

Thus large particles will grow at the expense of the smaller particles, whose chemical potential is greater, leading to an overall decrease in the surface energy of the system. According to this model the atomic mechanism of the sintering process may involve three steps[7]: 1) removal of a metal atom (or molecular unit) from the crystal, and transfer to the carrier; 2) migration of the atomic (or molecular) particle on the carrier surface; 3) capture of the migrating atoms (or molecules) by the crystals during collisions.

In this model the sintering process can be described with allowance for specific physicochemical features of the system. For example, in a supported Pt system the diffusing species are Pt atoms in a reducing medium and PtO_2 or PtO particles in an oxidising medium. The rate of growth of the particles is small in a reducing atmosphere because the sublimation energy (which appears in the exponential term of the rate constant) is 135 kcal mole^{-1} for Pt. On the other hand since the activation energy for the removal of a Pt atom as PtO_2 is only ~ 42 kcal mole^{-1} we expect the rate of growth to be substantially higher in an oxidising atmosphere.

This sintering mechanism predicts the following phenomena[3]:

1) the sintering rate should increase with the partial pressure of O_2;

2) stronger wetting of the carrier surface by the particles (or an increased interaction between the diffusing atom and the defects in the carrier) should lower the sintering rate, and in this way it should be possible to control the sintering process by adding impurities to the carrier or metal crystal surface;

3) the growth of particles in an O_2 atmosphere should be strongly dependent on the enthalpy of the reaction

$$M(s) + xO_2(g) = MO_{2x}(g).$$

On this basis we can define the following stability series for supported metals in an oxidising atmosphere: Os < Ru < Ir < Pt < Pd, Rh;

4) the stability under reducing conditions is determined by the heat of sublimation, leading to the following stability sequence: Pd < Rh, Pt < Ru < Ir < Os.

Neither of these theories can at present be accepted with full confidence, though a recent experimental paper[9] has confirmed the stability sequences predicted for Rh, Pt, and Ir supported on Al_2O_3. The problem is still being actively discussed[10,11], and a model of the sintering process allowing for the transfer of atoms has recently been proposed by Ruckenstein[8].

We shall now examine some examples of sintering phenomena which fall outside the scope of existing theories and need new conceptual approaches.

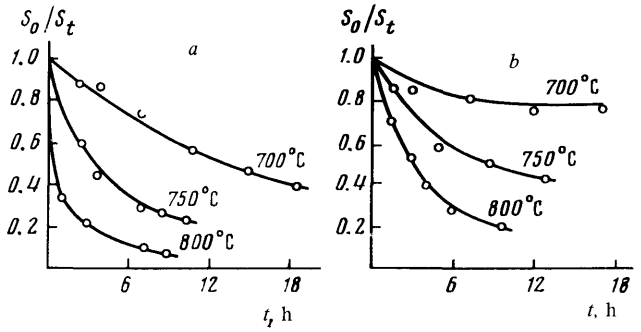


Figure 2. Sintering kinetics of Pt–Al_2O_3 catalysts: (*a*) in air and (*b*) in argon[12].

The sintering kinetics of a Pt–α-Al_2O_3 (0.036 wt.% Pt) catalyst[12] in air and in argon are shown in Figs. 2*a* and 2*b*. The sintering rate is much greater in air than in argon: the exponent n in Eqn. (1) takes the value 2 and 3 respectively, in keeping with the RP theory. However the sintering rate in N_2 quite unexpectedly goes through a maximum. This is ascribed[12] to chemical interaction between N_2 and Al_2O_3 at high temperatures (800 °C), leading to changes in the morphology of the carrier and in the sintering mechanism.

Electron microscopic studies[13] have confirmed that sintering is much faster in an oxygen atmosphere than in a vacuum. However the most fundamental result of this work was the first experimental observation of the motion of Pt crystals on the surface of graphite. The authors were able to monitor the tracks of particles moving on the graphite surface during combustion of the graphite in oxygen. Very surprisingly, particles of diameter ~ 1000 Å were found to move: this is theoretically impossible, but it can happen in this case because of the large decrease in interfacial energy resulting from the presence of O_2.

O_2 interactions on supported Pt crystals can lead to another effect not predicted by theory: dispersion of the crystals[14,15]. Pt crystals supported on Al_2O_3 whose diameter in air was initially 31 Å were found[14] to increase in size to 107 Å after a sintering treatment in air followed by slow cooling. However when the sample was re-heated in air to 500 °C and slowly cooled to 20 °C dispersion of the crystals was observed (to a diameter of 41 Å). This effect can be explained through the

formation of Pt(IV)–Al_2O_3 complexes, with a critical formation temperature of ~500 °C. This reaction at the interface between the metal and the carrier is accompanied by a large increase in the stresses applied to the metal, and these stresses are relieved by the cleaving of the crystals.

A different explanation of the same effect is given in Ref.15. It is pointed out that the PtO_2 molecules breaking away from the microcrystals can be stabilised on non-uniformities of the carrier surface and act as nuclei for new crystallites. Allowance for the inhomogeneity of the carrier surface is a significant refinement of the theoretical model, which is usually confined to a homogeneous surface. For example, the concept[16] of "trapping centres" from which microcrystallites can be released only by the expenditure of activation energy has been confirmed[17] by a demonstration that the disperseness of Pt on graphitised carbon increases (from a particle diameter of 68 Å to 19 Å) as the extent of burn-off is increased from 0 to 50%. In this case the dispersion effect arises from an increase in the energy non-uniformity of the carrier rather than from an increase in its surface area.

It is important to note that the re-dispersion of large metal crystals has been observed not only in supported platinum catalysts but also in metal–zeolite systems, in which cations are formed in an oxidising atmosphere and diffuse into the bulk of the zeolite[18,19].

Some of the most interesting publications discuss the chemical nature and the mechanism of action of the "trapping centres" which inhibit the sintering process. Thus it has been shown[20] that Pt microcrystals deposited on γ-Al_2O_3 by evaporation and decomposition of tetra-ammine complexes can be sintered in a N_2 or O_2 atmosphere, whereas crystals prepared from H_2PtCl_6 are stable up to 800 °C. It is suggested that sintering is inhibited by Cl^- ions. A similar inhibition effect by Mo^{2+} ions (added to the carrier) on the sintering of Pt and Pd was reported by Ermakov and coworkers[21].

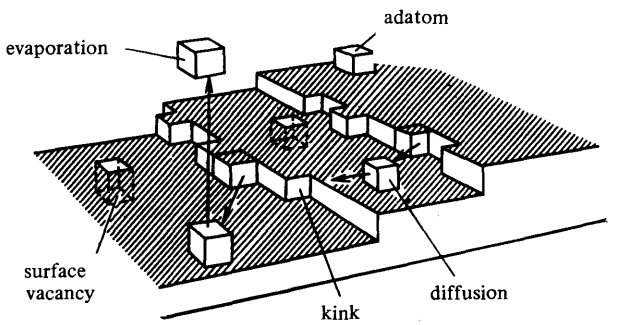


Figure 3. Elementary acts in diffusion on a crystal surface[24].

Takami and coworkers[22] made the important discovery that Rh–$MgWO_4$ catalysts have a high activity towards the reforming reaction of hydrocarbons with water vapour. Surprisingly, the surface area of the $MgWO_4$ sample was only 3–5 $m^2\ g^{-1}$, and most of the Rh was stabilised as large crystals. The high activity of these catalysts was explained by the formation of Rh^{3+} cations, which can replace Mg^{2+} in the tungstate lattice (isomorphous substitution). If tungstates of other metals (Be, Zn, Ca, Ba) are used as carriers the activity drops by a factor of 5–15. The possibility of dissolving atoms (or cations) of the metal in the lattice of the carrier was recently demonstrated (for Au atoms in MgO or Al_2O_3 lattices) by analysing the fine structure of the X-ray absorption spectra[23]. This possibility must be borne in mind when the structure and catalytic properties of supported catalysts are discussed.

The sintering processes discussed so far lead to a change in size of the metal crystals, and to a corresponding change in catalytic activity. However diffusion processes can occur not only between crystallites but also on the surface of a given crystallite[24]. The elementary steps in the diffusion of atoms on a crystal surface are shown in Fig. 3. Evidently, the "healing" of vacancies and the disappearance of kinks and steps can lower the activity without altering the size of the crystal. This process, termed "qualitative sintering", has been observed in Pd–Al_2O_3.SiO_2 catalysts[25], in which sintering is inhibited by the addition of Al^{3+}, La^{3+}, and Th^{4+} cations. The stabilisation mechanism associated with the presence of these cations is not fully understood, but one possible explanation is that the cations prevent "internal" sintering† by being adsorbed on defects contributed by surface centres.

III. STRUCTURE AND CATALYTIC PROPERTIES OF SMALL METALLIC CRYSTALS

For the last 20 years the key problem in the study of catalysis by supported metals has been to characterise the catalytic and structural properties of small metal crystals, and in more recent years this problem has attracted a great deal of attention[26–30]. We shall dwell on some aspects of this problem, i.e.: a) the structure of the crystals, and their catalytic and adsorption properties; b) interactions between the reaction system and the supported catalyst; c) the formation and properties of surface structures.

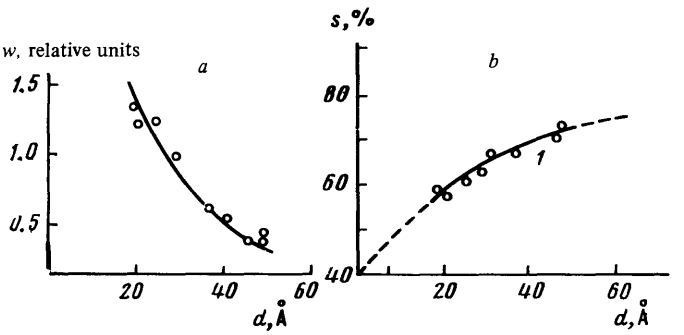


Figure 4. (a) velocity w and (b) selectivity s of the dehydrogenation of 2,3-dimethylbutane against disperseness of the Pt in a Pt–carbon catalyst[31] (curve *1*).

The number of publications on the effect of crystal size on catalytic activity and selectivity has continued to grow. It was shown[31] that the overall rate of dehydrogenation of 2,3-dimethylbutane by Pt–carbon catalysts decreases as the

† A process by which defects can be removed from the surface of microcrystals without sintering of the crystals.

average size of the Pt crystals increases, but the selectivity of the formation of 2,3-dimethylbut-1-ene increases (Fig. 4). This is ascribed to differences in the structure of intermediate complexes adsorbed on small and on large crystals, and is quoted as an example of a hindered reaction. Whether a reaction is hindered or unhindered is largely determined by the range of crystal size. The hydrogenation of benzene on $Pt-Al_2O_3$ is unhindered in the 10–50 Å crystal size range[32], whereas on Ni crystals ~5 Å in size the same reaction appears to be hindered[33]. A similar situation was observed in a study of the hydrogenolysis of ethane[34]: the specific activity was independent of the dispersion of the Ni catalyst in the range 15–70 Å, but it increased by a factor of 3 for a crystal size of ≤10 Å. The rate of oxidation of CO was found[12] to be extremely sensitive to the crystal size of the Pt catalyst.

This behaviour has been discussed both in terms of the structural features of small crystallites and by allowing for possible changes in electronic properties of the crystals (though these characteristics are often interrelated). For example, the decrease in specific activity of Ag crystals of increasing size, and the increase in their selectivity towards the formation of ethylene oxide or of CO_2 in the oxidation of ethylene, have been explained[35] by postulating two types of centre, corresponding to two forms of chemisorbed oxygen. Atomic oxygen, localised on atoms, occurs at the corners, edges, and growth steps of microcrystals: this form is very active, and leads to the formation of CO_2. Molecular oxygen, adsorbed on crystal faces, oxidises ethylene to ethylene oxide[35]. The 40-fold change in activity of Pt crystals towards the D_2 exchange with CH_4 on increasing the particle size from 9 to 100 Å is ascribed[36] to an increased proportion of the thermodynamically more stable (111) faces, which are not effective in catalysis. Thus the catalytic activity and selectivity of randomly oriented supported Ni crystals was found to be different from that of similar crystals in which the (111) and (110) faces were preferentially developed[37,38]. The oriented Ni crystals are more active towards the hydrogenation of ethylene, and they give a higher yield in the hydrogenolysis of n-heptane.

The concept of hindered and unhindered reactions is further developed in a study[39] of the isomerisation mechanism of 2-methylpentane and n-hexane on supported Pt crystals of different disperseness, allowing for the enhanced activity of atoms on corners or edges. The reaction mechanism (Fig. 5) includes the following steps:

1) weak adsorption on a Pt atom, localised on a crystal face (c_f);
2) surface diffusion to a reaction centre (edge atom, c_e);
3) formation of strongly dehydrogenated fragments on this centre;
4) rearrangement of the strongly adsorbed particles;
5) re-hydrogenation, surface diffusion, and desorption of the weakly adsorbed isomerised molecules.

A new classification of catalytic reactions has been proposed[39]. In reactions of type I all the surface atoms of the catalyst are equally active, and neither the rate nor the selectivity depends on the disperseness of the particles. In reactions of type II the number of reaction centres is greater than the number of weakly adsorbed molecules, and in this case the selectivity only is a function of disperseness. If the number of reaction centres is smaller than the number of weakly adsorbed molecules (type III) or if surface diffusion is very slow (type IV) both the selectivity and the specific reaction rate become a function of crystallite size.

Many workers have reported large differences in the adsorption and catalytic properties of metal atoms having different coordination. Thus it has been shown[40] that the n-heptane reforming reaction on supported rhodium catalysts involves atoms located on crystal faces, whereas the aromatisation reaction is due to edge atoms of Rh. Three types of centre have been defined[41] on a stepped metal surface: *A* centres (localised within a plane face), *B* centres (edge atoms), and *C* centres (corner atoms or atoms localised above the surface of a plane face). Each of these types of centre is thought to be responsible for a specific reaction involving olefins (*cis–trans*-isomerisation, migration of the double bond, hydrogenation). A similar explanation has been given[42] for the dependence of the rate of hydrogenation of cyclopropane, methylcyclopropane, and propylene on the disperseness of the Pt.

Calculations of the numbers of edge and corner Ni atoms in defect microcrystals have been used[43] to relate the amount of irreversible H_2 chemisorption to the disperseness of the Ni crystals.

Changes in catalytic activity and selectivity resulting from changes in crystal size may be due not only to structural differences between large and small crystals but also to a size dependence of the electronic properties of crystals. For example, the structure of the valence band of small crystals may be different from that of large crystals, since in small crystals: a) the potential may differ from the periodic lattice potential as a result of the presence of free valence electrons, b) the density of surface states may be greater than the density of electronic states, and c) the electronic state density may be affected by the presence of the carrier.

Thus in Pt crystals of 12–20 Å size supported on SiO_2 the edge of the valence band is shifted downwards by 1.5 eV relative to the Fermi level, and the valence band structure is quite different from that of a massive Pt crystal. On the other hand the electronic properties of Pt crystals 20 Å or more in diameter are identical to those of massive Pt.[44]

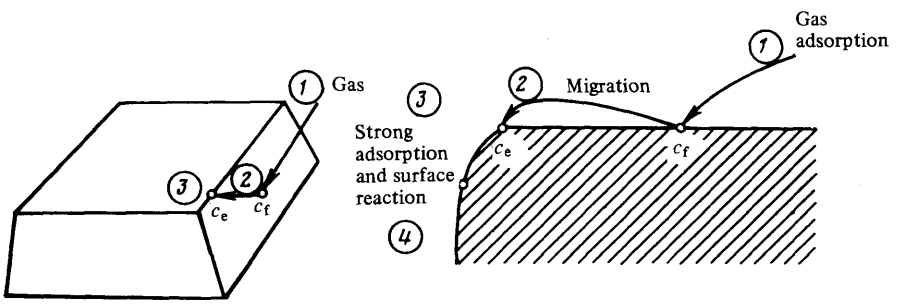


Figure 5. Mechanism of the isomerisation of 2-methylpentane and n-hexane[39].

Changes in crystal size have been shown[45] to influence the ratio of the ionisation potential to the electron affinity, and also the properties of the orbitals. Furthermore, the nature of the chemisorption bond may vary quite substantially under the influence of the carrier (and therefore as a function of the size of the crystals).[46] It is difficult at present to compare these theoretical calculations with experiment, but some workers have used calculated results to explain experimental findings. Thus the specific activity of Pt towards the methanation of CO increases by two orders of magnitude when the disperseness of the metal is increased 200-fold, an effect explained by the formation of the more weakly adsorbed, linear form of CO on the smaller crystals. On Pd, on the other hand, the activity is unaffected by the particle size of the metal though it is strongly dependent on the nature of the carrier (Al_2O_3, SiO_2), and this is ascribed to electronic interactions between the carrier and the metal microcrystals[47].

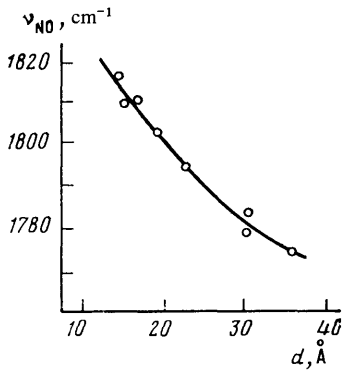


Figure 6. ν_{NO} against disperseness of the Pt.[48]

Changes in the nature of the chemisorption bond as a function of the disperseness of the metal must be allowed for when discussing catalytic systems, since this effect can influence both the rate and the selectivity of the process. As shown in Fig. 6, the frequency of stretching vibrations of NO irreversibly adsorbed on Pt crystals decreases as the crystal size increases, i.e. the energy of the N–O bond decreases[48]. The hydrogen bond strength and its charge also depend on the size of the Ni crystals[49]: these parameters can determine the reactivity of the adsorbed hydrogen. It has been shown that one form of ethylene adsorbed on Pd can be hydrated only by the negatively charged form of hydrogen, the positively charged form being completely inactive[50].

In this discussion of the structure and catalytic properties of supported metal microcrystals we have so far ignored changes induced by the reacting system. Yet very substantial effects of this type are possible: a) dispersion, or sintering, of the crystals, b) the development of facets which are more stable under the conditions of the catalytic reaction, c) internal reconstruction of the microcrystals without change in crystal size, and d) the formation of new phases on the catalyst surface.

Dispersion and sintering of supported metal crystals during a catalytic reaction are well known effects. Recently published data indicate a surprisingly fast reorganisation of a Ni surface under the influence of H_2 under conditions of hydrocarbon reforming with water vapour (due, no doubt, to the formation of different nickel hydrides[51,52]). It is interesting to note that the sintering of Ni in H_2 is much faster than the sintering of Pd.

A rearrangement of the surface facets of Pt [e.g. from (111) to (100)] under the influence of sulphur, leading to a decrease in surface free energy and in catalytic activity, has been demonstrated[53,54]. This effect may occur on other metals also.

The internal rearrangement of the microcrystals under the influence of the reacting species is particularly interesting. The main contribution to this work came from Boudart and coworkers[55–59], and it concerns the variations in the rate of the NH_3 synthesis on Fe crystals 15–300 Å in diameter stabilised on an MgO surface. The reaction rate increases as the particle size increases, but it also increases (for a constant crystal size of 15 or 40 Å) if the crystals are pre-treated in a mixture containing nitrogen. This pre-treatment causes a surface rearrangement (without changing the particle size) accompanied by a decrease in surface magnetic anisotropy and hence in the adsorption of CO. The underlying cause of these effects is shown to be the formation of C_7 centres#, which are active towards the NH_3 synthesis reaction.

The formation of a new phase on a catalyst surface during the reaction, and the structure of this phase, can influence the course of the reaction to a very large extent. This is clearly shown by studies of single-crystal faces[60,61]. For example, a disordered layer of carbonaceous products, which does not inhibit the reaction, is formed on the surface of stepped platinum faces during the hydrogenolysis of n-heptane. However the dehydrocyclisation reaction (with formation of toluene) occurs only on stepped crystal faces covered with an ordered carbon layer, and this layer is not formed on perfect (111) faces.

In addition to the oriented or non-oriented carbon structures formed by interactions with hydrocarbons on metal surfaces we can expect oxide, nitride, sulphide, and other structures to result from interactions with other compounds. A detailed analysis of the properties of these surface phases can be relevant to the identification of the mechanism of adsorption and catalytic processes. Experimental and theoretical studies of the interaction of oxygen with metal surfaces have been actively pursued in recent years[62–66]. By using monocrystal surfaces it has been possible to identify the various steps of surface and bulk reactions leading to the formation of two-dimensional and three-dimensional phases and to surface reconstruction.

Important results were obtained in studies of metal–oxygen structures formed by the action of O_2 on metal microcrystals. Fully disordered surface layers on Pt microcrystals following O_2 adsorption were observed[67] by the electron density radial distribution method. It was shown[68] that the deactivation of supported Pt microcrystals during the low-temperature oxidation of NH_3 is not due to a sintering process, but to the formation of an oxide layer several atoms thick or even to full oxidation of small crystals. These results force us to revise our views on the stability of the precious metals towards oxidation. Interactions with O_2 (under certain conditions) on Ni microcrystals stabilised by a carrier lead to the formation of surface nickel–oxygen structures of a quasi-metallic nature in which the oxygen shows a number of interesting properties[69], e.g.:

a) it acts as an additional centre for H_2 chemisorption, leading to a substantial increase in H_2 adsorption as compared with a clean Ni surface (Fig. 7);

b) it readily diffuses into the bulk of the crystal;

A surface centre with seven nearest-neighbour iron atoms.

c) the nickel–oxygen structure (unlike to NiO phase) is easily reduced by hydrogen.

We should note that the polarisation of the nickel atom is quite different in the nickel–oxygen structure and in NiO microcrystals, as shown by the large difference in adsorption capacity for ethylene (Fig. 8). This result suggests that the interaction of ethylene with the Ni^{2+} cation is much stronger than the interaction with the polarised nickel atom in the nickel–oxygen structure[70].

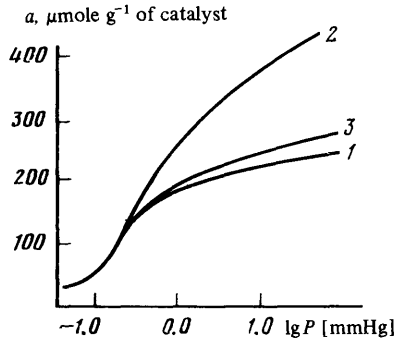


Figure 7. Adsorption of H_2 at 22 °C on supported Ni microcrystals[69]: *1*) clean surface, *2*) and *3*) surface covered with oxygen added at 150 and 300 °C respectively.

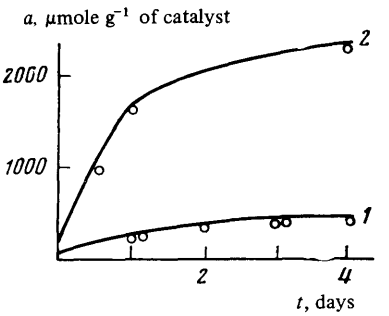


Figure 8. Kinetics of the adsorption of C_2H_4 at 22 °C: *1*) clean surface of supported Ni microcrystals and nickel–oxygen structure, *2*) supported NiO microcrystals[70].

IV. CATALYSIS BY METAL CLUSTERS

We shall now briefly consider the problems which arise in studies of catalysis by metal clusters (mainly, bimetallic clusters). These problems are attracting a great deal of attention because of their great theoretical and practical importance, and many recent results have already been critically reviewed[71–75].

There are several reasons for the current interest in this work: a) the prospects of a theoretical analysis of the interactions between atoms in a cluster and between the cluster and the carrier[76,77]; b) the large difference in selectivity between the bimetallic clusters and the component metals; c) the large difference in catalytic activity between the clusters and the component metals.

Theoretical analyses of the physical, adsorption, and catalytic properties of bimetallic clusters usually take account of two effects resulting from the addition of one metallic component to another:

1) the geometric factor (or "ensemble" effect),
2) the electronic factor (or ligand effect).

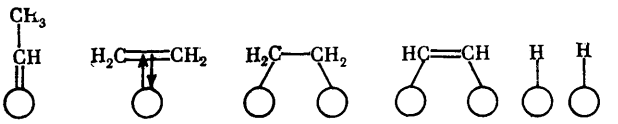


Figure 9. Adsorption forms of C_2H_4 on clusters of one, two, and four atoms respectively.

The geometric factor is clearly illustrated in Fig. 9, which shows various forms of ethylene adsorbed on nickel, requiring the presence of one-, two-, and four-atom ensembles on the surface respectively. Evidently, an increase in the amount of the second component (e.g. copper) on the surface lowers the probability of forming multi-atomic ensembles.

The electronic factor is far more complex. The "rigid band" model has long been used to discuss the physical and catalytic properties of alloys, and supported bimetallic clusters can be treated as a special case of alloy catalysts. Essentially the model states that an atom (for example, nickel) when introduced into the lattice of another component (for example, copper) loses its individuality, and its electronic levels are incorporated in the common *d*-band of the alloy. This model successfully describes the magnetic properties of alloys at relatively low concentrations of the additive, when the alloy remains ferromagnetic[78]. However there is evidence (experimental as well as theoretical) that the foreign atom can retain its individuality to a large extent[79,80].

The X-ray photo-emission spectra of the valence band of Ni–Cu alloys[81] are shown in Fig. 10. We note that the width and the shape of the Ni *d*-band are substantially unaffected by the addition of Cu. Characteristically, this *d*-band intersects the Fermi level at all compositions: the Ni atoms always have free *d*-levels and the electronic interaction with the Cu atoms is not very marked. This conclusion is confirmed by the failure to observe a shift in the frequency of the C–O bond vibration in the i.r. spectra of CO adsorbed on Ni–Cu alloys of increasing Cu content[82]: the only change was a decrease in the intensity of the band associated with the bridge form of CO adsorption. This decrease was ascribed to the geometric factor, i.e. to the decrease in the number of doublet centres on the alloy surface as the alloy is progressively diluted with copper.

However the existence of electronic interactions between the Ni and Cu atoms in this system has also been demonstrated[83]. As the alloy is made richer in copper both the intensity of the vibrations of the bridge form of adsorbed CO and the frequency of the vibrations of the CO bond in the

linear (*A*-band) as well as in the bridge (*B*-band) form decrease (Fig. 11), indicating an increase in the electron density on the nickel atoms. Magnetic data (Fig. 12) also show that an increase in the Cu content of the alloy is accompanied by a decrease in the number of bonds to the metal surface from 1.8 (for Ni) to 1.0 (for Cu), i.e. by a transition from the bridge to the linear adsorption form. It is interesting to note that Ni^{2+} ions in partially reduced $Ni-SiO_2$ catalysts lower the intensity of the band arising from the multi-centre form of CO adsorption, i.e. they act as diluents (like Cu atoms) by lowering the probability of finding clusters of several Ni atoms on the surface[84].

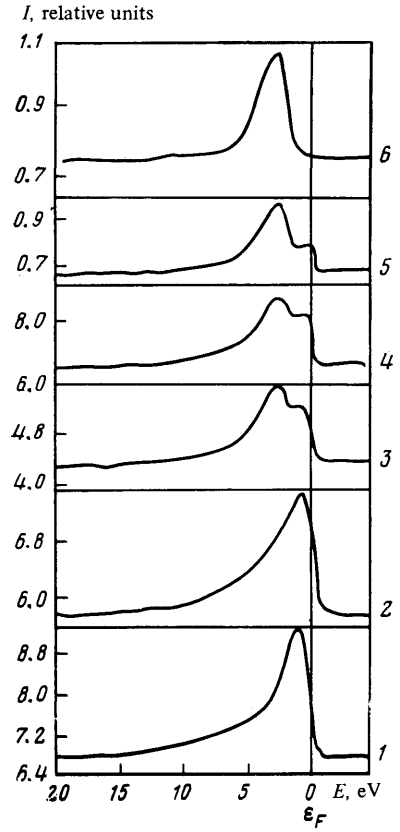


Figure 10. X-ray photo-emission spectra of the valence band of Ni–Cu alloys[81]: *1*) Ni, *2*) Cu(12%)–Ni(88%), *3*) Cu(44%)–Ni(56%), *4*) Cu(46%)–Ni(54%), *5*) Cu(74%)–Ni(26%), *6*) Cu.

In addition to demonstrating the presence of clusters in the Cu–Ni system recent work has shown that clusters can exist in other systems too. For example, Mössbauer spectral measurements have revealed the presence of Pd–Fe clusters in Pd and Fe supported on η-Al_2O_3.[85,86] The Mössbauer effect has proved very valuable in studies of electronic interactions in clusters. Thus iron in Pt–Fe clusters supported on γ-Al_2O_3 proved to be inactive (as compared to pure iron) towards the synthesis of hydrocarbons from CO and H_2.[87]

This effect may be related to the observed decrease in electron density on an Fe atom in a cluster due to interaction with the more electronegative Pt atom.

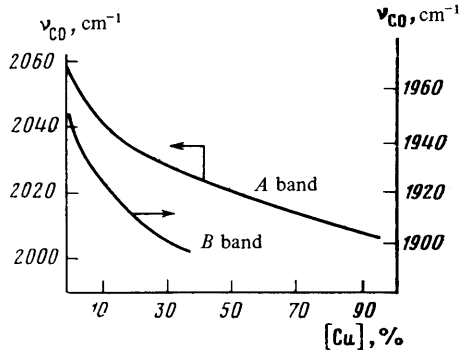


Figure 11. Variation of ν_{CO} for the *A* and *B* bands against Cu content of Ni–Cu alloys[83].

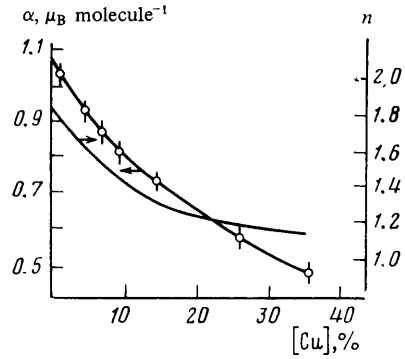


Figure 12. Effect of Cu concentration in a Ni–Cu alloy on the magnetisation (α) and number of bonds (n) per molecule of CO.[83]

Large electronic effects have been observed in clusters based on Pt and Sn as a result of electron transfer from Sn to Pt.[88] For example in the series $Pt < Pt_3Sn < PtSn < PtSn_2$ the surface is progressively enriched in Sn atoms, with a corresponding decrease in the strength of the bond between the surface and adsorbed CO, C_2H_4, and D_2 molecules. The downward shift of the ethylene desorption temperature on going from Pt_3Sn to PtSn is shown in Fig. 13. Typically, whereas the adsorption of ethylene on pure Pt is accompanied by a significant amount of self-hydrogenation the addition of Sn causes the adsorption of ethylene to be reversible. This is ascribed to the absence of Pt atomic ensembles on the surface of PtSn, but the effect could equally well be explained by an increase in electron density on the Pt atoms. Surprisingly, adsorbed CO molecules appear to "draw out" the Pt atoms from layers immediately below the surface and thus enrich the surface with Pt, but this effect is reversible and the initial state of the surface can be restored by pumping out the CO at room temperature.

Similar phenomena have been observed in the adsorption of O_2 on a Ni–Au alloy[89]. The alloy surface, initially consisting mainly of gold atoms, is found to be enriched in nickel atoms after O_2 adsorption: this effect is explained by the preferential attraction of Ni atoms towards the surface, resulting from the fact that the O–Ni bond energy is greater than the energy of the O–Au bond. These effects cannot be ignored when discussing the adsorption and catalytic properties of supported Bi- and polymetallic clusters.

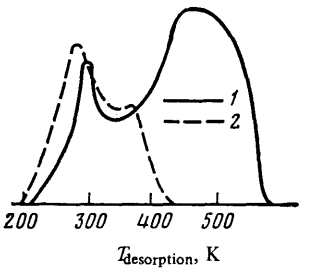


Figure 13. Desorption of ethylene from (*1*) Pt_3Sn and (*2*) PtSn surfaces.

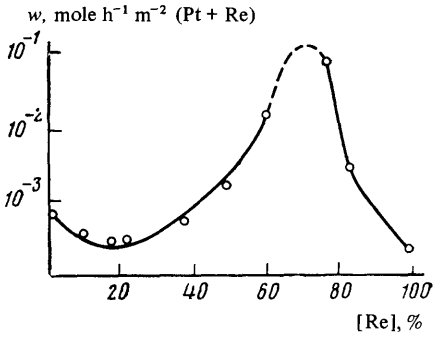


Figure 14. Specific catalytic activity *w* against concentration of Re in the hydrogenolysis of cyclopentane on $Pt–Re/Al_2O_3$ catalysts[93].

Thus in platinum–tin clusters the presence of the second component can have a powerful influence on the electronic state of the active centre[88], and hence on the type of interaction between the centre and adsorbed molecules. Similar effects were reported for additions of Sn to Pd or Ni supported on SiO_2.[90] The formation of carbonaceous deposits during the dehydrogenation of various compounds is suppressed if the Pd or Ni catalyst is alloyed with tin, suggesting a decrease in the energy of the bond between the reactants and the catalyst. According to measurements by X-ray photo-electron spectroscopy (XPES) the electronic structure of Pd and Ni is strongly affected by additions of Sn.

Another example of the decrease in bond energy between the reactant and the active centre is given in Ref. 91: the Pd–Au alloy (60 at.% Au) is approximately 50 times more active than Pd towards the oxidation of hydrogen by oxygen, showing that the energy of the bond between oxygen and a Pd atom is decreased by the presence of Au atoms on the surface.

Some of the most interesting Pt-containing clusters are the Pt–Re clusters supported on α- and γ-Al_2O_3. I.r. spectral data on CO adsorption have shown[92] that electron transfer from Re to Pt is responsible for the interactions in this alloy. The catalytic properties of this system towards the deuterium exchange and hydrogenation of benzene, the hydrogenolysis of cyclopentane and butane, and the dehydration of 1,1,3-trimethylcyclohexane suggest that in most cases the activity goes through a maximum (or several maxima): the maximum activity can be greater than the activity of the initial components, as shown by the change in specific activity as a function of composition of the cluster during the hydrogenolysis of cyclopentane (Fig. 14).[93] Within the framework of the "local" model these results can be explained[93] by the tendency of the cluster (depending on its composition) to acquire catalytic properties similar to those of Ir and Os as a result of electronic interactions between the components: these metals are known to be catalytically more active than Pt and Re towards the reactions under study.

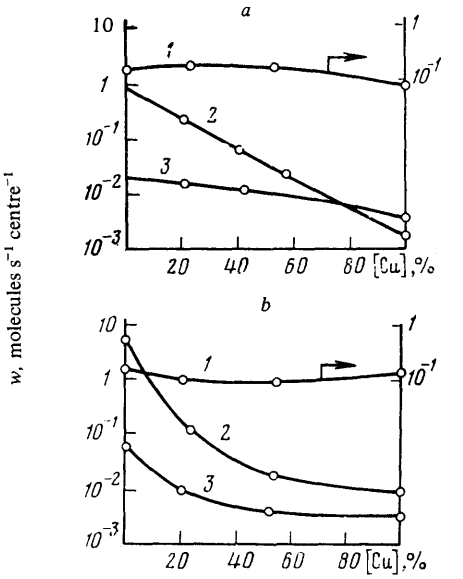


Figure 15. Specific catalytic activity *w* against composition of supported (on SiO_2) Cu–Ru (*a*) and Cu–Os (*b*) catalysts[94]: *1*) dehydrogenation of C_6H_{12}, *2*) hydrogenolysis of C_2H_6, *3*) hydrogenolysis of C_6H_{12}.

We shall close this review with a brief mention of the effect of composition on the selectivity and catalytic action of the cluster. This problem, as mentioned above, is currently one of the main areas of research on catalysis by clusters. The most important results obtained so far have already been critically reviewed[71–74]. Among the most interesting studies

in this area is Sinfelt's work[74] on the catalytic properties of Ni–Cu clusters towards the dehydrogenation of cyclohexane and the hydrogenolysis of ethane: a large increase in the amount of Cu in the alloy has practically no effect on the specific rate of dehydration of cyclohexane, whereas the rate of hydrogenolysis of ethane falls by about three orders of magnitude when as little as 5 at.% of Cu is added to the Ni. Similar results (Fig.15) were obtained for supported Ru–Cu and Os–Cu clusters in the same reactions[94]. Interactions in the Ru–Cu system have been studied by the XPES method[95]. It was shown that the Ru microcrystals are covered by Cu, and that heat treatment in H_2 produces a further increase in the surface concentration of Cu and a corresponding decrease in the rate of hydrogenolysis of ethane. No shifts of the absorption bands in the Cu and Ru XPE spectra were observed, but the conclusion[95] that electronic interactions between Cu and Ru are negligible does not seem justified.

A possible explanation of the reported effects is the following. Intermediate particles bound to several Ni atoms on the surface (i.e. bound to the cluster) are formed during the hydrogenolysis of C_2H_6. The addition of Cu lowers the probability of finding a cluster of several Ni (Ru,Os) atoms on the surface (geometric effect), and the rate of hydrogenolysis decreases. These intermediates are not formed during the dehydrogenation of cyclohexane, and therefore the rate of this reaction remains unaffected by the addition of copper over a wide range of composition.

This explanation is inconsistent with some of the considerations outlined above. Thus it has long been known that the adsorption of cyclohexane on Ni is accompanied by the formation of 8–12 bonds per molecule, i.e. it requires the presence of a much larger cluster of Ni atoms than does the conversion of a C_2H_6 molecule[96]. Hence the rate of dehydrogenation (or hydrogenolysis) of cyclohexane should be much more sensitive to the concentration of copper in the nickel than the rate of hydrogenolysis of ethane (if the geometric factor is predominant). In reality the situation is complicated by the possibility of changes in composition and in structure of the surface during the reaction, by the formation of carbonaceous surface structures, etc. Thus the problem of selectivity changes in the course of the reaction is still unsolved.

---o0o---

Though the problems presented by catalysis by supported metal crystals appear unrelated at first sight they have some important features in common, and progress in our understanding of any one of these problems can be expected to lead to progress in all directions.

REFERENCES

1. E.Ruckenstein and B.Pulvermacher, J.Catalysis, **29**, 224 (1973).
2. B.Pulvermacher and E.Ruckenstein, J.Catalysis, **35**, 115 (1974).
3. P.Wynblatt and Tae-Moon Ahn, Symposium "Sintering and Catalysis", New York–London, 1975, p.83.
4. K.Kinoshita, J.A.S.Bett, and P.Stonehart, Symposium "Sintering and Catalysis", New York–London, 1975, p.117.
5. J.C.Shlatter, Symposium "Sintering and Catalysis", New York–London, 1975, p.141.
6. P.Wynblatt, R.A.Dalla Betta, and N.A.Gjostein, "Physical Basis of Heterogeneous Catalysis", Battelle Institute Materials Science Colloquium, New York–London, 1975, p.501.
7. S.E.Wanke, Symposium "Sintering and Catalysis", New York–London, 1975, p.107.
8. E.Ruckenstein and D.B.Dadyburjor, J.Catalysis, **48**, 73 (1977).
9. R.M.J.Fiedorow, B.S.Chahar, and S.E.Wanke, J.Catalysis, **51**, 193 (1978).
10. C.G.Granqvist and R.A.Buhrman, J.Catalysis, **42**, 477 (1976).
11. S.E.Wanke, J.Catalysis, **46**, 234 (1977).
12. J.Zahradnik, E.F.McGarthy, G.C.Kuczynski, and J.J.Carberry, Symposium "Sintering and Catalysis", New York–London, 1975, p.199.
13. S.Wong, M.Flytzani-Stephanopoulos, M.Chen, T.E.Hutchinson, and L.D.Schmidt, J.Vac.Sci. Technol., **14**, 452 (1977).
14. E.Ruckenstein and M.L.Malhorta, J.Catalysis, **41**, 303 (1976).
15. R.M.J.Fiedorow and S.E.Wanke, J.Catalysis, **43**, 34 (1976).
16. J.Bett, K.Kinoshita, K.Routsis, and P.Stonehart, J.Catalysis, **29**, 160 (1973).
17. P.Ehrburger, O.P.Mahajan, and P.L.Walker, Jr., J.Catalysis, **43**, 61 (1976).
18. A.A.Slinkin, G.V.Antoshin, M.I.Loktev, E.S.Shpiro, E.A.Fedorovskaya, A.M.Rubinshtein, Yu.A.Yusibov, and Kh.M.Minachev, Kinetika i Kataliz, **19**, 754 (1978).
19. M.Che, J.F.Dutel, P.Gallezot, and M.Primet, J.Phys. Chem., **80**, 2371 (1976).
20. R.T.K.Baker, C.Thomas, and R.B.Tomas, J.Catalysis, **38**, 510 (1975).
21. Yu.I.Yermakov, B.N.Kuznetsov, and Yu.A.Ryndin, React.Kinet.Catal.Letters, **2**, 151 (1975).
22. K.Takami, A.Igorashi, and Y.Ogino, Bull.Jap.Petrol. Inst., **18**, 127 (1976).
23. I.W.Bassi, F.W.Lytle, and G.Paravano, J.Catalysis, **42**, 139 (1976).
24. G.Ehrlich, Symposium "Advances in the Study of Solid Surfaces" (Translated into Russian), No.1, Izd.Mir, Moscow, 1977, p.129.
25. I.Furuoya, Bull.Jap.Petrol.Inst., **13**, 78 (1971).
26. G.K.Boreskov, Zhur.Fiz.-Khim.Obshch.imeni Mendeleeva, **72**, 495 (1977).
27. G.C.Bond, "Electronic Structure and Reactivity of Metal Surfaces", New York–London, 1976, p.523.
28. T.E.Fischer, CRC Critical Rev. in Solid State Sci., **6**, 401 (1976).
29. A.Farkas, Catal.Rev.-Sci.Eng., **15**, 173 (1977).
30. J.H.Sinfelt, Symposium "Progress in Solid State Chemistry", No.10, Pt.2, Pergamon, New York, 1975, p.59.
31. M.Nakamura, M.Yamada, and A.Amano, J.Catalysis, **39**, 125 (1975).
32. J.M.Basset, G.Dalmai-Imelik, M.Primet, and R.Mutin, J.Catalysis, **37**, 22 (1975).
33. J.W.E.Coenen, R.Z.C.van Meerten, and H.Th.Rijnten, "Proceedings of the Fifth International Congress on Catalysis" (J.W.Hightower, Editor), North Holland, 1973, p.671.
34. Yu.A.Ryndin, B.N.Kuznetsov, and Yu.I.Yermakov, React.Kinet.Catal.Letters, **7**, 105 (1977).
35. J.C.Wu and P.Harriott, J.Catalysis, **39**, 395 (1965).
36. N.Sageret, Canad.J.Chem., **51**, 3588 (1973).
37. G.Dalamai-Imelik, C.Leclercq, J.Massardier, A.Maubert-Franko, and A.Zalhout, Japan.J.Appl. Phys., 1974, Suppl.2.
38. J.Massardier and G.Dalmai-Imelik, J.Chim.phys.Phys.-chim.biol., **73**, 90 (1976).

39. A.Chambellan, J.M.Dartiques, C.Corollour, and F.G.Gault, Nouv.J.Chim., **1**, 41 (1977).
40. E.Kikuchi, K.Ito, T.Ino, and Y.Morita, J.Catalysis, **46**, 382 (1977).
41. M.J.Ledoux, Nouv.J.Chim., **2**, 9 (1978).
42. P.H.Otero-Schipper, W.A.Wachter, J.B.Butt, R.L.Burwell, Jr., and J.B.Cohen, J.Catalysis, **50**, 494 (1977).
43. A.A.Slinkin, A.V.Kucherov, and A.M.Rubinshtein, Kinetika i Kataliz, **19**, 520 (1978).
44. P.N.Ross, K.Kinoshita, and P.Stonehart, J.Catalysis, **32**, 163 (1974).
45. R.C.Batzold, J.Catalysis, **29**, 129 (1973).
46. E.Ruckenstein, J.Catalysis, **30**, 309 (1973).
47. M.A.Vannice, J.Catalysis, **40**, 129 (1975); **44**, 152 (1976).
48. M.Primet, J.M.Basset, E.Garbowski, and M.V.Mathieu, J.Amer.Chem.Soc., **97**, 3655 (1975).
49. A.A.Slinkin, M.N.Loktev, and A.M.Rubinshtein, Dokl.Akad.Nauk SSSR, **207**, 1169 (1972).
50. R.Duš, Surface Sci., **50**, 241 (1975).
51. D.L.Trimm, Trans.Inst.Chem.Engineers, **54**, 119 (1976).
52. M.Moayeri and D.L.Trimm, J.Chem.Soc., Faraday Trans.I, **73**, 1245 (1977).
53. G.A.Somorjai, Catal.Rev., 7, 87 (1972).
54. G.A.Somorjai, J.Catalysis, **27**, 453 (1972).
55. M.Boudart, H.Topse, and J.A.Dumesis, "Physical Basis of Heterogeneous Catalysis", Battelle Institute Materials Science Colloquium, New York–London, 1975, p.337.
56. M.Boudart, A.Deloulle, J.A.Dumesic, S.Khammouma, and H.Topsøe, J.Catalysis, **37**, 486 (1975).
57. J.A.Dumesic, H.Topsøe, S.Khammouma, and M.Boudart, J.Catalysis, **37**, 503 (1975).
58. J.A.Dumesic, H.Topsøe, and M.Boudart, J.Catalysis, **37**, 513 (1975).
59. M.Boudart, J.A.Dumesic, and H.Topsøe, Proc.Nat. Acad.Sci.U.S.A., **74**, 806 (1977).
60. G.A.Somorjai, "Physical Basis of Heterogeneous Catalysis", Battelle Institute Materials Science Colloquium, New York–London, 1975, p.395.
61. G.A.Somorjai, Acc.Chem.Res., **9**, 248 (1976).
62. P.H.Holloway and J.B.Hudson, Surface Sci., **43**, 123 (1974).
63. K.A.Dadayan, V.I.Savchenko, and G.K.Boreskov, Kinetika i Kataliz, **18**, 189 (1977).
64. K.A.Dadayan, G.K.Boreskov, V.I.Savchenko, and N.N.Bulgakov, Kinetika i Kataliz, **18**, 574 (1977).
65. V.P.Ivanov, G.K.Boreskov, V.I.Savchenko, V.A.Tataurov, V.F.Egel'khoff, and V.G.Vainberg, Kinetika i Kataliz, **18**, 575 (1977).
66. V.A.Sobyanin, N.N.Bulgakov, and V.V.Gorodetskii, React.Kinet.Catal.Letters, 6, 125 (1977).
67. P.Ratnasamy, A.J.Leonard, L.Rodrique, and J.J.Fripiat, J.Catalysis, **29**, 374 (1973).
68. J.J.Ostermaier, J.R.Katzer, and W.H.Manogue, J.Catalysis, **41**, 277 (1976).
69. A.A.Slinkin, A.V.Kucherov, E.A.Fedorovskaya, and A.M.Rubinshtein, Kinetika i Kataliz, **18**, 742 (1977).
70. A.A.Slinkin, A.V.Kucherov, E.A.Fedorovskaya, and A.M.Rubinshtein, Kinetika i Kataliz, **19**, 403 (1978).
71. J.K.A.Clarke, Chem.Rev., **75**, 291 (1975).
72. G.K.Boreskov, Kinetika i Kataliz, **18**, 1111 (1977).
73. E.L.Muetterties, Science, **196**, 838 (1977).
74. J.H.Sinfelt, Science, **195**, 641 (1977).
75. Yu.I.Ermakov and B.N.Kuznetsov, Kinetika i Kataliz, **18**, 1167 (1977).
76. G.M.Zhidomirov, Kinetika i Kataliz, **18**, 1192 (1977).
77. K.H.Johnson, A.C.Balazs, and H.J.Kolari, Surface Sci., **72**, 733 (1978).
78. S.V.Vonsovskii, "Magnetizm" (Magnetism), Izd. Nauka, Moscow, 1971, p.615.
79. P.Soven, Phys.Rev., **156**, 809 (1967).
80. B.Velicky, S.Kirkpatrick, and H.Ehrenreich, Phys.Rev., **175**, 747 (1968).
81. C.Küfner, G.K.Wertheim, R.L.Cohen, and J.H.Wernick, Phys.Rev.Letters, **28**, 488 (1972).
82. Y.Soma-Noto and W.M.H.Sachtler, J.Catalysis, **34**, 162 (1974).
83. J.A.Dalmon, M.Primet, G.A.Martin, and B.Imelik, Surface Sci., **50**, 95 (1975).
84. M.Primet, J.A.Dalmon, and G.A.Martin, J.Catalysis, **46**, 25 (1977).
85. R.L.Garten and D.F.Ollis, J.Catalysis, **35**, 232 (1974).
86. R.L.Garten, J.Catalysis, **43**, 18 (1976).
87. M.A.Vannice and R.L.Garten, J.Molec.Catalysis, **1**, 201 (1975/76).
88. H.Verbeek and W.M.H.Sachtler, J.Catalysis, **42**, 257 (1976).
89. F.L.Williams and M.Boudart, J.Catalysis, **30**, 438 (1973).
90. M.Masai, K.Hohda, A.Kurota, S.Ohnaka, Y.Nishikawa, K.Nakahara, K.Kishi, and S.Ikeda, J.Catalysis, **50**, 419 (1977).
91. Y.L.Law, J.Criado, and M.Boudart, Nouv.J.Chim., **1**, 461 (1977).
92. C.Bolivar, H.Charcosset, R.Frety, M.Primet, L.Tournayan, C.Betizeau, G.Leclercq, and R.Maurel, J.Catalysis, **45**, 163 (1976).
93. B.Betizeau, G.Leclercq, R.Maurel, C.Bolivar, H.Charcosset, R.Frety, and L.Tournayan, J.Catalysis, **45**, 170 (1976).
94. J.H.Sinfelt, J.Catalysis, 29, 308 (1973).
95. C.R.Helms and J.H.Sinfelt, Surface Sci., **72**, 229 (1978).
96. P.W.Selwood, "Adsorption and Collective Paramagnetism", Academic Press, New York, 1962.

Zelinskii Institute of Organic Chemistry
of the USSR Academy of Sciences, Moscow

Translated from *Uspekhi Khimii*, 49, 789-813 (1980) U.D.C. 546.287;245:541.634

The Physical Chemistry of Silatranes

V.F.Sidorkin, V.A.Pestunovich, and M.G.Voronkov

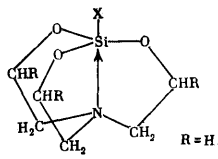
The present state and evolution of the theoretical ideas concerning the steric and electronic structures of silatranes as well as certain characteristics of their reactivity are analysed critically. The decisive influence of the hypervalent X-Si ← N bond on the physicochemical and spectroscopic characteristics of silatranes is demonstrated.
The bibliography includes 109 references

CONTENTS

I. Introduction 414
II. 1-Substituted silatranes 414
III. C-substituted silatranes 423

I. INTRODUCTION

The considerable interest in the chemistry of silatranes arose primarily because they have been found to include a number of substances with high and specific biological activities[1-4].



R = H, CH_3, or CF_3.

The molecular structure of silatranes is of special interest, since they are the first representatives of stable inner-complex organic derivatives of pentacoordinate silicon and have been studied in very high detail by a wide variety of physical methods. The development of the theory of their structure is undoubtedly an important contribution to the creation of the theoretical foundations and practical chemistry of metalloatranes. The aim of this review is to describe the present state and evolution of the theoretical ideas about the steric and electronic structures of silatranes and to discuss certain features of their reactivity.

II. 1-SUBSTITUTED SILATRANES

The first mention of silatranes appeared in 1960–1961 in a patent[5] and in a letter to the Editor[6]. They reported the formation of silatranes by the reaction of organyltriethoxysilanes $XSi(OC_2H_5)_3$ with tris-(2-hydroxyethyl)amine $(HOCH_2CH_2)_3N$:

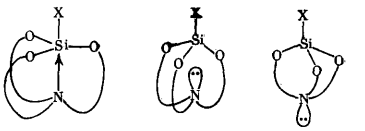
$$XSi(OC_2H_5)_3 + (HOCH_2CH_2)_3N \rightarrow XSi(OCH_2CH_2)_3N + 3C_2H_5OH .$$

The formation of silatranes in this reaction is unexpected, because the interaction of two trifunctional reagents as a rule results in the formation of polymers. Subsequent comparison of the chemical properties of silatranes and model compounds—organyltriethoxysilanes and triethanolamine—enabled the authors[6] to arrive at the following findings: (1) the nitrogen atom in silatranes is inert with respect to methyl iodide; (2) silatranes are more resistant to hydrolysis than the corresponding triethoxysilanes. On this basis, it was in fact suggested[6] that silatranes are the first representatives of organic compounds of pentacoordinate silicon containing the hitherto unknown intramolecular coordinate bond Si ← N.

Owing to the outward attractiveness and simplicity of this hypothesis, the absolute majority of the results of subsequent studies on silatranes were interpreted within its framework without further stipulations[1,2,7]. However, the above facts can be accounted for qualitatively without resorting to this hypothesis. For example, the reduced basicity of the nitrogen atom can be regarded as a consequence of the steric inaccessibility of its lone electron pair (LEP) in the *endo*-form of the silatrane molecule, stabilised by non-valence and electrostatic interaction. Below we shall attempt to analyse critically the results of physicochemical studies on silatranes from the standpoint of the choice of one of the two alternative hypotheses.

1. The Steric Structure

The classical theory of the structure of organic compounds permits three possible structures of silatranes[1]:



(Ia) (Ib) (Ic)

Structure (Ia) is planar-concave with a pentacoordinate silicon atom and a tetracoordinate nitrogen atom; structure (Ib) is convex-concave with a tetracoordinate silicon atom and a tervalent nitrogen atom; structure (Ic) (*exo*) is convex-convex and the heteroatoms are in the same valence state as in structure (Ib). Structure (Ic) can be rejected for silatranes on the grounds that the nitrogen atom in silatranes lacks basic properties[1,6,7]. Evidently the existence of silatranes in forms (Ia) and (Ib) would correspond to the first and second of the above hypotheses respectively.

It would seem that a decision can be reached concerning the alternative structures by resorting to X-ray diffraction. Table 1 presents the results of X-ray diffraction studies on a number of 1-substituted silatranes. In the molecules of the absolute majority of the compounds investigated the nitrogen atom is displaced from the plane of the neighbouring carbon atoms in the direction of the silicon atom (*endo*-orientation). The coordination polyhedron around the silicon atom consists of a distorted trigonal bipyramid, in the equatorial plane of which three oxygen atoms are accommodated, while the vertices contain the nitrogen atom and the α-atom of the substituent X. However, the deviations of the form of the coordination polyhedron from the ideal bipyramid are considerable. The average X–Si–O angles

(the values of which reflect to some extent the valence state of the silicon atom) are intermediate between the valence angles of compounds of tetravalent (109.5°) and pentacoordinate (90°) silicon atoms. On the basis of the valence angles, one cannot therefore decide reliably whether the steric structure of silatranes corresponds to distorted forms (Ia) or (Ib).

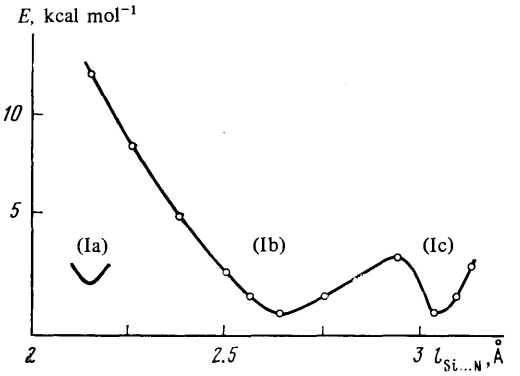
Table 1. The steric structures of 1-substituted silatranes.

X	Axial characteristics		Equatorial characteristics*		Refs.
	l_{X-Si}, Å	l_{Si-N}, Å	l_{Si-O}, Å	X-Si-O angle	
Cl	2.15	2.02	1.65	—	8
$ClCH_2$	1.91	2.12	1.67	97.4°	9
$Cl(CH_2)_3$	1.88	2.18	1.66	97.2°	10
mNO_2Ph	1.90	2.12	1.66	95.8°	11
Ph(α-form)	1.88	2.19	1.66	97.1°	12
Ph(β-form)	1.91	2.15	1.65	96.6°	13
Ph(γ-form)	1.89	2.13	1.65	96.0°	14
C_2H_5	1.88	2.21	1.66	—	15
$[(CH_3)_2C_6H_5P]_2ClPt$	2.29	2.89	1.65	108.8°	16,17

*The average Si–O bond lengths and X–Si–O angles are quoted.

The Si...N internuclear distances in the molecules of silatranes (Table 1) are much greater than the sum of the covalent values (1.8 Å), but are smaller than the sum of the van der Waals radii (3.1 Å) of the silicon and nitrogen atoms. This permitted the assignment of the structure of silatranes to form (Ia) without any ambiguity. On the basis of a qualitative inspection of the Si...N internuclear distance, one can be certain that there is a definite interaction between the silicon and nitrogen atoms in silatrane molecules. However, without additional arguments it is impossible to identify such interaction with the Si←N coordinate bond. Indeed one can assume with just as much certainty that the real structure of silatranes corresponds to a minimum in the conformational energy of form (Ib), in which the internuclear distance depends on the degree of non-valence interactions, the latter being in many respects determined by the nature of the substituent X. This hypothesis seemingly received indirect support by the detection of the *trans*-{PtCl[$Si(OCH_2CH_2)_3N$].[$P(CH_3)_2C_6H_5$]} molecule in a kind of *endo*-form[16,17]. The silicon atom in this molecule has a tetrahedral structure and the nitrogen atom is only slightly displaced from the plane of the three carbon atoms linked to it (by 0.07 Å). It is believed[16] that the tetrahedral structure of the silicon atom in this silatrane is caused by the considerable steric hindrance due to the structure of the Si-substituent as well as the low electronegativity of the latter. The nearly planar disposition of the nitrogen atom was explained by the intense steric interactions of the three methylene groups surrounding it.

To elucidate the relative role of the conformational and electronic factors determining the structure of silatrane molecules, the dependence of the chain energy on the Si...N internuclear distance has been investigated for the 1-methyl silatrane molecule by the Westheimer–Kitaigorodskii method[18,19]. It was found that the real structure of the 1-methyl silatrane molecule corresponds to the minimum conformational energy in form (Ia) alone; the latter is more stable to the extent of 8.5 kcal mole^{-1} than structure (Ib) (for the same Si...N internuclear distance). It was thus possible to demonstrate that conformational factors play a major role in the formation of the steric structure of silatranes, tending to increase the coordination number of the silicon atom to five. At the same time, the conformational energy of the *endo*-form (Ia) proved to be fairly close to the value calculated for the *exo*-form (Ic), which does not really exist and the barrier to the (Ic)→(Ia) transition does not exceed 2 kcal mole^{-1} (see Figure). Consequently conformational factors cannot account for the experimentally observed stability of the *endo*-form (Ia). This leads to the conclusion that the main factor determining the high stability of form (Ia) is the considerable contribution of the Si←N valence interaction energy to the overall energy of silatrane molecules†. Subsequently this conclusion was confirmed by quantum-chemical calculations[21].



Dependence of the conformational energy E of the 1-methylsilatrane molecule on the distance between the silicon and nitrogen atoms ($l_{Si...N}$).

According to X-ray diffraction data[8–15,22], the three five-membered heterocycles in the molecules of 1-substituted silatranes are non-planar. They have the shape of an envelope bent as a rule along the N–Cβ line. The molecules of all the silatranes investigated are distributed in crystals at distances which are determined by the van der Waals interactions. The crystal structures of 1-methylsilatrane[23,24] and 1-phenylsilatrane[12–14] exhibit polymorphism. The existence of several crystalline modifications (α, β, and γ) of the last compound was explained by the different conformations of the silatrane skeleton.

The dipole moments of silatranes are extremely high (5–9 D);[25–27] they are several times greater than the values for the corresponding organyltriethoxysilanes (1.5–2 D). This was assessed[25] as evidence for the existence of silatranes in form (Ia). The dipole moment of the $Si(OCH_2CH_2)_3N$ fragment in both the *exo*-form (Ic) and the *endo*-form (Ia), calculated by an additive scheme[25] without taking account the moment of the Si←N bond, proved to be significantly smaller

†It has been possible to show recently[20] that the stabilisation of structure (Ib) by electrostatic interaction is possible only for unrealistically high dipole moments of the polar bonds (Si–O, O–C).

(by 4–5 D) than the experimental value. Since data for the molecular structure had not yet been obtained in our calculations[25] it was necessary to employ bond lengths and angles which proved to be far from realistic. Analysis of the results led the authors[25] to the conclusion that silatranes exist in form (Ia) and have a very high (up to 8 D) dipole moment of the Si←N bond; however, this conclusion cannot be regarded as reliable for the reason stated above.

According to ^{1}H NMR data[1,28,29], three five-membered atrane half-rings in silatrane molecules are independent and completely identical. The chemical equivalence of the geminal protons of the methylene groups shows that the non-planar half-rings Si–O–C–C–N are involved in rapid (in terms of the NMR scale) conformational transitions. Analysis of the constants for the spin–spin coupling between the protons of the substituted ring of 3-methyl derivatives of silatranes indicates the *endo*-orientation of the LEP of the nitrogen atom in their molecules[30]. However, an unambiguous choice between forms (Ia) and (Ib) of silatrane molecules cannot be made on this basis.

2. Electronic Structure of 1-Substituted Silatranes

The adoption of the hypothesis that silatranes contain the Si←N bond imposes a number of requirements on their electronic structure[31,32]. Firstly the formation of such a bond must be accompanied by a rearrangement of the electron cloud of the silicon and nitrogen atoms and to some extent also of their immediate environment. This type of rearrangement should be manifested in a comparative analysis of the physicochemical properties of silatranes and the corresponding model systems sensitive to changes in electron distribution. Secondly, the collective properties# of silatranes cannot be understood without taking into account the characteristics of the Si←N bond. Thirdly, the nature of the dependence of the physicochemical properties of silatranes on the nature of the substituent at the silicon atom is determined by the presence of the Si←N bond. On the other hand, the hypothesis of the stabilisation of the silatrane skeleton as a result of non-valence interaction does not require the fulfilment of these conditions.

At the very beginning of the development of the chemistry of silatranes it was already claimed intuitively[1] that the degree of interaction between the nitrogen and silicon atoms and the length of the Si←N bond in silatrane molecules must be determined by the nature of the substituent X. With increasing electronegativity of the latter, a strengthening of the Si←N bond is to be expected. This was indeed established experimentally by X-ray diffraction analysis of silatranes (Table 1). The dependence of the Si...N internuclear distance in silatrane molecules on the Taft inductive constant (σ^*) of the substituent X at the silicon atom is linear[8,33]: $l_{Si\leftarrow N} = 2.20 - 0.0636\sigma^*$.

In silatrane molecules the displacement Δ of the silicon atom from the equatorial plane containing the three oxygen atoms in the direction of the substituent X is linked to the Si←N bond length by the relation[22] $l_{Si\leftarrow N} - \Delta = d$, where d is the distance from the nitrogen atom to the equatorial plane of the trigonal bipyramid; the value of d in the series of 1-substituted silatranes is then approximately the same and amounts to 2.00 ± 0.05 Å. It has been suggested that this is due to the competition of the non-valence interactions between the substituent and oxygen atoms, on the one hand, and the strain forces in the heterocycles, on the other. Later[15], on the basis of the analysis of more extensive experimental data, it was found that both Δ and d vary linearly with the Si←N bond length: $\Delta = -1.052 + 0.576 l_{Si\leftarrow N}$ and $d = 1.055 + 0.422 l_{Si\leftarrow N}$. Comparison of these relations shows that the length of the transannular Si←N bond in the molecules of 1-substituted silatrane changes mainly owing to the displacement of the silicon (and not nitrogen) atom relative to the equatorial plane of the distorted trigonal bipyramid. It was assumed that this indicates a decisive influence of the electronic interactions on the structure of silatrane molecules[15].

Despite the fact that this claim is valid, it in no way follows from the considerations presented above. For a more correct analysis of the changes in the degree of interaction between the silicon and nitrogen atoms, it is necessary to compare the values of Δ with the distance between the nitrogen atoms and the plane formed by the three neighbouring carbon atoms (Δ') and not with the value of d.[33] $\Delta = 0.48$ Å and $\Delta' = 0.13$ Å correspond to the minimum conformational energy of the 1-methylsilatrane molecule in form (Ib).[18] On the other hand, owing to the valence interaction in real 1-alkylsilatrane molecules the values of Δ and Δ' are lower and higher respectively than those indicated above. With increase of the Si←N bond strength, Δ diminishes and Δ' increases[34], the extent of the changes in these quantities being virtually identical in the series of silatranes whose structures have been investigated[33]. Consequently, under the influence of the substituent X, identical changes take place in the valence states of the nitrogen and silicon atoms. This agrees well with the results of studies of silatranes by other physical methods[35].

The value of $l_{Si\leftarrow N} = 1.83$ Å corresponds to the intercept which the plot of Δ against l_{Si-N} makes on the abscissa axis[15]. On this basis, it has been concluded[15] that the "ideal" length of the transannular Si←N bond is equal to the covalent Si–N bond length. The linear dependence of $l_{Si\leftarrow N}$ on the Taft inductive constant σ^*_X shows[8] that in an "ideal" silatrane the substituent X should have $\sigma^* = 5.4$. This value is extremely close to that known for the $R_3\overset{+}{N}$- group. It is therefore logical to assume that the 1-azaniasilatrane structure $[R_3N\rightarrow Si(OCH_2CH_2)_3N]^+A^-$ corresponds to the concept of the "ideal" silatrane. Hence it follows that there is no complete electron transfer from the nitrogen atom to the silicon atom in the molecules of the silatranes investigated hitherto.

Structural studies on silatranes have shown[14,15,22] that the Si–O bond lengths in their molecules and in model triethoxysilanes are virtually the same. It has come to be believed that this is due to the compensation of the enhancement of σ-bonding by the weakening of the $d_\pi - p_\pi$ interaction between the oxygen and silicon atoms when the silicon atom passes to the pentacoordinate state. However, evidence has been adduced (which must be regarded as incorrect) also in support of the $p_\pi - p_\pi$ interaction between the same atom[36].

In a series of 1-organylsilatranes the Si–O bond length hardly changes[14,15,22] and the longest Si←N bonds correspond to the shortest C–Si bonds[14]. This shows that the *trans*-influence of the substituents is characteristic of silatranes.

The parallel variation of the energies of the 2p levels of the silicon atom and the 1s level of the nitrogen atom in 1-substituted silatranes has been demonstrated by the method of photoelectron spectroscopy for chemical analysis (ESCA).[37] This finding is consistent with the hypothesis that the Si←N bond exists in silatranes (i.e. that there is a charge transfer from the nitrogen atom to the silicon atom). According to

#Properties which are determined, to a first approximation, by the sum of the properties of the individual bonds.

photoelectron spectroscopic (PES) data[38], the ionisation potentials of the 2*p* level of the nitrogen atom in the molecules of 1-hydro-, 1-methyl-, and 1-ethoxy-silatranes are higher than in triethanolamine. The authors explained this by the σ-donation of the LED of the nitrogen atom to the 3*d* orbital of the silicon atom. The approximate constancy of the first ionisation potentials for silatranes with X = H and C_2H_5O was somewhat unexpected. However, one should note that the interpretation of the PES data for silatranes in the study of Cradock et al.[38] is not reliable. The levels were assigned on the basis of symmetry considerations, which is clearly insufficient in the analysis of the PES of such complex molecules.

X-Ray electronic spectra of silatranes have been studied[36,39,40]. The chemical shifts of the K_α lines of the silicon atoms, calculated by an additive scheme on the assumption of the tetravalent state of the silicon atom, proved to be greater than the experimental values. The difference is fundamental and supports the structure with a pentacoordinate silicon atom. It has been suggested[39] that the Si←N bond in silatrane molecules is responsible for the reduced effective charge on the silicon atom (i.e. for the increased electron density at this atom) and hence for the reduced chemical shift of the K_α line. This conclusion cannot be regarded as rigorously justified, because the formula $\Delta E_l = Kq_{eff}$, used to determine the effective charges, presupposes the equality of the constant *k* for compounds of tetra- and penta-coordinate silicon, which is extremely doubtful.

A hypsochromic shift of the absorption band of the $N(CH_2)_3$ group relative to the spectrum of triethanolamine, in which the LEP of the nitrogen atom is free, has been observed in the ultraviolet spectra of 1-substituted silatranes (X = C_2H_5, CH_3, or H).[41] This confirms the hypothesis that the Si←N bond is present in silatranes, since the higher binding energy of the lone electron pair in silatrane is in fact responsible for the hypsochromic shift. Analysis of the ultraviolet absorption spectra of 1-aryloxysilatranes leads to the conclusion[42] that the bands due to the aryloxy-groups (200–300 nm) are insensitive to the coordination interaction of the silicon and nitrogen atoms.

Absorption bands in the range 560–590 cm^{-1}, which are absent from the spectra of model compounds, are characteristic of the infrared spectra of silatranes[1,43–48]. These frequencies were assigned to the stretching vibrations of the Si←N bond on the grounds that the vibrations of the covalent Si–N bonds in aminosilanes are in the range 780–830 cm^{-1}, while the vibration frequency of the coordinate bond should be lower[1,43]. The integral intensity *A* of this band in the spectra of a series of 1-organoxysilatranes of the type $RO\overset{\downarrow}{S}i(OCH_2CH_2)_3\overset{\downarrow}{N}$ depends on the nature of the substituent[44,45]. There should be strong kinematic interactions between the vibrations of the collinear X–Si and Si←N fragments, as a result of which the stretching vibration frequency of the Si←N bond should be displaced towards lower values with increase of the atomic weight of the substituent at the silicon atom. Such a shift has indeed been observed[44,49] in the series of 1-substituted silatranes with X = H, F, Cl, or Br, which also confirms the validity of the assignment of the ν band to the Si←N vibration. The introduction of symmetry coordinates permitted the calculation of the force field of the 1-hydrosilatrane molecule[45]. The force constant of the Si←N bond proved to be 1.2×10^6 cm^{-2}, which is several times smaller than the force constants of covalent bonds.

Evidence has recently been presented[46] showing that the assignment of the 560–590 cm^{-1} band in the infrared spectra of silatranes to the Si←N bond vibrations is erroneous. According to some data[44,45], the integral intensities A_ν of this band are as a rule inversely proportional to its intensity at the maximum. On the other hand, according to Voronkov et al.[46] (although the latter do not in fact quote specific results for the compound investigated previously[44,45]), the half-widths of such bands are constant, which led them to the belief that the measurements of the values of A_ν in the earlier investigations[44,45] were methodologically incorrect. The integral intensity of this band, measured for the first time for the series of 1-alkyl- and *C*-substituted silatranes, proved to be independent of the nature of the substituent at the silicon atom[46]; this constitutes important evidence against the assignment of the band in the range 560–590 cm^{-1} to ν(Si→N). It is so far difficult to solve ultimately the problem of the assignment of this band. For example, despite the use of the same method for the determination of the integral intensities (the Iogansen method) in the studies described in Refs. 44 and 46, the values of A_{570} obtained for 1-ethoxysilatrane differ sharply (9250 and 1612 litre cm^{-2} mol^{-1} respectively). Yet another argument against the assignment of the 560–590 cm^{-1} band to the Si←N vibration is based on the hypothesis that such vibrations (symmetry A_1) should be inactive in Raman spectra§. Furthermore, the intensity ratio $A_{570}/A_{790} = 0.1$ in the infrared spectrum of 1-ethylthiomethyl-3-methylsilatrane, while in the Raman spectrum it increases to **0.3.**[46]

On the basis of the above considerations and the presence of a band in the region of 600 cm^{-1} in the infrared spectra of certain di- and tri-cyclic structures (including those of metalloatranes), the 560–590 cm^{-1} band in the infrared spectra of silatranes has been assigned[46] to the skeletal vibrations. If this hypothesis is adopted, it is not clear why, despite the significant deformation of the atrane molecular skeleton on substitution of the $O_{(2)}$ atom by the methylene group[7] or after the introduction of methyl groups in the 3-, 7-, and 10-positions[1,7,46], the frequency of the above vibration remains constant. At the same time the 560–590 cm^{-1} band has not been observed[16] in the infrared spectrum of the bicyclic *trans*-{PtCl[$Si(OCH_2CH_2)_3N$][$P(CH_3)_2C_6H_5$]} molecule, in which there is virtually no Si←N bond according to X-ray diffraction data[16,17]. We believe that this factor shows unambiguously that the presence of the Si←N bond is an essential condition for the manifestation of the band at 560–590 cm^{-1} in the infrared spectra of silatranes.

We may note that the 560–590 cm^{-1} band in the infrared spectra of Si- and C-substituted silatranes has been assigned to the fully symmetrical vibrations of the SiO_3 group[47]. It has also been suggested[48] that the moderately intense bands in the region of 300 cm^{-1} should be assigned to the Si←N bond vibrations. Thus one must admit that the problem of the direct manifestation of the Si←N bond vibrations in the infrared spectra of silatranes still remains essentially open.

At the same time, the bathochromic shift of the ν(H–Si) band in the spectrum of hydrosilatrane relative to triethoxysilane[1,6,43] as well as the appreciably lower ν_{as}(C–Si) and ν(Hal–Si) frequencies in the infrared spectra of 1-alkyl-[43] and 1-halogeno-silatranes[49,51] compared with the corresponding derivatives of triethoxysilane confirm indirectly the presence of the Si←N bond in silatranes.

A change in the nature of the substituent at the silicon atom has approximately the same influence on the degrees of electronic shielding of the protons of both OCH_2 and CH_2N groups in the ^1H NMR spectra of silatranes[1,28,29,38],

§This is a clear misunderstanding, since the A_1 vibrations are active in both Raman and infrared spectra[50].

[52–54]. This is responsible for the constancy of the difference between the chemical shifts of these protons (in a given solvent) for all 1-substituted silatranes (Table 2). The results show that the electronic influence of the substituent at the silicon atom is transmitted not only via the system of σ-bonds of the atrane half-rings (SiOCCN) but also via the Si←N bonds. The same feature can be seen also in the variation of the spin–spin coupling constants $^1J(^{13}C-^1H)$ for the OCH_2 and CH_2N groups[53]. It follows from statistical considerations that the Si←N bond transmits the influence of the substituent X more effectively than each of the Si–O bonds. Thus ^1H NMR data indicate one of the most significant features of silatranes—the *trans*-influence of the substituent at the silicon atom on the nitrogen atom.

Table 2. NMR parameters of 1-substituted silatranes.

X	^1H chemical shifts, p.p.m.*		^{29}Si chemical shifts, p.p.m.	
	δ_{OCH_2}	δ_{CH_2N}	δ_{Si}	$\Delta\delta_{Si}^{**}$
H	3.830	2.868	−83.6	17.6
CH_3	3.779	2.806	−65.7	21.7
CH_3CH_2	3.777	2.802	−67.1	21.2
$ClCH_2$	3.858	2.886	−77.2	21.1
$BrCH_2$	3.853	2.879	−77.7	21.5
ICH_2	3.839	2.860	−77.0	22.3
$H_2C=CH$	3.829	7.850	−83.5	23.2
Cl_2CH	3.930	2.962	−83.2	14.8
C_6H_5	3.905	2.915	−80.5	21.1
CH_3CH_2O	3.837	2.836	−94.7	12.3
F	3.906	2.950	−101.1	16.1

*Values extrapolated to infinite dilution in $CHCl_3$.

**$\Delta\delta_{Si} = \delta_{Si}(X-Si(OCH_2CH_2)_3N) - \delta_{Si}(X-Si(OCH_2CH_3)_3)$.

When the nitrogen atom passes to the cationic state or its LEP is involved in a coordinate bond, the ^1H NMR absorption line of the protons of the methylene group linked to the nitrogen atom usually undergoes a paramagnetic shift of approximately 0.5–0.8 p.p.m. However, the chemical shifts of the CH_2N protons in the ^1H NMR spectra of silatranes are only slightly greater than in those of the acyclic and monocyclic analogues[29,52], where there is no Si←N bond. The observed difference between the chemical shifts of the CH_2N protons of silatranes and their analogues shows that the degree of transfer of the LEP of the nitrogen atom to the silicon atom is insignificant. This purely qualitative conclusion (which conflicts with the hypothesis put forward at one time[1,25] that the Si←N bond is highly polar) was later proved quantitatively[21,27,35,55].

The chemical shifts of the OCH_2 and CH_2N protons of 1-alkyl- and 1-alkenylsilatranes are correlated with the inductive substituent constant σ*.[29,52,56] However, 1-aryloxy- and 1-alkoxy-silatranes deviate from this relation. This has been explained[29,52] by the superposition of the effect due to the $d_\pi - p_\pi$ interaction of the silicon atom with the oxygen atom of the aryloxy- or alkoxy-group.

An equation for joint correlation of the σ_{CH_2N} and the field and resonance constants (F and R) of the substituent X has been found for a number of 1-alkyl or aryl- and 1-aryloxy- or alkoxy-silatranes[53]. ^1H NMR data also show that the distribution of electron density in silatranes depends also on the steric influence of the substituent at silicon atom[29,52]. The chemical shifts of the ^{13}C NMR signal of the atrane skeleton in silatrane molecules depend comparatively little on the nature of the substituent on the silicon atom [$\delta(C_N) = 51$ p.p.m. and $\delta(C_0) = 57$ p.p.m.].[53] This is probably caused by the damping effect of the readily polarisable C–H bonds in the silatrane molecules, which can compensate for the change in the charges on the α- and β-carbon atoms induced by the substituent X.

Despite the involvement of the nitrogen atom of silatranes in the Si←N coordinate bond, the ^{14}N NMR lines in their spectra are appreciably broadened (X = CH_3, $\Delta\nu = 2211$ Hz; X = H, $\Delta\nu = 638$ Hz).[57] The authors explain this by the local asymmetry of the nitrogen atom in the silatrane molecules and by the increase of the C–N–C valence angles. The isolation of the contribution of the Si←N bond to the ^{14}N shielding constant for silatranes is complicated by a number of factors. Among these, the main one is the cyclisation effect, which is of a distinctly diamagnetic type. At the same time, the change in the ^{14}N chemical shifts (by 9 p.p.m.) when the hydrogen atom in the 1-hydrosilatrane molecule ($\delta_N = -355$ p.p.m.) is replaced by the methyl group[57] is approximately equal to the downfield shift of the ^{14}N resonance of trialkylamines or their salts when the hydrogen atom at α-carbon atom is substituted by the methyl group. This kind of analogy in the behaviour of δ_N is caused by the formally similar mechanisms of the transmission of the effective substituent to the indicator centre (^{14}N) in the X–C–N and X–Si–N fragments.

In the NMR spectra of 1-substituted silatranes the ^{29}Si line is displaced upfield with increase of the electronegativity of the substituent X.[53,58,59] A similar dependence has been observed also for Si-substituted triethoxysilane $XSi(OCH_2H_5)_3$.[53,59] Consequently the presence of the Si←N bond in silatranes cannot be inferred from the nature of the change in the $\delta(^{29}Si)$ as the substituent X is varied. At the same time, the ^{29}Si signals in the NMR spectra of silatranes are appreciably displaced upfield compared with the signals observed in the NMR spectra of model Si-substituted triethoxysilanes (Table 2). This increase of the shielding cannot be accounted for either by the cyclisation effect (usually causing a downfield shift of the signals[60]) or by the influence of the high electronegativity of the nitrogen atom. The implication is that the factors which do not characterise directly the presence of the Si←N bond are unable to explain the upfield shift of the ^{29}Si NMR signal of silatranes relative to Si-substituted triethoxysilanes.

However, the increase of the shielding constants of the nuclei with increase of the coordination number of the atom, a fact which has not so far been accounted for theoretically, is widely known in ^{11}B, ^{29}Si, ^{119}Sn, ^{199}Hg, etc. NMR. On this basis one must conclude that the nature of the ^{29}Si NMR spectra of silatranes rigorously demonstrates the presence of the Si←N bond in their molecules. If one adopts the reasonable, at first sight, hypothesis that the presence of the Si←N bond is responsible for the increased electron density at the silicon atom (compared with model systems) and one takes into account the familiar[60,61] V-shaped relation between the chemical shift and the atomic charge, then one should expect a downfield shift of the ^{29}Si signal of silatranes. It was therefore necessary to assume[53,59] that, in contrast to Si-substituted triethoxysilanes, the ^{29}Si shifts of silatranes are determined not only by the effective charge of silicon atom but also by a certain positive coordination contribution δ_{coord}. The magnitude of the latter increases with increasing degree of the Si←N interaction.

The proposed interpretation explains why the absolute values of $|\Delta\delta Si = \delta Si(silatrane) - \delta Si(triethoxysilane)|$ decrease in parallel with increase of the degree of the Si←N interaction in silatrane molecules[53]. On the other hand, the hypothesis of the reduced electronic charge on the silicon atom in silatranes hinders the explanation of the observed relations, although it does provide a formal explanation of the upfield shift of the ^{29}Si signal in their NMR spectra. All these findings show that, like the majority of other spectroscopic characteristics of silatranes, their ^{29}Si NMR chemical shifts are not determined solely by the contribution of the charge on the central atom.

An increase of the degree of shielding (compared with the corresponding Si-substituted triethoxysilanes) of the nuclei of the atoms forming part of the composition of the substituent at the silicon is also characteristic of silatranes[1,29,52,53,58]. ^{13}C and ^{19}F linked directly to the silicon atom are the only exceptions[58]. The pentacoordinate state of the silicon atom in silatrane molecules is responsible for the increase of the spin–spin coupling constants $^1J(^{29}Si^{13}C)$ and $^2J(^{29}Si^1H)$ and for the decrease of $^1J(^{29}Si^1H)$ and $^1J(^{29}Si^{19}F)$ compared with the corresponding derivatives of tetravalent silicon[58]. The above properties are probably common to all derivatives of Group IVB elements containing a heteroatom with an increased coordination number.

Before silatranes were studied by ^1H NMR,[29,52] the hypothesis of the high polarity of the Si←N bond in their molecules aroused no doubts. This conviction was based on the determination and calculations of the dipole moments of silatranes[1,25]. The appearance of new data on the geometry of the silatrane molecules enabled one of the present authors and his coworkers[27,55] to recalculate their dipole moments on the basis of an additive scheme. It was found[55] that the Si←N bond dipole moment in 1-alkyl- and 1-aryl-silatranes does not exceed 2.20 D, which corresponds to the transfer of approximately 0.2*e* from the nitrogen to the silicon atom. At the same time the validity of the earlier conclusion[25] that the high dipole moments of silatranes cannot be explained without taking into account the contribution of the Si←N bond moment was demonstrated. Similar results were obtained in another study[27], where the dipole moment of the Si←N bond in 1-methylsilatrane was estimated as 1.38 D.

The dipole moments of silatranes depend not only on the electronic effect of the substituent X and hence also on the internuclear Si...X distance, as assumed before, but also on the conformational features of the heterocyclic skeleton of the molecules[55]. The revised values of μ(Si←N) are of fundamental importance for the theory of the structure of silatranes. In the study of 1-methylsilatrane solutions in dioxan measurements were made of the molar Kerr constants, the total polarisation, and the molecular anisotropy[62]. The determination of these molecular characteristics made it possible to establish, within the framework of the additive scheme for the calculation of bond polarisabilities, that the Si←N bond in silatranes is characterised by an appreciable anisotropy of its polarisability. The conformations of a number of silatranes containing a carbofunctional substituent were established by the same methods[63].

The molecular ions $(M-X)^+$ in the mass-spectra of silatranes[64,65] exhibit a high intensity (from 48.5 to 33.9%). This indicates the stability of the silatrane ring on electron impact, which can be accounted for by the presence of the Si←N coordinate bond. When the substituent X is extracted, the latter is converted into the "covalent" Si–$\overset{+}{N}$ bond, where the nitrogen atom is in the ammonium state.

The influence of the silatrane skeleton on the properties of the Si-substituent have been frequently considered. The ^{35}Cl NQR frequencies for 1-chloroalkyl- and 1-chlorovinyl-silatranes are somewhat lower than for the corresponding acylic analogues[54]. This is consistent with the hypothesis that there is a coordination interaction in silatranes between the silicon and nitrogen atoms, which increases the +*I* effect of the silatranyl group. The inductive constant of the silatranyl group has been determined as −1.2 by employing familiar[66,67] linear relations between the ^{35}Cl NQR frequencies and the σ_X^* constants for the $H_2C{=}CClX$ and $XX'CCl_2$ series. This value indicates a distinctly σ-donor character of the $-\overset{\downarrow}{Si}(OCH_2CH_2)_3N$ group. The high σ-donor capacity of the silatranyl group has also been confirmed by ^1H, ^{13}C, and ^{19}F NMR.[28,29,52,53,58,68–70]

The quantitative estimate of the inductive effect of the silatranyl group, obtained[70] on the basis of ^{13}C NMR data for 1-phenyl silatrane ($\sigma^* = -0.9$) is lower in absolute magnitude than that determined[54] by ^{35}Cl NQR. This discrepancy is most probably independent of the difference between the reliabilities of the correlation equations employed, based on data found by different methods (^{35}Cl NQR and ^{13}C NMR). It can probably be explained by the fact that the σ-donor properties of the silatranyl group are not constant and depend on the nature of the substituent at the silicon atom. The latter in fact determines the degree of transannular interaction in silatrane molecules and hence the increased, compared with $Si(OR)_3$ groups, electron-donating capacity of the silatranyl fragment $-\overset{\downarrow}{Si}(OCH_2CH_2)_3N$ (see below). The quantitative estimate of the inductive effect of the silatranylmethyl group $-CH_2-\overset{\downarrow}{Si}(OCH_2CH_2)_3N$ ($\sigma^* = 0.8$) [69] is consistent with the value of $\sigma^*[-\overset{\downarrow}{Si}(OCH_2CH_2)_3N]$ obtained from ^{35}Cl NQR data.

It has been suggested[54] that there may be a coordination interaction between the chlorine and silicon (oxygen) atoms in the 1-(γ-chloropropyl)silatrane molecule. However, this was subsequently disproved experimentally[10].

Thus, despite the fact that, in the majority of the studies examined the isolation of the contribution of the Si←N bond to the properties of silatranes investigated has been achieved only at a qualitative level (and frequently very artificially), the results obtained convincingly demonstrate a significant change in the electron clouds of the silicon and nitrogen atoms as well as their immediate environment in silatrane molecules. Together with the characteristic influence of the nature of the substituent at the silicon atom on the properties of silatranes this indicates unambiguously the presence of the Si←N bond in their molecules. The existing experimental data cannot be accounted for within the framework of the alternative model (the stabilisation of the silatrane skeleton by non-valence and electrostatic interactions). At the same time, in view of the lack of experimental and theoretical estimates of the Si←N bond energy, the problem of the causes of the stability of silatranes, which is crucial for the theory of their structure, remained in fact open for a long time.

To solve this problem, the total energies of the 1-hydrosilatrane molecules and the most significant points on the potential function for the *endo–exo* transition were calculated[21] by the CNDO/2 method in terms of a novel parametrisation. It was shown that the *endo*-form is energetically more favourable than the *exo*-form (by 60 kcal mol^{-1}). The high value of the calculated barrier to the transition of the *endo*-form (Ia) into the *exo*-form (Ic) (~64 kcal mol^{-1}) and its low value (~4 kcal mol^{-1}) for the reverse transition demonstrated that the *exo*-form does not exist.

The energies of the skeletal bonds of the silatrane molecule do not actually change on transition from the *endo*- to

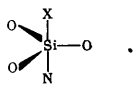
the *exo*-form (more precisely the changes in them are negligible compared with their absolute values). The decrease of the Si←N bond energy by more than an order of magnitude is unique and extremely symptomatic. Hence we may conclude that the main factor stabilising the *endo*-form of the silatrane molecule is the bonding interaction between the silicon and nitrogen atoms. The energy of the Si←N bond in the *endo*-form (Ia) of the 1-hydrosilatrane molecule can be regarded as close to 24–25 kcal mol^{-1}¶.

Analysis of the populations of the hybrid orbitals of the nitrogen atom indicates unambiguously the involvement of its LEP in the formation of the Si←N bond. The calculated degree of transfer of electron density from the nitrogen to the silicon atom in the hydrosilatrane molecule (~0.2*e*) agrees well with the earlier estimate obtained by analysing the dipole moments of silatranes[55].

The results of conformational[18,19] and quantum-chemical[21] analyses suggest[35,72] that the cause of the existence of the intramolecular Si←N bond in silatranes and the virtual absence of the formation of a similar intermolecular bond when organyltriethoxysilanes react with amines consists in the fundamental difference between the free energy profiles for the formation of the intra- and intermolecular hypervalent X–Si–N linkages. The energetically favourable transition of the silatrane molecule from the *exo*- to the *endo*-form occurs with retention of the conformational entropy. This follows from the existence, as the reaction coordinate r_{Si-N} is altered, of only two stable states and the dissociation of the intermolecular complex is characterised by a monotonic increase of the entropy.

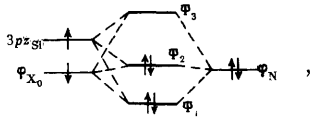
The problem of the nature of the interaction between the silicon and nitrogen atoms in silatranes is particularly significant. Only one mechanism of their mutual binding was in essence considered in previous studies: the donor–acceptor interaction of the LEP of the nitrogen atom with the vacant 3*d* orbitals of the silicon atom having a suitable symmetry[1,28,38,73]. However, as shown above, this mechanism cannot explain logically certain results of physicochemical studies on silatranes. Futhermore, the concept of hybridisation involving 3*d* orbitals, particularly in the case of non-transition elements, has been recently subjected to serious and constructive criticism[74]. The problem of both the nature of the Si←N bond in silatranes and of the influence of the substituents at the silicon atom on the energetics of the molecule and the steric structure of the silatrane skeleton therefore clearly had to be reconsidered.

An attempt has been made[75] to treat the electronic and steric structures of silatranes within the framework of the model of hypervalent linkages[76]. A significant factor in the consideration of the electronic structure of silatranes is the isolation of the molecular fragment of greatest structural and chemical importance. This is the silicon atom and its immediate environment, which has approximately the symmetry of a trigonal bipyramid:



For a more logical determination of the influence of the substituent X on the equilibrium properties of silatranes, one can assume that, for a "standard" substituent X_0, the geometry of the local environment of the silicon atom corresponds rigorously to the ideal trigonal bipyramid†. Three sp^2-hybridised orbitals can be constructed from the four valence orbitals of the silicon atom (3*s*, $3p_x$, $3p_y$, and $3p_z$). The hybrid orbitals are involved in the formation of three "normal" equivalent equatorial Si–O bonds. The orbitals of the axial atoms (one from each atom) can then interact with the single $3p_z$ orbital of the central silicon atom common to all of them. According to the molecular orbital (MO) theory, this should lead to the formation of three three-orbital, three-centre MO.

In the case where the central atom is less electronegative than the axial atoms, this can be represented schematically as follows:



where ϕ_{X_0} and ϕ_N are the hybrid or the pure orbitals of the axial atoms used to construct the MO, ψ_1 is a bonding MO, ψ_2 a weakly bonding MO with a node in the region of the weaker bond (for the X–A–X fragment, the ψ_2 orbital becomes non-bonding), and ψ_3 an antibonding MO. The filling of ψ_2 with electrons corresponds to the model of hypervalent linkages and distinguishes such linkages from the "normal" bonds for which only bonding MO are filled with electrons. It can be readily shown that the filling of the ψ_1 orbital with electrons in the model of hypervalent linkages ensures the required energy gain in the interaction of three atomic orbitals.

The first evident consequence arising from the model is that the influence of the σ-linked substituent can be transmitted only via the $3p_z$ orbital of the central atom. This explains the *trans*-influence of the substituent characteristic of silatranes. The expression defining the effect of the bonding between the Si and N atoms can be formulated as follows for a three-level system:

$$\Delta E_{SiN} = \beta^2_{Si^0N} \Big/ \left(\alpha^0_{Si} + \frac{\beta^2_{Si^0X^0}}{\alpha^0_{Si} - \alpha^0_X} - \alpha^0_N \right),$$

where α and β are the Coulombic and resonance integrals, subscript 0 refers to the initial atomic levels, and the ratio $\beta^2_{Si^0N}/(\alpha_{Si^0N} - \alpha_{X^0})$ characterises the decrease of the effect of the bonding between the Si and N levels as a result of the X_0–Si interaction.

It follows from this expression that, with increase of the X–Si bond strength, the Si–N interaction in silatranes is weakened. Furthermore, the change in the Si←N bond energy depends significantly also on the electronegativities of the silicon and nitrogen atom (the Coulombic integrals α_{Si} and α_N). The conclusion that the silicon atom is displaced from the equatorial plane formed by the three oxygen atoms on transition from X_0 to X_i is natural. Indeed, the strengthening of one part of the X–Si–N fragment and the weakening of the other constitutes in essence the "expulsion" of the silicon atom from the equatorial plane. The greater the effect of the strengthening (and weakening) of one of the components of the fragment compared with the standard value, the greater should be the displacement Δ from this plane#.

¶The presence of the Si←N bond in the 1-methylsilatrane molecule was also confirmed by the 4NDO method[71].

†Such a "standard" substituent is the $R_3\ddot{N}$ group.

#The sign of Δ depends on the relative values of α_{X_0} and α_{X_i}.

When the contribution of the 3*s* orbital is neglected and for $|\alpha_{X_i}| > |\alpha_{Si}|$, an increase of the electronegativity of the substituent X should weaken the X–Si bond and enhance the Si←N interaction. If $|\alpha_X| < |\alpha_{Si}|$, variation of the substituent X leads to a parallel variation of the X–Si and Si←N bond strengths. Analysis of the experimental data for the steric structure of silatranes[14] fully confirmed the conclusions of Voronkov and coworkers[75]. In agreement with the theory, the weakest Si←N interaction is observed for a silatrane in which the silicon atom is linked to the atom of a transition metal (Pt: $|\alpha_{Pt}| \ll |\alpha_{Si}|$).[16,17] In this molecule the non-valence interactions make the dominant contribution to the stabilisation of the silatrane skeleton. Indeed, the optimum geometry of the silatrane ring in relation to the non-valence interactions, corresponding to a structure without bonding[18], is fairly close to the experimental structure[16,17].

The proposed model readily explains the destabilising resonance§ influence of the *p*- or π-donor Si-substituents in silatrane molecules, which is caused by the filling with electrons of the antibonding level of the hypervalent X–Si–N linkage as a result of which the degree of Si→N bonding diminishes.

The X–Si bond in silatranes is known[8,14,22,64] to be weakened¶, i.e. its length is increased, compared with the corresponding $X-Si_{sp^3}$ bond. This can apparently be accounted for by the fact that the hypervalent linkages are always weaker than the normal covalent bonds. The disposition and filling with electrons of the atomic levels corresponding to the experimental and theoretical results[21], which is illustrated in the diagram, clearly show that the degree of charge transfer from the donor orbital ϕ_N to the $3p_z$ orbital of the silicon atom is less than unity. The Si←N bond strength should increase with increase of the polarity of the bond. As the ionisation potential of the central atom increases, the energy of the bonding orbital falls, i.e. the hypervalent structure in fact becomes less stable (other conditions being equal). Comparison of the ionisation potentials of the carbon and silicon atoms (11.25 and 8.15 eV) explains why it is difficult to obtain carba-atrane†. On this basis, one may expect an increase of the bonding effect when the silicon atom in silatranes is replaced by a germanium or tin atom and also when the nitrogen atom is replaced by a phosphorus atom.

Thus the above investigation shows that the interaction between the silicon and nitrogen atoms in silatranes is due to the hypervalent bonding between these atoms and the substituent at the silicon atom. Despite a number of assumptions, the hypervalent bond model describes more realistically, in our view, the electronic and steric structures of silatranes than the widely held hypothesis of the sp_3d hybridisation of the silicon atom.

---

§This influence has not been established experimentally quite so convincingly as the inductive effect. It has been observed in the analysis of the ^1H NMR and ESCA spectra as well as the kinetics of the hydrolysis of silatranes.

¶In the limiting case which obtains under electron impact, the hypervalent X–Si–N linkage is converted into the usual covalent linkage in the substituted ammonium ion $[\overbrace{Si(OCH_2CH_2)_3N}]^+$ formed.

†A recent analysis[77] demonstrated the possibility of the existence of the stable hypervalent linkage X–C←P.

3. Donor–Acceptor Properties of Silatranes

The study of the mechanism of the hydrolysis of silatranes provided definite ideas about their donor–acceptor properties. The influence of the substituent at the silicon atom on the rate of hydrolysis of silatranes has been studied in both neutral[7,78,79] and in acid media[79–81]. The hydrolysis in a neutral medium is described satisfactorily by a first-order equation. The silatranes investigated can be divided into two reaction series. The first includes 1-alkylsilatranes and the second 1-alkoxy-derivatives. Linear relations between the logarithms of the rate constants for the hydrolytic reactions ($\lg k$) and the inductive constants of the substituent at the nitrogen atom (σ^*) have been observed for both series.

In the reaction series of 1-alkylsilatranes an increase of the inductive constant of the substituent X accelerates the hydrolysis. The high reaction constant $\rho = +4.76$ indicates a high degree of polarity of the transition state in which the silicon atom acquires a considerable negative charge.

The values of $\lg k$ for 1-vinyl- and 1-phenyl-silatranes deviate significantly from the linear correlation plot for 1-alkyl derivatives. This can be explained by the $p\pi-d\pi$ interaction of the above substituents at the silicon atom, which reduces the electron-accepting effect of X. A better explanation, from modern standpoints, consists in π-donation to the antibonding orbital of the hypervalent X–Si←N linkage. The same causes are probably responsible also for the lower than expected (in view of the high electronegativity of the alkoxy-groups) rate constants for the hydrolysis of 1-alkoxysilatranes. The reaction constant $\rho = 2.60$ for these compounds is smaller than for 1-alkylsilatranes. The results led to the conclusion that the rate-limiting stage in hydrolysis in a neutral medium is nucleophilic attack by a water molecule or an OH^- ion on the silicon atom.

The rate of hydrolysis of silatranes in an acid medium[79–81] is considerably higher than in a neutral medium. The influence of the substituent at the silicon atom is also different. With increase of the electronegativity of the latter, the rate constants for the hydrolysis of silatranes decrease appreciably, which made it necessary to assume[79,80] that the rate-limiting stage in the acid hydrolysis of silatranes is electrophilic attack by a hydronium ion on the oxygen atom with simultaneous transfer of the hydration shell to the silicon atom. The subsequent stages of the hydrolysis (in the first place the rupture of the Si–O) bond are probably very fast.

A somewhat different mechanism[82] has been proposed for the acid hydrolysis of the Si-substituted derivatives of tribenzosilatrane $X-\overbrace{Si(OC_6H_4)_3N}$. The protonation of the oxygen atom is fast; on the other hand, the slow stage of the reaction is the dissociation of the Si–O bond in the protonated molecule. In both cases the possibility of the protonation of the nitrogen atom (as the initial and slowest step of the hydrolytic reaction in an acid medium) is rejected owing to its weak nucleophilic properties due to the steric inaccessibility of the LEP. On the other hand, evidence has been obtained[81] showing that the slowest stage of the hydrolytic reaction is the *endo–exo* transition of the silatrane molecule accompanied by the cleavage of the Si←N bond, which is followed by the protonation of the nitrogen atom in the transition state. This evidence is based on the analysis of the kinetic isotope effect observed in the hydrolysis. The proposed mechanism explains naturally the influence of the nature of the substituent at the silicon atom on the rate of the process.

The experimental activation energy for the hydrolysis of 1-phenylsilatrane (22 kcal mol^{-1}) [81] agrees satisfactorily with the Si←N bond energy in 1-hydrosilatrane estimated by the CNDO/2 method[21].

One of the most important pieces of chemical evidence for the involvement of the nitrogen atom in the transannular interaction with the silicon atom and hence for the pentacoordinate state of the latter in silatrane molecules is their inability to form methiodides as well as the low rate of their interaction with perchloric acid[1,6,7,73]. It is therefore not surprising that a number of studies have been made on the possibility of the formation of complexes of silatranes with other electron-accepting reagents. 1:1 complexes with certain Lewis acids ($TiCl_4$, $AlCl_3$) have been obtained for a series of 1-substituted silatranes; the structure of these complexes has been studied by infrared spectroscopy[83]; after the interaction of 1-ethoxysilatrane with $TiCl_4$, it was possible to isolate a 2:1 complex. In the infrared spectra of these complexes the bands assigned previously[1,7,43] to the Si←N coordinate bond persist, while the ν(Si–O) bands undergo a regular displacement. This led to the hypothesis[83] that the nitrogen atom in the silatrane molecule is not involved in the donor–acceptor interaction with Lewis acids. One of the oxygen atoms functions as the nucleophilic centre of the silatrane molecules in the complexes.

The isolation of the pure 1:1 hydrochloride of 1,3,7,10-tetramethylsilatrane, which is unstable in air, and analysis of its infrared spectrum led to the assertion[84] that the nitrogen atom is the centre of coordination with the HCl molecule. Evidence for this has been based on the fact that the infrared spectrum of the hydrochloride contains absorption bands of the stretching vibrations of the hydroxy-groups, which usually appear in the region of 3200–3300 cm^{-1}. This indicates the retention of the Si–O–C bonds in the complex-formation process. A group of bands characteristic of trialkylamine hydrochlorides was observed in the range 2500–2800 cm^{-1}. It was found that in the infrared spectrum of the hydrochloride of 1,3,7,10-tetramethylsilatrane all the absorption bands characteristic of the silatrane itself, including the 560–590 cm^{-1} band, are retained. Since this band has been assigned to the vibrations of the silatrane skeleton[46], its presence in the spectrum has been interpreted[84] as evidence for the retention of this skeleton in the complex. In this connection we may note that there is no absorption at 560–590 cm^{-1} in the infrared spectrum of the platinum derivative, which contains no transannular Si←N bond[16]. It is correct to assume[83] that the presence of the 560–590 cm^{-1} band in the infrared spectra of the complexes of silatranes with Lewis acids is evidence for the retention of the Si←N bond in these compounds. One cannot rule out the possibility that the hydrochloride of 1,3,7,10-tetramethylsilatrane is an oxonium derivative or a clathrate compound.

The ability of the nitrogen atom in certain 1-substituted silatranes to participate in complex formation with tetracyanoethylene (TCE) has been reported[84]. However, later convincing evidence was obtained[81] showing that the nitrogen atoms in silatrane molecules do not interact with TCE. The application of the EPR method and analysis of data published previously[84] established[85] that the absorption bands in the range 20000–25000 cm^{-1}, assigned[84] to the silatrane–TCE complex, are in fact due to the TCE radical-anion (and its conversion product). The formation of the TEC radical-anions is due to the electron transfer from the nitrogen atoms of impurity molecules present in the test substances in very small amounts. Carefully purified 1-alkylsilatranes do not give rise to a colour and EPR signals in systems with TCE.[85]

At the same time, it has been shown by ultraviolet spectroscopy[69] that 1-phenyl- and 1-benzyl-silatranes form charge-transfer complexes with TCE. However, in these two cases the donor centre is the aromatic substituent at the silicon atom. Analysis of the absorption bands in the spectra of these complexes shows convincingly that the silatranyl substituent is a better electron donor than the $Si(OC_2H_5)_3$ group. Silatranes are able to form hydrogen bonds with chloroform[26,52]. The composition of some of these associated species has been established by measuring the dielectric losses[86]; the proton acceptors in these compounds are oxygen atoms.

1-Methylsilatrane is capable of forming complexes with lanthanide shift reagents[87]. The interpretation of the paramagnetic shifts in the ^1H NMR spectrum of 1-methylsilatrane induced by europium trisdipivaloylmethanate [Eu(DPM)$_3$] (a lanthanide shift reagent) was based[88] on a comparison of the relative observed chemical shifts with the values calculated from McConnell's formula[89]. The best agreement (in terms of the *R*-factor) with experiment is obtained on the hypothesis that 90% of the 1-methylsilatrane molecules are involved in coordination with the acceptor via the oxygen atoms, while the remaining 10% are coordinated via the nitrogen atom. The 1-methylsilatrane molecule assumed to be coordinated with the shift reagent via the nitrogen atom should exist in the *endo*-form according to the calculation. However, the electron pair of the nitrogen atom in such a structure is known to be inaccessible to electrophilic attack. We believe that the results of the calculation[88] cannot be regarded as convincing demonstration of the involvement of the nitrogen atom in silatrane molecules in complex formation with Eu(DPM)$_3$. This is due to a number of fundamental difficulties which arise when the method of shift reagents is used in structural chemistry[90,91].

The conclusion that the nitrogen atom in silatranes is able to participate in complex formation was reached also on the basis of the study of the ^1H NMR of certain representatives of this class (X = CH_3, $ClCH_2$, or Cl) in the presence of paramagnetic complexes of $NiCl_2$ or $CoCl_2$ with 1-ethylimidazole[92]. In the systems investigated the induced shifts could be recorded reliably only in the presence of an excess of the paramagnetic complex by a factor of 1.5–2, which indicates an exceptionally low capacity of silatranes for coordination (the addition of individual $NiCl_2$ or $CoCl_2$ salts does not cause any changes in the ^1H NMR spectra of silatranes). It was found that there is a significant upfield shift of the signals due to the CH_2N protons, and not OCH_2 protons, in the ^1H NMR spectra of silatranes under the influence of these paramagnetic complexes. This served as the basis for the assumption that the nitrogen atom is a centre of coordination. However, the shifts induced by the Ni^{2+} and Co^{2+} complexes are largely of the contact type. Consequently, their values depend not only on the geometrical factor but also on the nature of the distribution of spin density in the adducts.

Thus there are at present no convincing grounds for the assertion that the lone electron pair of the nitrogen atom can be involved in the formation of complexes by silatranes with weak Lewis acids.

By virtue of the high dipole moments of silatranes, many of their properties should depend significantly on the polarity of the medium. The mechanism of the influence of the polar solvent reduces to non-specific interactions which induce the formation of solvates and the dissociation of the self-associated silatrane species, which leads ultimately to the perturbation of the most readily polarisable hypervalent X–Si←N linkage.

The phenomenon is illustrated by the recently observed dependence of the stretching vibration frequencies of the Si–H bonds in 1-hydrosilatrane (but not trialkoxysilane) on the solvent polarity and temperature[93]. With increase of the dielectric constant of the medium, the frequencies ν(Si–H) diminish, which corresponds to a weakening of the H–Si bond owing to the enhancement of the interaction between the silicon and nitrogen atoms. A significant influence of the medium on the properties of silatranes has also been observed in the study of the ^{1}H NMR spectra[53].

Further investigation of the interaction in silatrane–solvent systems may throw light also on the hitherto completely obscure problem of the mechanism of the formation of complexes by silatranes.

III. *C*-SUBSTITUTED SILATRANES

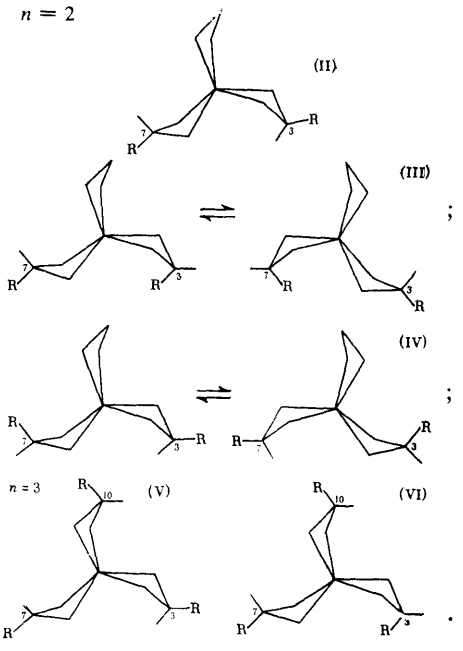
The study of the influence of the substituents R at the carbon atoms of the silatrane skeleton yields interesting information about the steric and electronic structures of silatranes. Successive substitution of the hydrogen atoms in the 3-, 7-, and 10-positions in chloroalkylsilatranes by methyl groups (i.e. R=CH_3) leads to an increase of the dipole moments[27]. It has been suggested that this is due to the conformational distortions of the atrane skeleton induced by the introduction of the methyl groups or by changes in its electronic structure.

At the same time the dipole moment of 1-phenyl-2-homosilatrane $C_6H_5Si(OCH_2CH_2CH_2)(OCH_2)_2N$ hardly changes when methyl groups are introduced into the 8- and 11-positions[94]. The intensity of the $(M-X)^+$ ions in the mass-spectra of 3-mono-, 3,7-di-, and 3,7,10-trimethyl derivatives of 1-chloroalkylsilatranes decreases linearly with increase of the number of methyl groups in the molecule[64]. The authors explained this by the increased strength of the Si–C bond, since, owing to the inductive influence of the *C*-methyl substituents, there is an increase of the electron density at the silicon atom and a weakening of the degree of the transannular interaction of the latter with the nitrogen atom. The ^{35}Cl NQR frequencies for 1-chloroalkyl-3,7-10-trimethylsilatranes are higher than for their *C*-unsubstituted analogues[54]. These data are consistent with the decrease following the introduction of the *C*-methyl group in the electron-donating capacity of the silatrane skeleton, which is caused by the weakening of the Si←N bond. Previously[54] this decrease was attributed to the distortion of the geometry of the silatrane skeleton arising when methyl groups are introduced.

The introduction of methyl groups in the 3-, 7-, and 10-positions in the silatrane skeleton reduces the hydrolysis rate constant[79,81]. This has been explained[79] by the increased order and hence strength of the Si–O bond. Within the framework of the proposed mechanism of the hydrolytic process (with the protonation of oxygen atoms as the rate-limiting stage), this hypothesis appears likely. In terms of the alternative concept (where protonation of the nitrogen atom is the primary step), the observed behaviour cannot be explained[81]. However, on the basis of the proposed mechanism for the hydrolytic reaction[81], one can assume that the introduction of *C*-methyl groups into the silatrane skeleton reduces its conformational mobility, hindering thereby the *endo–exo* isomerisation of the molecule.

As methyl groups accumulate, the intensity of the band in the range 560–590 cm^{-1} increases in the infrared spectra of 3-mono-, 3,7-di-, and 3,7,10-trimethylsilatranes[46]. However, without a correct identification of the band under discussion, it is so far impossible to explain the effect.

According to ^{1}H NMR data, Si-substituted 3-methylsilatranes exist as a single diastereoisomer with a pseudoequatorrial orientation of the substituent[30,52]; Si-substituted 3,7-dimethylsilatranes and 3,7,10-trimethylsilatranes consist of mixtures of the following diastereoisomers[53,95]:



Judging from the spin–spin coupling constants between the protons of the substituted atrane half-rings, all the methyl groups of isomer (V) as well as the 7- and 10-groups of isomer (VI) are oriented pseudoequatorially, while the 3-CH_3 group of isomer (VI) is disposed pseudoaxially. In diastereoisomer (II) both methyl groups are pseudoequatorial, but the substituted atrane half-rings are non-equivalent. On the other hand, in diastereoisomers (III) and (IV) the substituted half-rings are equivalent in pairs owing to the high conformational mobility of these isomers, the conformational changes being accompanied by a rapid *ae–ea* reorientation of the *C*-substituents.

A change in the temperature of solutions of 3,7-dimethyl-, and 3,7,10-trimethylsilatranes in various solvents from −80° to +200 °C does not alter the relative positions of their ^{1}H NMR lines[95]. This shows that the height of the barrier to the conversion of the *C*-substituted rings in silatrane molecules is very small (<2 kcal mol^{-1}). However, the differences between the strain energies of the rings substituted pseudoequatorially and pseudoaxially are fairly large. These two factors fully explain the existence of molecules of 3-methyl-substituted silatranes as well as diastereoisomers (V) and (VI) in a single energetically favourable conformation. The same causes are responsible for the ease of the conformational transitions between the two states (III) and (IV) which are degenerate with respect to energy. Furthermore, the equatorial–axial and not equatorial–equatorial orientation of the 3,7-substituents in isomers (III) and (IV) shows that the non-concerted conversion of the three five-membered rings is forbidden by virtue of the high strain energies of the asymmetric structure. This is confirmed by the results of conformational calculations[20]. Thus the conformational transitions of the silatrane skeleton are collective and take place with retention of C_3 symmetry.

Analogous conclusions were reached[96] in a ^{19}F NMR study of the stereochemistry of the *C*-(trifluoromethyl)silatranes# ($R = CF_3$). Naturally, the strain arising in the axial orientation should influence the extent of the transannular Si←N interaction. The shielding constants for the protons of the substituent at the silicon atom and the ^{29}Si nuclei in the case of *C*-substituted silatranes are greater for the less strained diastereoisomers[53].

The sum total of the data presented above requires a reconsideration of the problem of the influence of *C*-substituents on the spectroscopic and physicochemical properties of silatranes substituted in the 3-, 7-, 10-positions and the formulation of a series of new experimental approaches to its solution. The point is that all the characteristics of 3,7-di- and 3,7,10-tri-substituted silatranes obtained hitherto must be regarded as integral characteristics referring to a mixture of stereoisomers. This constitutes one of the causes of the evident conflict between the conclusions based on the change in the properties of silatranes following their successive *C*-substitution. Hence it is necessary to separate the above mixtures into individual components and to study in detail the physicochemical and spectroscopic properties of the latter. In analysing the results, particular attention must be paid to the stereodynamic characteristics of each isomer§. The solution of the problem formulated here can play a significant role in the practical applications of the silatranes. Data indicating the biological activity of *C*-substituted silatranes already exist[97]. One must assume that their optically active isomers will be still more effective.

---o0o---

The structural studies on silatranes make a fundamental contribution to the development of a general theory of the structure of organic compounds containing the atoms of pentacoordinate silicon and its neighbours in the Periodic System.

Analysis of the results of physicochemical studies on silatranes indicates a significant influence of the hypervalent—Si←N linkage on their steric and electronic structures and in many instances also on their reactivity. At the same time, the extensive experimental data accumulated point to an urgent need for the solution of a number of new vital problems in the structural chemistry of silatranes. These involve in the first place a theoretical study of the structure and spectroscopic characteristics, an experimental determination of the thermodynamic parameters, and a systematic study of the reactivity and of the influence of the medium on the physical and chemical properties of silatranes.

The solution of all these problems will not only prove to be extremely useful for the theory of chemical structure and reactivity but will also permit a deeper understanding of the nature of the biological activity of silatranes.

During the preparation of the manuscript for the press, a number of new studies, extending the available ideas about silatranes, were published. A monograph[97] and a brief review[98] devoted to silatranes appeared. The concept of the hypervalent nature of the bonding in the axial fragments of silatrane molecules has been confirmed[99] by the CNDO/2 method (in terms of two parametrisations) in relation to 1-hydro- and 1-fluoro-silatranes. The constancy of the hypervalent X–Si←N bond order when the nature of the substituent X is varied has been demonstrated[33]. An increase of the degree of Si←N interaction in silatrane molecules with increasing proton-donating capacity, polarity, and polarisability of the medium has been observed by infrared spectroscopy[100] and ^{15}N and ^{29}Si NMR.[101,102] The solvent effects diminish with increasing strength of the Si←N bond under the influence of the 1-substituent[102]. According to ^{29}Si NMR data for the solid state[103], the influence of the crystal field on the state of the Si←N bond in silatrane molecules does not exceed the effect of a highly polar solvent. The influence of the nature of the 1-substituent in silatranes on the ^{15}N NMR chemical shifts has been studied[104,105]. The spin–spin interaction between the ^{15}N and ^{29}Si nuclei has been observed[104] in relation to 1-chloromethylsilatrane. The relaxation times of the ^{29}Si and ^{13}C nuclei have been studied by NMR.[106] The pathways leading to the dissociative ionisation of 1-substituted silatranes on electron impact have been examined[107]. Arguments supporting the manifestation of the ν(Si←N) stretching vibration band in the infrared spectra at frequencies below 400 cm^{-1} have been obtained[108]. It has been shown by EPR [109] that unstable silatranyl radicals are formed in the oxidation-reduction reactions of 1-hydrosilatrane.

#For these diastereoisomers, a further spin–spin interaction between the fluorine nuclei separated by eight valence bonds was observed for the first time.

§This must be taken in account also in a more detailed analysis of the known properties of *C*-unsubstituted and 3-substituted silatranes.

REFERENCES

1. M.G.Voronkov, Pure Appl.Chem., **13**, 35 (1966).
2. M.G.Voronkov, Vestnik Akad.Nauk SSSR, **38**, No.10, 48 (1968).
3. M.G.Voronkov, E.Zelcans, and E.Lukevics, "Kremnii i Zhizn'"" (Silicon and Life), Izd.Zinatne, Riga, 1978.
4. M.G.Voronkov, in "Biochemistry of Silicon and Related Problems", Plenum Press, New York–London, 1978, p.395.
5. A.B.Finestone, US P.2953545 (1960); Chem.Abs., **55**, 4045 (1961).
6. C.L.Frye, G.E.Vogel, and I.A.Hall, J.Amer.Chem. Soc., **83**, 996 (1961).
7. G.Zelcans, Candidate's Thesis, Institute of Organic Synthesis, Academy of Sciences of Latvian SSR, Riga, 1967.
8. A.Kemme, J.Bleidelis, V.A.Pestunovich, V.P.Baryshok, and M.G.Voronkov, Dokl.Akad.Nauk SSSR, **243**, 688 (1978).
9. A.Kemme, J.Bleidelis, V.M.D'yakov, and M.G.Voronkov, Zhur.Strukt.Khim., **16**, 914 (1975).
10. A.Kemme, J.Bleidelis, V.M.D'yakov, and M.G.Voronkov, Izv.Akad.Nauk SSSR, Ser.Khim., 2400 (1976).
11. J.W.Turley and F.P.Boer, J.Amer.Chem.Soc., **91**, 4129 (1969).
12. J.W.Turley and F.P.Boer, J.Amer.Chem.Soc., **90**, 4026 (1968).
13. L.Parkanyi, K.Simon, and J.Nagy, Acta Cryst., **30B**, 2328 (1974).
14. L.Parkanyi, J.Nagy, and K.Simon, J.Organometal. Chem., **101**, 11 (1975).

15. A.Kemme, Candidate's Thesis, Institute of Organic Synthesis, Academy of Sciences of Latvian SSR, Riga, 1977.
16. C.Eaborn, K.J.Odell, A.Pidcock, G.R.Scollary, J.J.Daly, and F.Sanz, J.Chem.Soc.D, 2051 (1974). [This reference appears to be in error: it refers to a paper by Daly and Sanz only (Ed. of Translation)].
17. G.R.Scollary, Austral.J.Chem., **30**, 1007 (1977).
18. M.G.Voronkov, V.V.Keiko, V.F.Sidorkin, V.A.Pestunovich, and G.Zelcans, Khim.Geterotsikl. Soed., 613 (1974).
19. M.G.Voronkov, V.F.Sidorkin, V.A.Shagun, V.A.Pestunovich, and G.Zelcans, Khim.Geterotsikl. Soed., 715 (1975).
20. V.F.Sidorkin, Z.A.Shagun, V.A.Pestunovich, and M.G.Voronkov,Khim.Geterotsikl.Soed., 1347 (1976).
21. V.F.Sidorkin, V.A.Pestunovich, V.A.Shagun, and M.G.Voronkov, Dokl.Akad.Nauk SSSR, **233**, 386 (1977).
22. J.Bleidelis, A.Kemme, G.Zelcans, and M.G.Voronkov, Khim.Geterotsikl.Soed., 617 (1973).
23. M.G.Voronkov and G.Zelcans, Geterotsikl.Soed., 51 (1962).
24. D.Schmid, Z.anorg.Chem., **425**, 17 (1976).
25. M.G.Voronkov, I.Mazeika, and G.Zelcans, Khim. Geterotsikl.Soed., 58 (1965).
26. V.A.Chetverikova, V.A.Kogan, G.Zelcans, M.G.Zoronkov, and O.A.Osipov, Khim.Geterotsikl. Soed., 446 (1969).
27. E.A.Ishmaeva, O.A.Samarina, V.M.D'Yakov, M.G.Voronkov, and A.N.Pudovik, Dokl.Akad.Nauk SSSR, **222**, 876 (1975).
28. M.G.Woronkow, G.I.Seltschan, A.Lapsina, and W.A.Pestunowitsch, Z.Chem., **8**, 214 (1968).
29. V.A.Pestunovich, M.G.Voronkov, G.Zelcans, E.Lukevics, L.Liberts, A.N.Egorochkin, and A.I.Burov, Khim.Geterotsikl.Soed., **2**, 339 (1970).
30. V.A.Pestunovich, M.G.Voronkov, G.Zelcans, A.Lapsina, E.Lukevics, and L.Liberts, Khim. Geterotsikl.Soed., 348 (1970).
31. K.Ruedenberg, "The Physical Nature of the Chemical Bond" (Translated into Russian), Izd.Mir, Moscow, 1964.
32. I.B.Bersuker, "Elektronnoe Stroenie i Svoistva Koordinatsionnykh Soedinenii" (The Electronic Structure and Properties of Coordination Compounds), Izd.Khimiya, Leningrad, 1976, p.7.
33. V.A.Pestunovich, V.F.Sidorkin, O.B.Dogaev, and M.G.Voronkov, Dokl.Akad.Nauk SSSR (in the press).
34. P.Hencsei, "Conference on Advances in Elementoorganic Chemistry", Abstracts of Papers, Liblice, 1977, p.7.
35. V.A.Pestunovich, V.F.Sidorkin, S.N.Tandura, and M.G.Voronkov, "Conference on Advances in Elementoorganic Chemistry", Abstracts of Papers, Liblice, 1977, p.C-19.
36. A.T.Shuvaev, A.P.Zemlyanov, Yu.V.Kolodyazhnyi, O.A.Osipov, V.N.Eliseev, and M.M.Morgunova, Zhur.Strukt.Khim., **15**, 433 (1974).
37. R.C.Gray and D.M.Hercules, Inorg.Chem., **16**, 1426 (1977).
38. S.Cradock, E.A.V.Ebsworth, and J.B.Muiry, J.Chem.Soc.D, 25 (1975).
39. A.P.Zemlyanov, A.T.Shuvaev, V.V.Krivitskii, and M.G.Voronkov, Izv.Akad.Nauk SSSR, Ser.Fiz., **36**, 255 (1972).
40. A.P.Zemlyanov, V.V.Krivitskii, and A.T.Shuvaev, Izv.Zys.Ucheb.Zaved., Fizika, **103**, 149 (1970).
41. V.A.Petukhov, L.V.Gudovich, G.Zelcans, and M.G.Voronkov, Khim.Geterotsikl.Soed., 968 (1969).
42. M.G.Voronkov, Yu.L.Frolov, O.A.Zasyadko, and I.S.Emel'yanov, Dokl.Akad.Nauk SSSR, **213**, 1315 (1973).
43. Yu.B.Egorov, M.G.Voronkov, T.B.Lutsenko, and G.Zelcans, Khim.Geterotsikl.Soed., 24 (1966).
44. E.E.Shestakov, M.G.Voronkov, V.O.Reikhsfel'd, and G.Zelcans, Zhur.Obshch.Khim., **43**, 308 (1973).
45. E.E.Shestakov, Candidate's Thesis, Leningrad Technological Institute, 1973.
46. M.G.Voronkov, Yu.L.Frolov, E.I.Brodskaya, S.G.Shevchenko, V.M.D'yakov, and M.S.Sorokin, Dokl.Akad.Nauk SSSR, **228**, 636 (1976).
47. S.G.Shevchenko, E.I.Brodskaya, Yu.L.Frolov, V.P.Baryshok, V.M.D'yakov, and M.G.Voronkov, "Tezisy Dokladov I Vsesoyuznogo Simpoziuma 'Stroenie i Reaktsionnaya Sposobnost' Kremnii-organicheskikh Soedinenii', Irkutsk, 1977" (Abstracts of Reports of the Ist All-Union Symposium on 'The Structure and Reactivity of Organosilicon Compounds', Irkutsk, 1977), p.51.
48. V.P.Anosov, Yu.A.Pentin, A.G.Popov, V.V.Antipina, T.L.Krasnova, and E.A.Chernyshev, "Tezisy Dokladov I Vsesoyuznogo Simpoziuma 'Stroenie i Reaktsionnaya Sposobnost' Kremnii-organicheskikh Soedinenii', Irkutsk, 1977" (Abstracts of Reports of the Ist All-Union Symposium on 'The Structure and Reactivity of Organosilicon Compounds', Irkutsk, 1977), p.57.
49. M.G.Voronkov, V.P.Baryshok, V.A.Pestunovich, S.N.Tandura, T.I.Safonova, and Z.N.D'yakov, Izv.Akad.Nauk SSSR, Ser.Khim., 1665 (1979).
50. M.V.Vol'kenshtein, L.A.Gribov, M.A.El'yashevich, and B.N.Stepanov, "Kolebaniya Molekul" (Molecular Vibrations), Izd.Nauka, Moscow, 1972, p.486.
51. C.L.Frye, G.A.Vincent, and W.A.Finzel, J.Amer. Chem.Soc., **93**, 6805 (1971).
52. V.A.Pestunovich, Candidate's Thesis, Institute of Organic Synthesis, Academy of Sciences of Latvian SSR, Riga, 1970.
53. S.N.Tandura, Candidate's Thesis, Institute of Organic Chemistry, Siberian Division of the USSR Academy of Sciences, Irkutsk, 1977.
54. M.G.Voronkov, V.P.Feshin, V.M.D'yakov, L.S.Romanenko, V.P.Baryshok, and M.V.Sigalov, Dokl.Akad.Nauk SSSR, **223**, 1133 (1975).
55. V.A.Pestunovich, M.G.Voronkov, V.F.Sidorkin, B.Kh.Kopylovskaya, V.A.Shagun, and G.Zelcans, Khim.Geterotsikl.Soed., 1052 (1975).
56. V.A.Pestunovich, Yu.Yu.Popel, E.Lukevics, L.Liberts, and M.G.Voronkov, Izv.Akad.Nauk Latv. SSR, Ser.Khim., 365 (1973).
57. M.Witanowski, L.Stefaniak, H.Janiszewski, M.G.Voronkov, and S.N.Tandura, Bull.Acad.Polon. Sci., Ser.Sci.Chim., 281 (1976).
58. V.A.Pestunovich, S.N.Tandura, M.G.Voronkov, V.P.Baryshok, G.I.Zelchan, V.J.Glukhikh, G.Engelhardt, and M.Witanowski, Spectroscopy Letters, **11**, 339 (1978).
59. V.A.Pestunovich, S.N.Tandura, M.G.Voronkov, G.Engelhardt, E.Lippmaa, T.Pehk, V.F.Sidorkin, G.Zelcans, and V.P.Baryshok, Dokl.Akad.Nauk SSSR, **240**, 914 (1978).

60. J.Schraml and J.M.Bellama, "Determination of Organic Structure by Physical Methods", Acad.Press, New York–London, 1976, Vol.6, p.203.
61. G.Engelhardt, R.Radeglia, H.Jancke, E.Lippmaa, and M.Magy, Org.Magnet.Resonance, **5**, 561 (1973).
62. O.A.Samarina, A.N.Vereshchagin, E.A.Ishmaeva, S.G.Vul'fson, V.M.D'yakov, V.P.Baryshok, M.G.Voronkov, and A.N.Pudovik, Izv.Akad.Nauk SSSR, Ser.Khim., 785 (1977).
63. O.A.Varnavskaya, T.A.Ishmaeva, V.M.D'yakov, N.S.Sorokin, M.G.Voronkov, and A.N.Pudovik, Izv.Akad.Nauk SSSR, Ser.Khim., 1671 (1977).
64. R.Müller and H.F.Uref, Z.anorg.Chem., **368**, 113 (1969).
65. M.G.Voronkov, I.S.Emel'yanov, V.Yu.Vitkovskii, L.V.Kapranova, V.M.D'Yakov, and V.P.Baryshok, Zhur.Obshch.Khim., **47**, 382 (1977).
66. I.P.Biryukov and M.G.Voronkov, Coll.Czech.Chem. Communs., **32**, 830 (1967).
67. V.P.Feshin, M.G.Voronkov, V.D.Simonov, V.Z.Estrina, and Ya.B.Yasman, Dokl.Akad.Nauk SSSR, **218**, 1400 (1974).
68. J.Lipowitz, J.Amer.Chem.Soc., **94**, 1582 (1972).
69. A.Daneshrad, C.Eaborn, and D.R.M.Walton, J.Organometall.Chem., **85**, 35 (1975).
70. V.I.Glukhikh, S.N.Tandura, G.A.Kuznetsova, V.V.Keiko, V.M.D'yakov, and M.G.Voronkov, Dokl.Akad.Nauk SSSR, **239**, 1129 (1978).
71. G.I.Kartsev and Zh.E.Grabovskaya, "Tezisy Dokladov I Vsesoyuznogo Simpoziuma 'Stroenie i Reaktsionnaya Sposobnost' Kremniiorganicheskikh Soedinenii', Irkutsk, 1977" (Abstracts of Reports at the Ist All-Union Symposium on 'The Structure and Reactivity of Organosilicon Compounds', Irkutsk, 1977), p.15.
72. V.F.Sidorkin, V.A.Pestunovich, V.A.Shagun, and M.G.Voronkov, "Tezisy Dokladov I Vsesoyuznogo Simpoziuma 'Stroenie i Reaktsionnaya Sposobnost' Kremniiorganicheskikh Soedinenii', Irkutsk, 1977" (Abstracts of Reports at the Ist All-Union Symposium on 'The Structure and Reactivity of Organosilicon Compounds', Irkutsk, 1977), p.37.
73. I.I.Solomennikova, G.Zelcans, and E.Lukevics, Khim.GeterotsikI.Soed., 1299 (1977).
74. D.A.Bochvar, N.P.Gambaryan, and L.M.Epshtein, Uspekhi Khim., **45**, 1316 (1976)[Russ.Chem.Rev., No.7 (1976)].
75. V.F.Sidorkin, V.A.Pestunovich, and M.G.Voronkov, Dokl.Akad.Nauk SSSR, **235**, 1363 (1977).
76. J.J.Musher, Angew.Chem., Int.Ed., **8**, 54 (1969).
77. M.G.Voronkov, V.F.Sidorkin, V.A.Pestunovich, and V.A.Shagun, "Tezisy Dokladov Mezhdunarodnoi Konferentsii po Kvantovoi Khimii, Biologii i Farmakologii, Kiev, 1978" (Abstracts of Reports at the International Conference on Quantum Chemistry, Biology, and Pharmacology, Kiev, 1978), Part III, p.9
78. M.G.Voronkov and G.Zelcans, Khim.Geterotsikl. Soed., 450 (1969).
79. M.G.Voronkov, I.S.Emel'yanov, V.M.D'yakov, V.Yu.Vitkovskii, L.V.Kapranova, and V.P.Baryshok, Khim.Geterotsikl.Soed., 1344 (1976).
80. M.G.Voronkov, I.S.Emel'yanov, G.Zelcans, V.M.D'yakov, and I.G.Kuznetsov, Khim.Geterotsikl. Soed., 35 (1975).
81. A.Daneshrad, C.Eaborn, R.Eidenschink, and D.R.M.Walton, J.Organometall.Chem., **90**, 139 (1975).
82. R.E.Timms, J.Chem.Soc.A, 1969 (1971).
83. V.A.Chetverikova, V.A.Kogan, G.Zelcans, O.A.Osipov, and M.G.Voronkov, Zhur.Obshch. Khim., **40**, 1382 (1970).
84. M.G.Voronkov, S.G.Shevchenko, E.I.Brodskaya, Yu.L.Frolov, V.P.Baryshok, I.N.M.Deriglazov, E.S.Deriglazova, and V.M.D'yakov, Dokl.Akad. Nauk SSSR, **230**, 627 (1976).
85. V.A.Pestunovich, L.P.Petukhov, T.I.Vakul'skaya, V.K.Turchaninov, V.P.Baryshok, Yu.L.Frolov, and M.G.Voronkov, Izv.Akad.Nauk SSSR, Ser. Khim., 1470 (1978).
86. V.A.Chetverikova, A.S.Gritsenko, V.A.Kogan, Yu.V.Kolodyazhnyi, O.A.Osipov, G.Zelcans, and M.G.Voronkov, Zhur.Obshch.Khim., **40**, 1285 (1970).
87. V.K.Voronov, Izv.Akad.Nauk SSSR, Ser.Khim., 2110 (1976).
88. V.K.Voronov, V.V.Keiko, V.P.Baryshok, V.M.D'yakov, and M.G.Voronkov, Dokl.Akad.Nauk SSSR, **236**, 147 (1977).
89. H.M.McConnell and R.E.Robertson, J.Chem.Phys., **29**, 1361 (1958).
90. V.K.Voronov, V.V.Keiko, and T.E.Moskovskaya, Zhur.Strukt.Khim., **18**, 917 (1977).
91. J.Reuben, Progress in NMR Spectroscopy, **9**, 1 (1973).
92. V.K.Voronov, M.G.Voronkov, V.M.D'yakov, and V.P.Baryshok, Izv.Akad.Nauk SSSR, Ser.Khim., 1457 (1978).
93. M.G.Voronkov, E.I.Brodskaya, P.Raich, S.G.Shevchenko, V.P.Baryshok, and Yu.L.Frolov, Dokl.Akad.Nauk SSSR, **241**, 1117 (1978).
94. I.S.Yankovska, I.I.Solomennikova, I.Mazeika, G.Zelcans, and E.Lukevics, Izv.Akad.Nauk Latv. SSR, Ser.Khim., 366 (1975).
95. S.N.Tandura, V.A.Pestunovich, M.G.Voronkov, G.Zelcans, V.P.Baryshok, and Yu.A.Lukina, Dokl. Akad.Nauk SSSR, **235**, 406 (1977).
96. S.N.Tandura, V.A.Pestunowich, V.I.Glukhikh, V.P.Baryschok, and M.G.Voronkov, Spectroscopy Letters, **10**, 163 (1977).
97. M.G.Voronkov and V.M.D'yakov, "Silatrany" (Silatranes), Izd.Nauka, Novosibirsk, 1978.
98. I.I.Solemennikova, G.Zelcans, and E.Lukevics, Khim.Geterotskl.Soed., 1299 (1977).
99. V.F.Sidorkin, Candidate's Thesis, Institute of Organic Chemistry of the Siberian Division of the USSR Academy of Sciences, Irkutsk, 1978.
100. M.G.Voronkov, E.I.Brodskaya, P.Reich, S.G.Shevchenko, V.P.Baryshok, and Yu.L.Frolov, J.Organometall.Chem., **164**, 35 (1979).
101. V.A.Pestunovich, S.N.Tandura, B.Z.Shterenberg, V.P.Baryshok, and M.G.Voronkov, Izv.Akad.Nauk SSSR, Ser.Khim., 2653 (1978).
102. V.A.Pestunovich, S.N.Tandura, B.Z.Shterenberg, V.P.Baryshok, and M.G.Voronkov, "Tezisy Dokladov Vsesoyuznoi Konferentsii 'Spektroskopiya YaMR Tyazhelykh Yader Elementoorganicheskikh Soedinenii', Irkutsk, 1979" (Abstracts of Reports at the All-Union Conference on 'The Spectroscopy of the NMR of Heavy Nuclei of Organoelemental Compounds', Irkutsk, 1979), p.34.
103. M.Ya.Myagi, A.D.Samson, E.Lippmaa, V.A.Pestunovich, S.N.Tandura, B.Z.Shterenberg, and M.G.Voronkov, Dokl.Akad.Nauk SSSR (in the Press).
104. E.Liepins, I.Birgele, G.Zelcans, and E.Lukevics, Zhur.Obshch.Khim., **49**, 1537 (1979).

105. V.A.Pestunovich, S.N.Tandura, B.Z.Shterenberg, Z.P.Baryshok, and M.G.Voronkov, Izv.Akad.Nauk SSSR, Ser.Khim., 2159 (1979).
106. R.K.Harris, J.Jones, and S.Ng, J.Magn.Res., **30**, 521 (1978).
107. M.G.Voronkov, V.Yu.Vitkovskii, and V.P.Baryshok, Izv.Akad.Nauk SSSR, Ser.Khim., 626 (1979).
108. V.P.Anosov, Candidate's Thesis, Moscow State University, 1979.
109. M.G.Voronkov, L.P.Petukhov, T.I.Vakul'skaya, V.P.Baryshok, S.N.Tandura, and V.A.Pestunovich, Izv.Akad.Nauk SSSR, Ser.Khim., 1665 (1979).

Irkutsk Institute of Organic Chemistry, Siberian Division of the USSR Academy of Sciences

Translated from *Uspekhi Khimii*, 49, 814-847 (1980) U.D.C. 547.836.3:547.75

Advances in the Chemistry of Azaindoles

L.N.Yakhontov and A.A.Prokopov

The results of research into the chemistry of azaindoles during the last ten years are examined and the advances in the development of new methods for the synthesis and the study of the chemical and physicochemical characteristics of the behaviour of azaindole systems containing condensed rings with an excess and a deficiency of π-electrons are discussed. The studies on the nature of the biological activity of various derivatives of isomeric azaindoles are summarised.
The bibliography includes 267 references.

CONTENTS

I. Introduction 428
II. Methods of synthesis of azaindole structures 428
III. Physicochemical studies on azaindoles 433
IV. Synthetic studies based on azaindoles 435
V. Biological properties of azaindole derivatives 439

I. INTRODUCTION

As a result of vigorous research by Soviet and foreign investigators, new significant results have been obtained in the chemistry of azaindoles during the ten years which have elapsed since the publication of two previous reviews on this field[1,2]. The methodological possibilities of the synthesis of azaindole structure have greatly expanded and the study of the characteristics of the structure of azaindoles compared with indoles revealed new chemical transformations (the cleavage of the N-N bond in hydrazones with simultaneous alkylation of the nitrogen atom[3-5], etc), which are outside the framework of the problem under consideration.

Azaindoles proved to be convenient models for the study of the mutual influence in condensed systems of *N*-heteroaromatic rings with opposite shifts of the π-electron density within each ring—a problem which is of general interest for the chemistry of heterocyclic compounds and theoretical organic chemistry.

Studies on the tautomerism of hydroxy-, amino-, and acylamino-azaindoles[6] served as the starting point of the investigation of a number of general problems of tautomeric equilibria involving *N*-heteroaromatic compounds[7-10], while consideration of the protonation of azaindoles showed that these compounds are effective models for a more detailed study of the mechanisms of protolytic equilibria[11-13].

Studies on the interrelations between tryptophan, heteroauxin, and other biologically important indole compounds, on the one hand, and their 7-aza-analogues on the other, in biochemical processes have been greatly expanded and carried out in greater depth. The observation of a high activity of new antibiotics—tubercidin, toyocamycin, and sangivamycin—which are *N*-glycosylated derivatives of diazaindoles[14], stimulated research into the synthesis and activities of *N*-glycosylated indoles as the antimetabolites in the metabolism of nucleic acids[15,16].

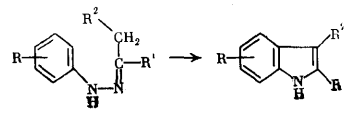
The above factors as well as the psychotropic and cardiovascular activities of a wide variety of synthetic azaindole derivatives, discovered in recent years, led to an extensive development of synthetic research into this series of compounds. Chemical and biochemical investigations in the field of porphobilinogens—derivatives of azaindoles linked to porphyrins, protoporphyrins, and their analogues, have been prosecuted vigorously[17-19].

Within the framework of a single review, it is difficult to cover the entire wide range of problems associated with azaindoles and we therefore decided to disregard in the present review studies on condensed azaindole systems (a small section dealing with the formation of new condensed heterocyclic systems based on 7-azaindole derivatives is an exception) as well as studies on fully or partly hydrogenated azaindoles (with the exception of azaindolines and systems in which aromaticity breaks down as a result of tautomerism). The studies on the chemistry and biology of azaindoles published up to 1967 and discussed in earlier reviews[1,2] are quoted in exceptional instances where it is necessary to describe the general characteristics of the state of the problem.

II. METHODS OF SYNTHESIS OF AZAINDOLE STRUCTURES

1. Syntheses Based on Pyridylhydrazines

The attempts to apply to the series of azoindoles the Fischer reaction, on which one of the main methods for the synthesis of indole derivatives is based[20], yielded few positive results under the usual conditions of acid catalysis:

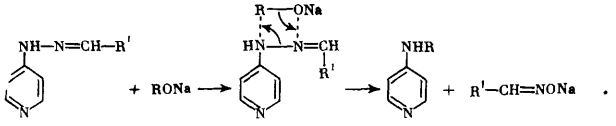


azaindole derivatives were isolated in low yields or were not obtained at all, owing to the relative inertness of the pyridine ring with respect to electrophilic attack on the carbon atoms and the ease of such attack on the pyridine nitrogen atom[21]. Modification of the reaction conditions, involving a transition to "non-catalytic" thermal cyclisation, extended somewhat the possibilities of the method[22]. Thus the 4-pyridylhydrazones of isobutyraldehyde and ethyl methyl ketone were converted into 2,3-dimethyl-5-azaindole on being refluxed in diethylene glycol, while the 4-pyridylhydrazones of propionaldehyde and 2-methylbutyraldehyde were converted into 3-methyl- and 2-ethyl-3-methyl-5-azaindoles[23-25].

1,2-Dialkyl (or-diaryl)-4-methyl-7-azaindoles have been obtained from 4-methyl-2-pyridylhydrazones of propionaldehyde, phenylacetaldehyde, acetophenone, and deoxybenzoin[26], while the analogous 4-azaindole derivatives have been synthesised from 3-pyridylhydrazones of propionaldehyde, ethyl methyl ketone, acetophenone, and certain others[25]. 4-Substituted 5-azaindoles have been synthesised on the basis of 2-hydroxy-6-methyl-4-pyridylhydrazine[27].

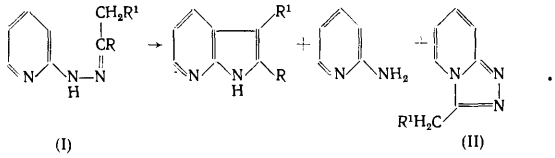
Studies designed to optimise the conditions of the "normal" Fischer reaction in the synthesis of azaindoles have not ceased either. It has been established[28-35] that the yields of the "normal" products of the conversion of 2- 4-pyridylhydrazines by the Fischer reaction vary within wide limits, depending on the nature of the initial hydrazine and that of the substituents in the hydrazine component, as well as the structure of the carbonyl component and the catalyst employed. The introduction of electron-donating substituents into the pyridine ring facilitates the "normal" Fischer cyclisation; on the other hand, electron-accepting groups hinder this process and promote an "anomalous" course of the reaction with formation of aminopyridines of products of cyclisation via the pyridine nitrogen atom.

It has been possible to carry out the Fischer reaction in the presence of not only acid but also alkaline catalysts[34,35]. In the course of this research a new type of cleavage of the N-N bond in isomeric 2-, 3-, and 4-pyridylhydrazones under the influence of alkali alkoxides was discovered; it results in the formation of monoalkylaminopyridines and *syn*-oximes of the carbonyl components of the hydrazones[4,35]:



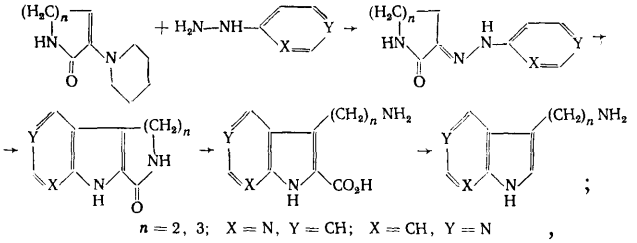
The use of aromatic aldehydes as the carbonyl component in those cases where the "normal" course of the Fischer reaction becomes impossible led to the development of a new preparative method of synthesis of *N*-monoalkylaminopyridines[4,36].

Azaindole structures are formed also in the Fischer cyclisation under the conditions of high-temperature heterogeneous catalysis[37,38]. 7-Azaindole and its 2-methyl- and 2,3-dimethyl-derivatives have been obtained from the 2-pyridylhydrazones of acetaldehyde, acetone, and ethyl methyl ketone (I) by the above method in the presence of alumina. The reaction was accompanied by the formation of 2-aminopyridine and the product of the cyclisation via the pyridine nitrogen—3-methyl-*s*-triazolo[4,3-*a*]pyridine (II).



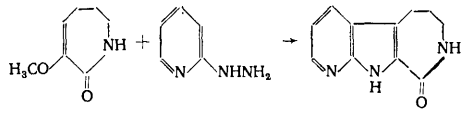
(I) (II)

The synthesis of 5- and 7-azatryptamines and 5- and 7-azahomotryptamines from α- or γ-pyridylhydrazines and lactam α-enamines[39] via the mechanism



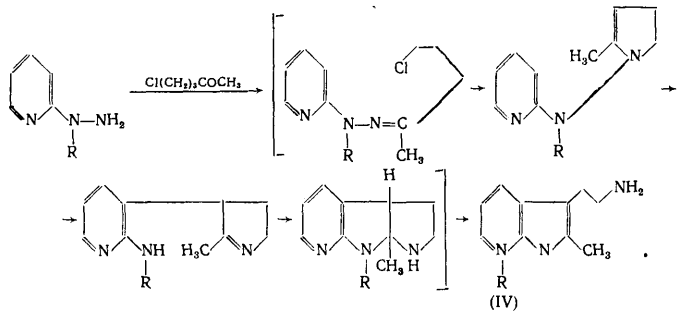
$n = 2, 3$; X = N, Y = CH; X = CH, Y = N

has been described. The use of pyridylhydrazine and 3-methoxy-2-oxo-2*H*,1,5,6,7-tetrahydroazepine (III) in the Fischer reaction yielded the new system of 1-oxo-9-aza-1*H*,2,3,4,5-tetrahydrazepine[3,4,-*b*]indole[40]:



(III)

The synthesis of 2-methyl-7-azatryptamine (IV, R = H) and 1,2-dimethyl-7-azatryptamine (IV, R = CH_3) has been achieved[41,42] by the reaction of 2-pyridylhydrazine with γ-chloropropyl methyl kentone:

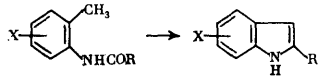


(IV)

2. Syntheses Based on *o*-Nitro- or *o*-Acylamino-picolines and Their Derivatives

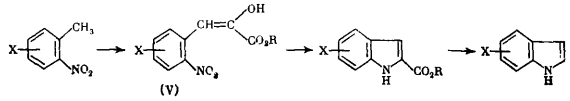
This group of methods includes primarily the Madelung and Reissert reactions which are widely used in the chemistry of indoles.

The Madelung synthesis, which consists in the cyclisation of *o*-acylaminomethyl derivatives of aromatic compounds, was of the greatest importance in the synthesis of azaindole compounds until the last decade:



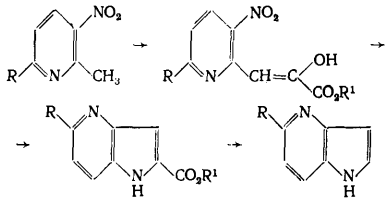
Unsubstituted 4-, 5-, and 7-azaindoles and some of their alkyl derivatives have been synthesised with the aid of this reaction[1]. However, during the last 10 years the Madelung method has not been specially developed for the synthesis of azaindoles owing to inadequate yields and the limited range of substituents which can be introduced into the azaindole system. Among the studies carried out in this field mention should be made of the confirmation[26] of the superiority of sodium *N*-methylanilide over sodium ethoxide as the catalyst in the synthesis of 2-methyl, 2-phenyl-, and 2-pyridyl-7-azaindoles, which agrees well with the hypothesis[43] concerning the roles of amidines as intermediates in the Madelung reaction. The 2-phenyl derivatives of 4-, 5-, 6-, and 7-azaindoles have been synthesised in low yields by the cyclisation of *o*-benzamidopicolines under the conditions of alkaline catalysis[44].

The Reissert method, which consists in the condensation of *o*-nitromethyl derivatives of aromatic compounds with diethyl oxalate, further reductive cyclisation of the intermediates (V) followed by the hydrolysis of indole-2-carboxylic acid esters, and decarboxylation has found extremely limited applications in the series of azaindoles[2]:



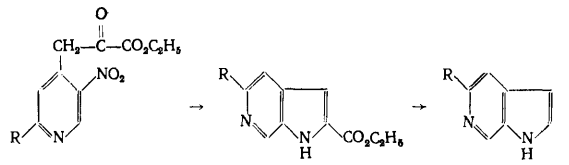
(V)

It was not until 1968 that the Reissert method began to be used successfully[45-48] in preparative synthesis of 4-azaindole and 5-alkoxy-derivatives:

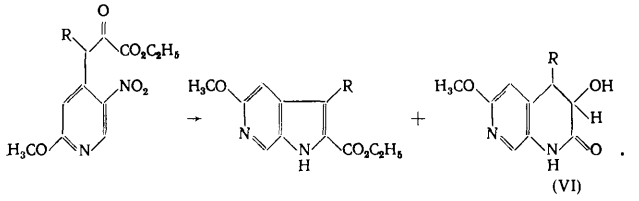


The greatest difficulty in this synthesis was the decarboxylation of 4-azaindole-2-carboxylic acids, for which satisfactory conditions could not be found initially[46]. Later a convenient method was developed[45,47,48] for the direct elimination of the carboxy-group by refluxing the acids in biphenyl in the presence of copper bronze.

The Reissert method has been used widely also in the synthesis of 6-azaindole derivatives[17,18,46,49,50]:

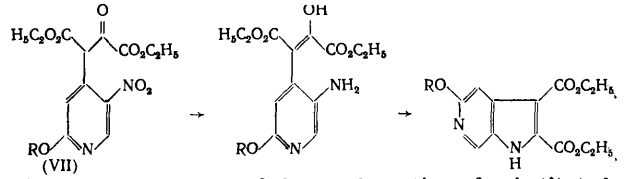


The presence of substituents in the α-methylene group of the side chain complicates the process: together with 6-azaindole derivatives, partly hydrogenated 1,7-naphthyridines (VI) are produced[51]:



(VI)

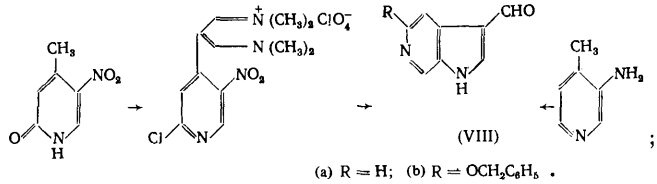
The reduction of the diethyl esters (VII) leads to the preferential formation of 3-aminopyridine derivatives, which are converted into 2,3-diethoxycarbonyl-6-azaindoles in the presence of phosphoryl chloride[51]:



(VII)

Among the products of the condensation of substituted 2-chloro-3-nitropyridine with malonic[52] or cyanoacetic[53,54] esters, 4-azaoxindole and its derivatives were synthesised.

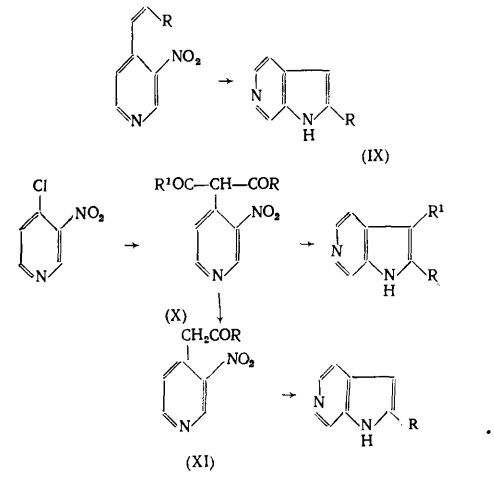
The synthesis of 3-formyl-6-azaindole (VIIIa) [55] and its 5-benzyloxy-derivative (VIIIb) [9] has been achieved in low yields under the conditions of the Wilsmeyer reaction:



(VIII)

(a) R = H; (b) R = $OCH_2C_6H_5$.

2-Substituted 6-azaindoles (IX), R = alkyl or heteroaryl, have been synthesised in yields of 12–22% by the reductive cyclisation of 3-nitro-4-vinylpyridines with triethyl phosphite[44]:

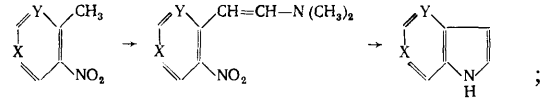


(IX)

(XI)

Various 2-substituted and 2,3-disubstituted 6-azaindoles have been synthesised by the reaction of 4-chloro-3-nitropyridine with β-dicarbonyl compounds (malonic, acetoacetic, and benzoylacetic ester, etc) or with cyanoacetic ester followed by reductive cyclisation of compounds (X) obtained or their reaction products (XI).[52,56-58]

The use of condensation of *o*-nitropicolines (XII) with the dimethylformamide (DMF) acetal followed by the reductive cyclisation of nitroenamines (XIII) proved to be fruitful in the synthesis of isomeric 4- and 6-azaindoles[59,60]. The yields of the azaindoles (XIV) (with respect to the readily available *o*-nitropicolines) are nearly quantitative when this method is used:



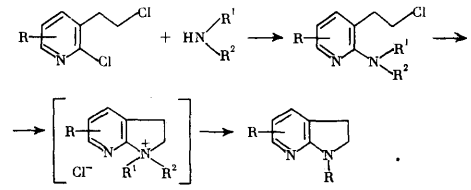
(XII) (XIII) (XIV)

X = CH, Y = N; X = N, Y = CH .

The employment of 3-bromo-5-nitro-γ-picoline as the starting compound yielded 4-bromo-6-azaindole[61], while the introduction of (3-nitro-4-pyridyl)acetone or ethyl (3-nitro-4-pyridyl)acetate instead of *o*-nitropicolines led to 3-substituted 6-azaindoles[62].

3. Syntheses from Halogeno-Derivatives of 3-(β-Chloroethyl)Pyridines via the Corresponding Azaindolines

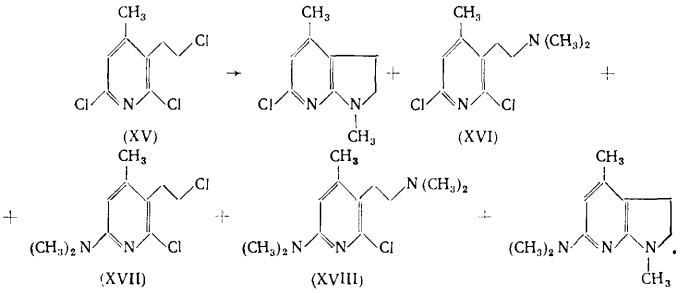
A general method of synthesis of a wide variety of derivatives of 5- and 7-azaindoles had been developed previously[1] on the basis of the reaction of 3-(β-chloroethyl)pyridines, containing halogen atoms in the 2- or 4-positions, with ammonia and primary or secondary amines:



During the last ten years, the study of this method was continued in relation to the reaction of 2,6-dichloro-3-(β-chloroethyl)-4-methylpyridine (trichlorocollidine) (XV) with

asymmetric secondary amines[63]. It was established that the ease of elimination of the substituent at the pyrroline nitrogen atom in the intermediate quaternary azaindoline salt increases in the sequence aryl < alkyl < benzyl, while for alkyl substituents the sequence is hexyl < ethyl < methyl[64].

Detailed study of the side reactions occurring when compound (XV) interacts with dimethylamine[65] established the possibility of controlling the process by altering the reactant ratio, temperature, the reaction time, the polarity of the medium, and the catalytic effect of metal salts. It was shown that side processes leading to the monocyclic products (XVI)–(XVIII) can be suppressed by increasing the polarity of the medium:



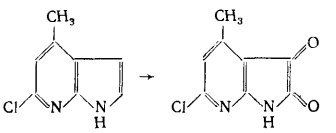
(XV) (XVI) (XVII) (XVIII)

Trichlorocollidine (XV) reacts with sterically hindered primary amines of the type of β-phenylisopropylamine as well as *N*-substituted anilines to form 6-chloro-7-azaindolines and not the 6-amino-derivatives[66]. On passing to t-butylamine, the nucleophilic attack on the α,α′ positions in the pyridine ring becomes sterically impossible and the main reaction pathway becomes the dehydrohalogenation of compound (XV) to 2,6-dichloro-4-methyl-3-vinylpyridine.

5-Azaindolines have been obtained in analogous processes from 4,6-dichloro-3-(β-chloroethyl)pyridine[47,67], while 4-chloro-(5-chloroethyl)pyrimidines gave rise to derivatives of 5,7-diazaindoles[68].

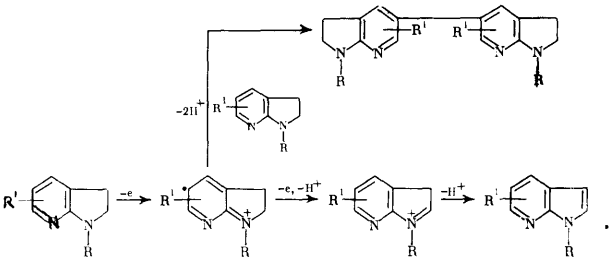
The hydrogenation of azaindolines, i.e. conversion into aromatic azaindole systems, has been achieved successfully by reaction with chloranil and dichlorodicyanoquinone and catalytically in the presence of palladium[47,63,66,69–71]. The dehydrogenation reaction involves *N*-debenzylation[63] and even *C*-dealkoxylation[69].

Studies on the polarographic dehydrogenation of azaindolines and the mechanism of this process have been published[72–77]. It has been shown that azaindolines with an oxidation potential $E_{1/2}$ < 1.1 V are capable of being dehydrogenated by chloranil, those with $E_{1/2}$ up to 1.2 V can be dehydrogenated by dichlorodicyanoquinone, and those with a potential up to 1.4 V can be dehydrogenated by activated manganese dioxide[78]. Azaindoles are oxidised by chromium trioxide to azaisatins[79]:



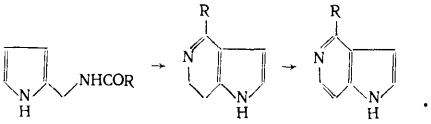
The conversion of 7-azaindolines into indolines without electron-accepting pyridine nitrogen is facilitated by dehydrogenation[72–74], while the conversion to 5-azaindolines and 5,7-diazaindolines gives rise to a successively enhanced hindrance to this process[75].

A mechanism has been proposed for the polarographic oxidation of 7-azaindolines via the formation of intermediate radicals of the semiquinonoid type with further aromatisation to give7-azaindoles or dimerisation to give the corresponding 5,5-bis-7-azaindolines, which have been isolated on a preparative scale[76]:

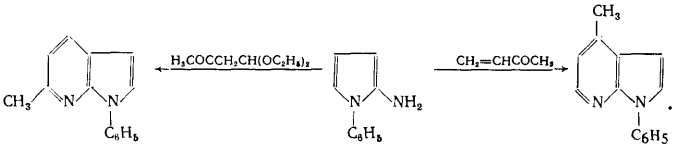


4. Syntheses Based on Pyrrole Derivatives

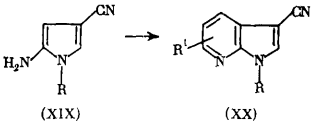
Up to 1968 there were only isolated publications concerning the syntheses azaindole systems based on pyrrole derivatives which dealt[1] with the preparation of 5-azaindoles from acylated 1-(β-aminoethyl)pyrroles by the Bischler–Napieralski reaction:



The synthesis (with a yield of 18–23%) of 4-methyl- and 6-methyl-1-phenyl-7-azaindoles by the reaction of 2-amino-1-phenylpyrrole with methyl vinyl ketone and the acetal of acetoacetaldehyde in the presence of zinc and iron chlorides was reported in 1973 [80]:



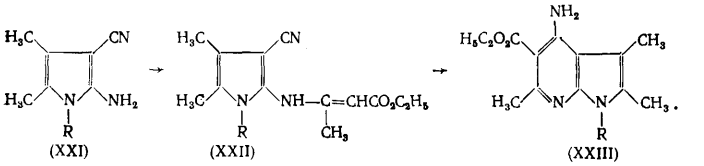
The use of cyanaminopyrroles as the starting materials for the extension of the range of dicarbonyl compounds employed led to the synthesis of a wide variety of 7-azaindole derivatives[81,82]. Thus 1-alkyl(or aryl)-2-amino-4-cyanopyrroles (XIX) undergo cyclocondensation with 1,3-dicarbonyl compounds and their acetals to form unsubstituted 1-alkyl(or aryl)-3-cyano-7-azaindoles (XX) or derivatives substituted in the pyridine ring[81]:



(XIX) (XX)

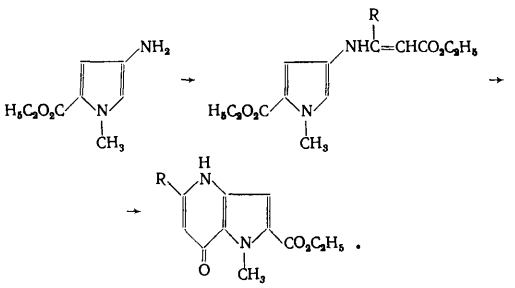
R′ = H or alkyl.

When 1,4,5-trisubstituted 2-amino-3-cyanopyrroles (XXI, R = aryl or cyclohexyl) were allowed to react with acetoacetic ester, the products were propenylaminopyrroles (XXII), which were converted by reductive cyclisation into bifunctional polysubstituted 7-azaindoles (XXIII) [82]:

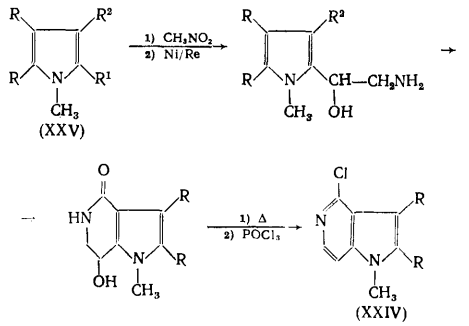


(XXI) (XXII) (XXIII)

The successful use of the 2-ethoxycarbonyl derivative of the isomeric 4-amino-pyrrole in syntheses of substituted 4-azaindoles has been reported[83]. The reaction with β-dicarbonyl compounds proceeds in this case also via propenylaminopyrroles, whose cyclisation can yield 2-ethoxycarbonyl-1-methyl-4-azaindoles with substituents in the pyrridine ring:



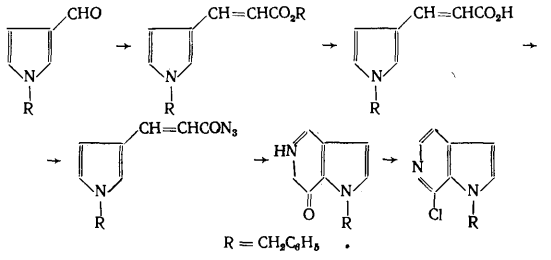
The method of synthesis of 4-chloro-1-methyl(or benzyl)-5-azaindole (XXIV, R = H) and its 2,3-dichloro-derivative (XXI, R = Cl) from 3-ethoxycarbonyl-2-formyl-*N*-methyl(or benzyl)pyrrole and its 4,5-dichloro-derivative (XXV, R = Cl, R^1 = CHO, $R^2 = CO_2C_2H_5$) [84,85] via the mechanism



is of interest.

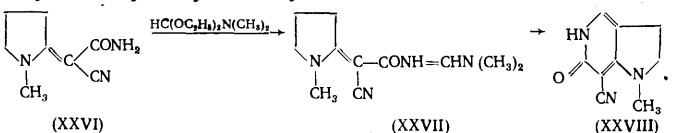
Compound (XXIV, R = H) has also been obtained[86,87] by the reaction of 2-formyl-*N*-methylpyrrole (XXV, $R = R^2 = H$, R^1 = CHO) with malonic acid and by the cyclisation of the azide of the resulting substituted acrylic acid derivative (XXV, $R = R^2 = H$, $R^1 = CHCHCO_2H$) followed by treatment with phosphoryl chloride[88].

1-Benzyl-7-chloro-6-azaindole has been synthesised using an analogous scheme[87] from 1-benzylpyrrole-3-aldehyde via 1-benzyl-3-pyrrolylacrylic acid:



The synthesis of 4,6-dihydroxy-5-azaindole (3,7-didesazaxanthine) has been achieved recently by the alkaline cyclisation of 3-ethoxycarbonyl-2-pyrrolylacetamide[89].

In the reaction of 2-(2′-cyano-2′-carbamoylmethylene)-1-methylpyrrolidinone (XXVI) with the DMF acetal the condensation involves the amide NH_2 group and the resulting substituted acylformamidine (XXVII) readily cyclises to the 7-cyano-6-hydroxy-1-methyl-5-azaindoline (XXVIII) [90,91]:

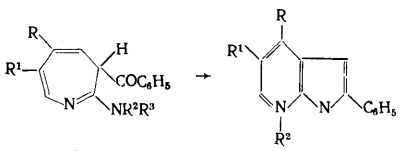


(XXVI) (XXVII) (XXVIII)

An analogous synthesis based on the *N*-benzyl derivative of pyrrolidinone makes it possible to obtain 1-benzyl-7-cyano-6-hydroxy-5-azaindoline, which splits off the cyano- and benzyl groups simultaneously on being refluxed with hydrobromic acid and gives rise to a high yield of 6-hydroxy-5-azaindoline[92].

5. Other Syntheses

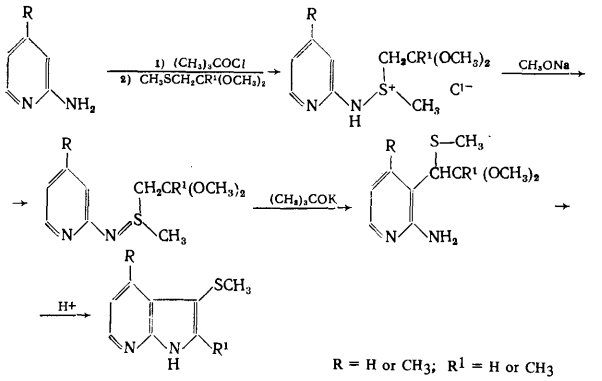
Certain syntheses of azaindolines by specific methods have been described in the literature. An example is provided by the thermal rearrangement of 3-acyl-2-amino-3*H*-azepines (XXIX) to 7-azaindoles (XXX) [93]:



(XXIX) (XXX)

R, R^1 = H, Cl; R^2 = H, C_6H_5, or n-C4H9.

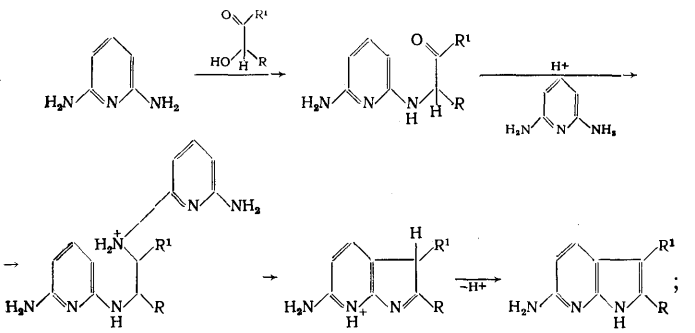
The synthesis of 3-methylthio-7-azaindoles from 2-aminopyridines via the mechanism



R = H or CH_3; R^1 = H or CH_3

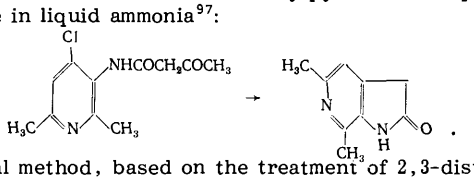
has been reported.

The use of the Bischler reaction, which involves the interaction of α-hydroxy-ketones with 2,6-diaminopyridine, for the synthesis of 7-azaindoles has also proved to be successful[96]:

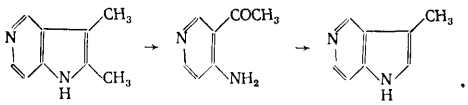


R, R^1 = H, alkyl, or aryl.

5,7-Dimethyl-6-azaoxindole has been obtained by cyclising 3-acetoacetamido-4-chloro-2,6-dimethylpyridine with potassium amide in liquid ammonia[97]:

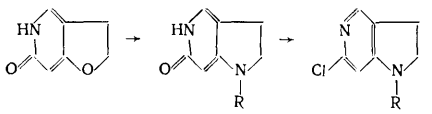


An unusual method, based on the treatment of 2,3-disubstituted 5-azaindoles or 6,7,8,9-tetrahydro-γ-carbolines with hydrogen peroxide in acetic acid, has been proposed[98] for the synthesis of 3-substituted 5-azaindoles. The process takes place with the opening of the pyrrole ring and further cyclisation of the resulting *o*-aminopyridyl ketones or *o*-aminopyridinecarboxylic acids with dimethylsulphonium methyid:



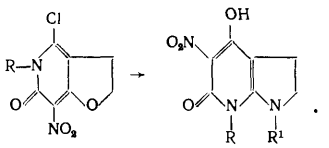
An analogous closure of the pyrrole ring is believed[98] to be possible also for 7-azaindoles. However, the yields in both stages of the process are low so that the method is of no practical value.

Satisfactory results have been obtained in the synthesis of 1-phenyl and 1-benzyl-5-azaindolines[47,70,99,100] by the reaction of 6-oxo-2,3-dihydro-5-azabenzofuran (XXXI) with primary amines:



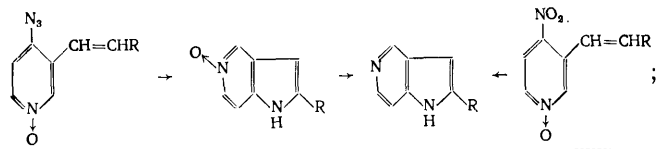
(XXXI)

The interaction of 4-chloro-7-nitro-6-oxo-2,3-dihydro-5-azabenzofurans (XXII) with primary and secondary amines involves the substitution of the chlorine atoms by amine residues and recyclisation of the compounds to 7-azaindoline derivatives[101]:



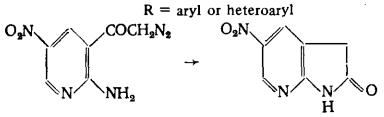
(XXXII)

The synthesis of azaindoles by the thermal cleavage of 4-azido-3-styrylpyridine 1-oxide (XXXIII) with subsequent *N*-deoxidation of the resulting 2-phenyl-5-azaindole 5-oxide[44] as well as the synthesis of 5-nitro-7-azaoxindole by the thermal decomposition of 2-amino-3-diazoacetyl-5-nitropyridine[102] have been described:



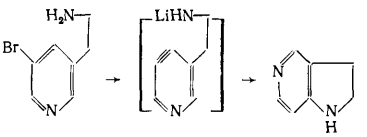
(XXXIII) (XXXIV)

R = aryl or heteroaryl



2,3-substituted 5-azaindoles have been obtained[44] by the reduction of the *N*-oxides of 4-nitro-3-styrylpyridines (XXXIV).

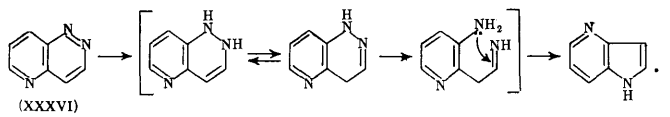
The reaction of 3-(2-aminoethyl)5-bromopyridines with lithium diethylamide proceeds via the hetaryne (XXXV) and gives rise to 5-azaindoline[103] in 56% yield:



(XXXV)

We may note that the above reaction is the first example of the intramolecular addition of a base in the series of hetarynes.

A novel synthesis of unsubstituted 4-azaindoles has been achieved by the reduction of 5-azacinnoline (XXXVI) [104] via the mechanism



(XXXVI)

III. PHYSICOCHEMICAL STUDIES ON AZAINDOLES

1. Ionisation Constants and Electronic Structures of Azaindoles and Their Protonated Forms. The Study of Azaindole Bases and Their Cations by Spectroscopic Methods

As mentioned previously[1,2], the properties of azaindoles are determined by the involvement in their condensed bicyclic system of two *N*-heteraromatic rings with opposite shifts of π-electron density within each ring: pyridine with a deficiency of π-electrons and pyrrole with an excess of π-electrons. During the last decade a number of theoretical and experimental studies have been carried out on the interaction of π-electron systems of this kind. The study of the ionisation constants of a large group of derivatives of 4- and 5-azaindoles using correlation methods made it possible to generalise the relations governing the transmission of the influence of such substituents and to calculate the transmission factors for isomeric 4-, 5-, 7-azaindoles and 5- and 7-azaindolines[105].

In order to estimate the ability of isomeric azaindoles to undergo electrophilic substitution reactions, a study was made of the kinetics of deuterium exchange involving 4-, 5-, and 7-azaindoles[106]. The penetration integrals have been determined[107] for isomeric azaindoles and indole by the Pariser–Parr method, the calculated π–π* transition energies agreeing satisfactorily with experimental data.

Calculations have been made for the molecules of isomeric azaindole and indole by the Hückel and Pariser–Parr–Pople methods, the nature of the mutual influence of the five- and six-membered rings has been examined within the framework for the π-electron approximation, and the energies of the lowest excited states have been calculated by the method of limited interaction of the configurations[108,109]. The results indicate a relatively large π-electron charge on $C_{(3)}$ in all azaindoles and indole. The distribution of π-electron density in the $C_{(1)}$–$C_{(2)}$–$C_{(3)}$ atomic group changes little from molecule to molecule, i.e. the rotation of the pyridine ring has little effect on the electronic structure of the five-membered ring. The π-electronic charges in the six-membered ring are as it were rotated when the position of the pyridine nitrogen atom is altered, without undergoing significant distortions in this process[109].

Calculations for the cations of isomeric azaindoles indicate a relatively high charge on the $C_{(3)}$ atom, which enables the protonated azaindoles to react via an electrophilic mechanism.

The shielding of the positive charge of the cation as a result of solvation enhances this possibility[110]. It has been found that the electron affinity increases in the sequence indole < 5- < 6- < 7- < 4-azaindoles. The ionisation potentials increase in the sequence indole < 5- < 7- < 6- < 4-azaindoles[109].

On the other hand, the experimental basicities of azaindoles are correlated neither with the charge on the nitrogen atom of the six-membered ring nor with the analogous value for the protonated molecules. The discrepancy between the experimental and theoretical data has been attributed[110] to the characteristic features of the structure of the σ-skeleton of azaindoles, as a result of which the basicity of azaindoles can be influenced by the relatively positively charged nitrogen atom of the pyrrole ring.

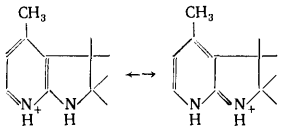
Attempts have been made[111,112] to estimate experimentally the electron distribution in the 7-azaindole system. This was done taking into account the measured chemical shifts (with a correction for the shielding influence of the ring), the magnetic anisotropy of the neighbouring atoms, and the electric field of the free electron pair of the heteroatom dipole. However, in this case too the agreement between the experimental and calculated data was not very satisfactory. In particular the positive charge on the carbon atoms of the rings proved to be greater than the calculated value, experiment revealing an excess negative charge on the heteroatoms and on the bridging carbon atoms. The authors[111,112] do not rule out the possibility that the contradictory data are due to insufficient allowance for the mutual influence on the five-and six-membered rings in the condensed azaindole systems.

^{1}H NMR has been used to investigate the protonation of 5-azaindoles and 5-azaindolines in media with different dielectric constants[11-13]. It has been shown that the structures of the monocations of 5-azaindole, 5-azaindoline, and their 1-substituted derivatives indicate an appreciable contribution of quinonoid structures with transfer of the positive charge to the nitrogen atom of the pyrrole or pyrroline fragment.

The dependence of the chemical shifts of the proton signals of 1-substituted 5-azaindoles or 5-azaindolines on the concentration of trifluoroacetic acid in methylene chloride, acetonitrile, and deuteroacetone led[11,12] to a protonation mechanism in which the proton transfer from the donor to the acceptor in media of low polarity takes place via the formation of a hydrogen-bonded molecular complex of the base and the acid, which is followed by conversion into an ion pair and dissociated ions.

The relative equilibrium position in reactions involving proton transfer via a hydrogen bond and dissociation of hydrogen-bonded complexes with formation of solvated ions has been determined as a function of the concentration of acids on the basis of a model of the amine—acid system in which the amine component is 4-methyl-7-azaindoline[113]. Near the equimolar reactant ratio in the amine—trifluoroacetic acid system, the protolytic equilibrium is fully displaced towards hydrogen-bonded complexes of the ion pair type. The interaction with acetic acid under the same conditions involves a molecular complex ⇌ ion pair equilibrium. The enthalpy and entropy of the proton transfer reaction have been determined.

In a neutral molecule the greatest sensitivity to the effects of the medium and to the formation of hydrogen bonds is shown by the proton in the α-position with respect to the nitrogen atom of the pyridine ring ($H_{(6)}$). On passing from the neutral molecule to the cation, the changes in the ^{1}H NMR spectrum, particularly the upfield shift of the $H_{(6)}$ signal, correspond to the addition of a proton to the pyridine nitrogen with formation of a conjugated ion of the amidinium type (XXXVII)[113]:

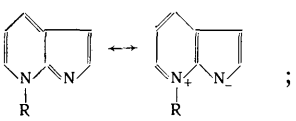


(XXXVII)

A detailed study[114] of the ^{1}H NMR spectra of 5-azaindole and its 1- and 3-methyl derivatives showed that the protons in the 3- and 7-positions interact, while the $H_{(1)}$—$H_{(3)}$—$H_{(2)}$—$H_{(6)}$ and $H_{(4)}$—$H_{(6)}$ interactions were not observed in any one spectrum.

Mass-spectrometric studies on 7-azaindole and a large number of its derivatives established[115] that, on fragmentation on electron impact, the common intermediates for many compounds are naphthyridines and pyrido[2,3d]pyrimidines.

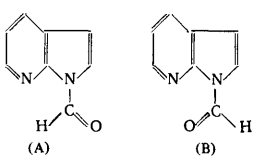
The structure of anhydro-salts of the (XXXVIII) series was determined with the aid of absorption spectroscopy[116] and the contribution of each resonance structure, which varies as a function of the type of solvent, was estimated:



(XXXVIII)

R = alkyl or aryl.

The rotation of the acyl groups about the N—C bond has been studied by ^{1}H NMR for a set of *N*-acylindoles[117] and it has been shown that, in contrast to other *N*-acyl derivatives, 1-formyl-7-azaindole exists predominantly in form A:

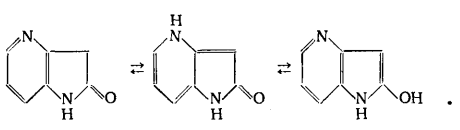


(A) (B)

The chromatographic mobilities of azaindole derivatives have been investigated[118] by thin-layer chromatography.

2. Problems of the Tautomerism of Azaindole Systems

Studies in recent years on tautomeric transformations of isomeric azaindoles have dealt mainly with problems of the lactam—lactim tautomerism of hydroxy-derivatives. It has been established[52,54] that 4-azaoxindole exists in the lactam form (a) in the crystalline state; in protic solvents it has been possible to detect by ultraviolet spectroscopy all three tautomeric forms (a, b, and c) [54]:

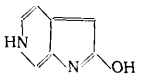


a b c

A change of solvent or the introduction of substituents into the molecule influences significantly the position of the tautomeric equilibrium.

6-Azaoxindole exists as a mixture of comparable amounts of the tautomeric lactam and lactim forms in solution in dimethyl sulphoxide and in the crystalline state[52,56,119], although the possibility of the presence of form (XXXIX) as

well is not ruled out:



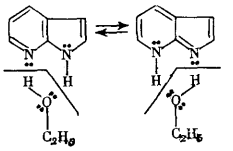
(XXXIX)

In the crystalline state 3-ethoxycarbonyl-6-azaoxindole exists as a mixture of two tautomeric forms, the equilibrium being strongly displaced towards the lactam, in contrast to 3-ethoxycarbonyl-4-azaoxindole, which exists in the lactim form in the crystalline state[52,56].

The lactam—lactim tautomerism of 7-azaindole and 7-azaindoline systems containing the oxo-group in the α-position with respect to the pyridine hydrogen atom had been studied fairly completely previously[1]. It was noted that, in contrast to other analogous *N*-heteroaromatic systems, a complete shift of equilibrium towards lactams is not observed in 6-hydroxy-7-azaindolines and 6-hydroxy-7-azaindoles. This is due to the inductive effect of the nitrogen atom of the pyrrole ring on the α-hydroxy-*N*-heteroaromatic system which exhibits a tendency towards tautomerism. On passing from 7-aza-compounds to the analogous 5-aza-derivatives, the inductive effect on the nitrogen atom of the five-membered ring is greatly weakened, which is responsible, in particular, for the shift of the lactam—lactim tautomeric equilibrium involving 6-hydroxy-5-azaindolines[120] and 4-hydroxy-5-azaindoles[84] almost completely towards the lactam forms. The tautomeric lactam form predominates also in derivatives of 2-ethoxycarbonyl-7-hydroxy-1-methyl-4-azaindole containing a methyl or phenyl group in the 5-position[83].

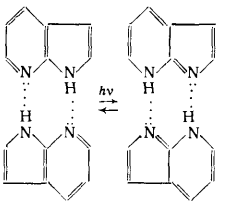
A study of the temperature dependence and the thermodynamic characteristics of the lactam—lactim tautomeric equilibrium of 1-substituted 6-hydroxy-4-methyl-7-azaindoles established[121] that the conversion of the lactim into the lactam is an exothermic process in most of the forms investigated. On passing to less polar solvents, the process becomes less exothermic and in dioxan, where the lactim form predominates to a large extent, the process becomes endothermic. An increase of temperature in more polar solvents promotes a decrease of the content of the lactam forms; the opposite behaviour is observed in less polar solvents.

Examination of the optical, absorption, and luminescence spectra of 7-azaindole in ethanol revealed a two-proton phototautomerism[122]. The influence of the tunnel effect and of the migration of the excited proton cannot explain the changes in the luminescence but does show that the excited state of the molecule is the cause of the ready two-sided migration of the two combined protons:



The spectra of solutions of 7-azaindole in aprotic solvents have two fluorescence maxima, the relative intensities of which depend on the concentration of the solution, temperature, pH, wavelength, and irradiation intensity. The second maximum is apparently caused by the tautomeric form produced as a result of the rapid intramolecular migration of the proton doublet in the excited state, and constitutes a doubly hydrogen-bonded dimer[122-128].

A study of the cleavage of the 7-azaindole dimer in 3-ethylpentane by investigating its fluorescence at 77 and 4.2 K led to the determination[127] of the potential energy barrier to the double prototropic intermolecular reaction. The rate of deuterium exchange involving the excited 7-azaindole molecule and the rate of migration of the proton in the excited non-deuterated 7-azaindole molecule have been determined[127]:



IV. SYNTHETIC STUDIES BASED ON AZAINDOLES

The characteristic features of the chemical behaviour of condensed pyrrolopyridines (azaindoles), associated with the nature of the electron density distribution in their molecules, have been examined in fair detail in earlier reviews[1,2]. Further studies did not alter the fundamental ideas concerning the chemical properties of compounds of this class but greatly extended the synthetic possibilities in the series of azaindole derivatives and led to the discovery of new ways of constructing condensed heterocyclic systems on the basis of 7-azaindole derivatives.

1. Reactions of Azaindoles Involving Nitrogen Atoms

One of the commonest reactions of isomeric azaindoles is alkylation at the pyrrole nitrogen atom[24,114,129-131]. This process takes place fairly readily in the presence of strong bases (sodium amide, sodium hydride, etc.) which convert azaindole compounds into the corresponding anions[1]. In the absence of strong bases the reaction usually takes place via several pathways and leads to a mixture of products of alkylation at the pyrrole and pyridine nitrogen atoms[132-135]. In some instances the alkylation of 7-azaindole derivatives in the presence of alkali involves the expansion of the pyrrole ring with formation of 1,8-naphthyridine derivatives[26].

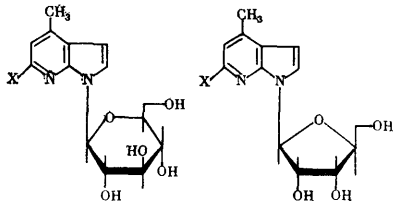
7-Azaindole reacts with ethylmagnesium iodide to form a Grignard compound, which is converted into the 1-acetyl and 1-ethoxycarbonyl derivatives on treatment with acetyl chloride and ethyl chloroformate respectively[26].

Oxidation of 5- and 7-azaindoles with *m*-chloroperbenzoic acid converts them into the *N*-oxides[52,136], which like the *N*-oxides of other six-membered *N*-heteroaromatic compounds, are capable of rearrangement under the influence of acetic anhydride, phosphoryl chloride, and other analogous reagents.

Certain mercury derivatives of 7-azaindole substituted at the pyrrole nitrogen atom[137] as well as cobalt[138] and copper[139] complexes of 7-azaindole, which exhibit antiferromagnetic properties of practical interest, have been synthesised.

The synthesis of *N*-glycosylated azaindoles by fusing 7-azaindole with 1,2,3,5-tetra-*O*-acetyl-β-*D*-ribofuranose did not give positive results[140]. The use of the indoline—indole method[15,16], which consists in the glycosylation of 7-azaindoline derivatives by *D*-glucose or 5-*O*-trityl-*D*-ribofuranose residues with subsequent dehydrogenation to 1-β-*D*-glucopyranosyl-7-azaindole (XL) and 1-β-*D*-ribofuranosyl-7-

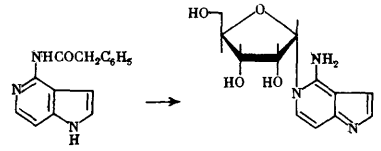
azaindole (XLI), was more successful:



(XL) X = H or Cl. (XLI)

1-Glycosyl derivatives of 5-azaindole have been obtained by the glycosylation of the chloromercury salt of 5-azaindole by acetylated bromosugars[141].

Direct glycosylation of 4-benzamido-5-azaindole (XLII) by 2,3,3-tri-*O*-benzoyl-*D*-ribofuranosyl bromide takes place at the nitrogen atom of the pyridine ring, subsequent debenzoylation yielding 4-amino-5-β-*D*-ribofuranosyl-5-azaindole (XLIII) [87,142]:



(XLII) (XLIII)

2. Electrophilic Substitution Reactions in the Series of Isomeric Azaindoles and Azaindolines

The influence of the π-electron-deficient pyridine ring is responsible for certain characteristic features in the behaviour of azaindole molecules under the conditions of the electrophilic substitution reaction in relation to indoles[1,2]. The earlier investigations of the Mannich, Vilsmeier, cyanomethylation, halogenation, and nitration reactions of 7-azaindoles have been extended during the last decade to 4-, 5-, and 6-azaindoles[26,62,71,133,134,143-148], which exhibited the same features as 7-azaindoles. It is of interest to note that 7-azagramine has been used as a model of a polymer oxidation inhibitor[149]. New literature data[145] disproved earlier conclusions[1,2,150] that 5-azaindole is incapable of undergoing electrophilic substitution reactions.

A quantitative study of the comparative reactivities in the electrophilic substitution reactions of isomeric azaindoles has been carried out in relation to the acid-catalysed deuterium exchange involving the 3-position[106].

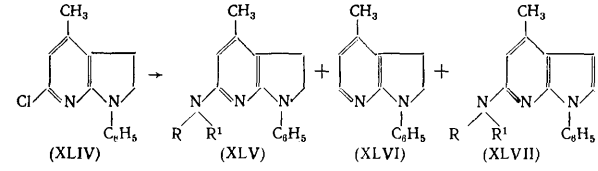
Electrophilic substitution reactions of azaindolines have been studied in relation to 6-chloro-7-azaindolines[151,152], which, in contrast to 7-azaindolines, lacking a halogen atom in the α-position with respect to the pyridine nitrogen, are readily brominated, chlorinated, and nitrated with formation of 5-substituted 6-chloro-7-azaindolines. In the absence of an *N*-acyl protecting group, nitration yields the 1-nitro-isomer in addition to the 5-nitro-isomer.

3. Nucleophilic Substitution Reactions in the Series of Isomeric Azaindoles and Azaindolines

Nucleophilic substitution reactions of azaindole and azaindoline compounds are difficult[1,2]. Thus 4-methyl-7-azaindoline and its 1-phenyl derivative are not aminated under the conditions of the Chichibabin reaction[153]. The pyrrole ring in 1-phenyl-5-azaindole is opened under the influence of sodium amide and 4-phenylamino-3-vinylpyridine is formed. Nor was it possible to achieve the Chichibabin amination of 4-azaindole[153]. These results can be accounted for by the enhanced electron density, compared with pyridine, in the pyridine ring of azaindoles.

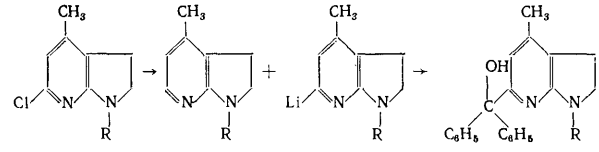
Substitution of the chlorine atom in the 6-position by hydrogen in derivatives of 7-azaindoline[63,66,71] and 5-azaindoline[67,70] as well as the chlorine atom in the 4-position in 5-azaindole[87] proceeds smoothly in the presence of a palladium catalyst. Nucleophilic substitution of chlorine by alkoxy-groups[67] by reaction with alkali metal alkoxides requires severe conditions. Even more severe conditions are necessary for the substitution of chlorine atoms in the pyridine component of the molecules of 5- and 7-azaindoles by nucleophiles such as primary or secondary amines[84,85,87,154-158]. A kinetic study of the nucleophilic substitution of chlorine in 4-chloro-1-methyl-5-azaindole by the piperidine residue revealed an autocatalytic effect[156].

In the reactions of primary and secondary amines with 6-chloro-4-methyl-1-phenyl-7-azaindolines (XLIV), which take place under severe conditions, the normal nucleophilic substitution process is accompanied by the reduction of the hitherto unreacted compound (XLIV) by the *N*-substituted 6-amino-4-methyl-1-phenyl-7-azaindole (XLV) formed to 4-methyl-1-phenyl-7-azaindoline (XLVI) with simultaneous oxidation of compound (XLV) to *N*-substituted 6-amino-4-methyl-1-phenyl-7-azaindole (XLVII) [154,155]:



(XLIV) (XLV) (XLVI) (XLVII)

The interaction of 6-chloro-7-azaindolines with lithionaphthalene at temperatures between -35° and -40 °C in tetrahydrofuran followed by treatment with benzophenone yielded substituted 7-azaindoline-6-yldiphenylmethanols together with 6-unsubstituted 7-azaindolines[159]:

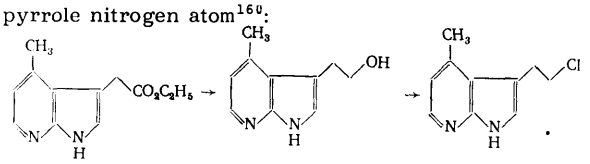


4. Transformations of Azaindole Compounds Associated with Reactions Involving the Carbon Side Chain

The characteristics of the distribution of electron density in azaindole systems do not interfere with a number of classical reactions involving their side chains. Thus 3-formyl-1-phenyl-7-azaindole has been reduced to the alcohol, the hydroxy-group of which is readily acetylated and substituted by chlorine; the latter can in its turn be substituted by various acyloxy-groups[146].

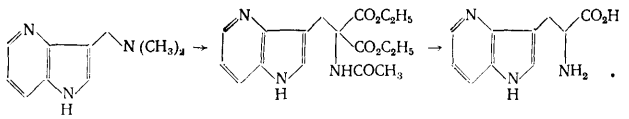
The reduction of the ethyl ester of 4-methyl-7-azaindole-3-acetic acid led to the synthesis of the alcohol (XLVIII), the hydroxy-group of which is also readily substituted by chlorine; the resulting compound is fairly readily acetylated at

the pyrrole nitrogen atom[160]:



(XLVIII)

During the last decade considerable interest has been shown in azaindoles containing nitrogen in the side chain[39,41,42,144,147]. 4-Azatryptamine has been obtained by the reduction of 4-azaindole-3-acetamide and 4-azatryptophan (XLIX) has been synthesised[161] by the reaction of 4-azagramine (L) with acetamidomalonic ester followed by hydrolysis or partial decarboxylation:

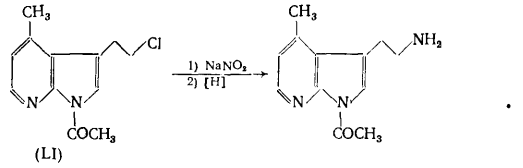


(L) (XLIX)

The method of synthesis of 3-aminoalkyl-7-azaindoles[1,2], consisting of the condensation of 3-formyl-7-azaindoles with nitroalkanes and subsequent reduction of the intermediates, has been developed further[71,143,147,162]. In particular, 7-azatryptamines, substituted at the pyrrole nitrogen atom by aliphatic or aliphatic-aromatic residues[71], have been synthesised by this procedure; 3-aminomethyl derivatives of 7-azaindole have been obtained by reducing the oximes of the corresponding 3-aldehydes[143,147].

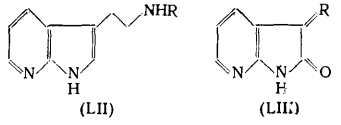
It has been shown that the oxime of 6-chloro-3-formyl-4-methyl-7-azaindole consists of *syn*- and *anti*-isomers in the crystalline state[163], while the crystalline oxime of 3-formylindole exists as the *anti*-isomer.

The synthesis of 1-acetyl-4-methyl-7-azatryptamine from 1-acetyl-3-(β-chloroethyl)-4-methyl-azaindole (LI), based on the substitution of a chlorine atom in the side chain by the nitro-group with subsequent reduction, has been investigated[160]. The interaction of compound (LI) with ammonia, potassium bis(dimethoxysilyl)amide, and potassium phthalimide (with subsequent removal of the phthalimide protecting group) involves the elimination of the *N*-acetyl group:



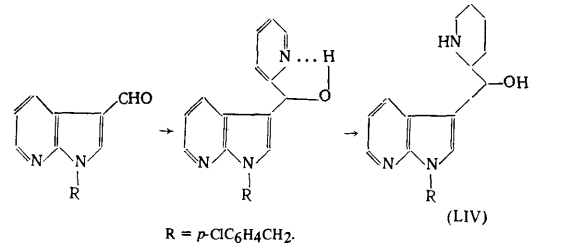
(LI)

Derivatives (LII) of 7-azatryptamine substituted in the amino-group have been synthesised from 7-azatryptamine itself[164]. The interaction of 7-azaoxindole with nitrosoketones yielded the oximes (LIII, R = CCH_3CH = NOH or CC_6. .H_5CH = NOH), which were then reduced to 2-(7-azaoxindol-3-yl)propylamines (LIII, R = $CCH_3CH_2NH_2$) [164]:



(LII) (LIII)

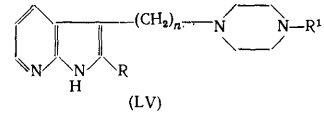
1-(*p*-Chlorobenzyl)-7-azaindol-3-yl-α-piperidinylmethanol (LIV) has been synthesised[133,134] by the interaction of 3-formyl-7-azaindole with 3-pyridyl-lithium and selective reduction of the product to a mixture of diastereoisomers:



(LIV)

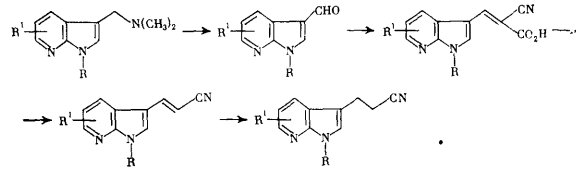
R = *p*-$ClC_6H_4CH_2$.

A large group of compounds of the type (LV, R = H or CH_3; n = 1–3; R^1 = alkyl, aryl, or heteroaryl) have been synthesised from 7-azaindole-3-ylalkanecarboxylic acids via the corresponding piperazides with reduction of the amide group by lithium tetrahydroaluminate[148,165]:



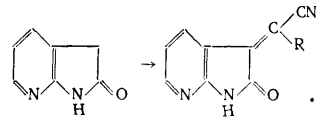
(LV)

3-Cyanoethyl derivatives of 7-azaindoles have been obtained from 7-azagramines, which were converted into 3-formyl-7-azaindoles under the conditions of the Duff reaction (with urotropine in aqueous acetic acid solutions) and were then condensed with cyanoacetic acid. The subsequent decarboxylation of the substance and catalytic reduction of the double bond leads to the required products[131]:



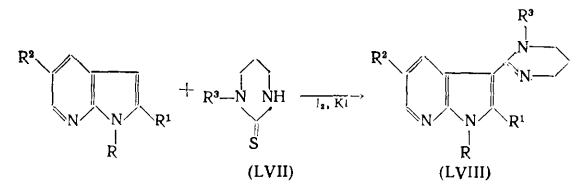
3-[β-(2-Imidazoline-2-yl)ethyl]-7-azaindoles have been synthesised from 3-cyanoethyl-7-azaindoles[131].

On reaction with compounds of the type RCOCN (R = CH_3, C_2H_5, or C_6H_5), 7-azaoxindole is converted into acetonitriles (LVI) [164]:



(LVI)

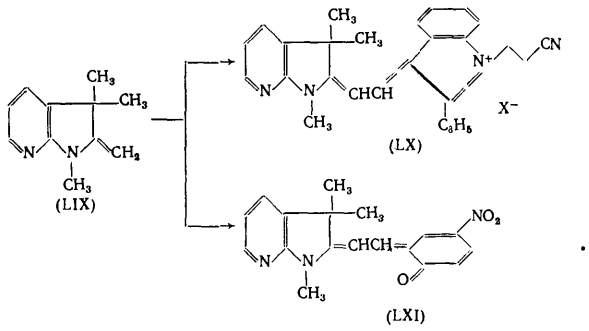
Compounds (LVIII), containing tetrahydropyrimidine residues in the 3-position in 7-azaindoles, have been obtained on condensing 7-azaindoles with tetrahydropyrimidinethione (LVII) in the presence of iodine[166,167]:



(LVII) (LVIII)

The interaction of 2,3-dihydro-1,3,3-trimethyl-2-methylene-7-azaindole (LIX) with 1-(2-cyanoethyl)-3-formyl-2-phenylindole leads to the cyanine (LX, X = *p*-$CH_3C_6H_4SO_3^-$ or

ClO_4^-) [168], while the reaction of compound (LIX) with nitrosalicylaldehyde makes it possible to obtain compound (LXI) [169]:

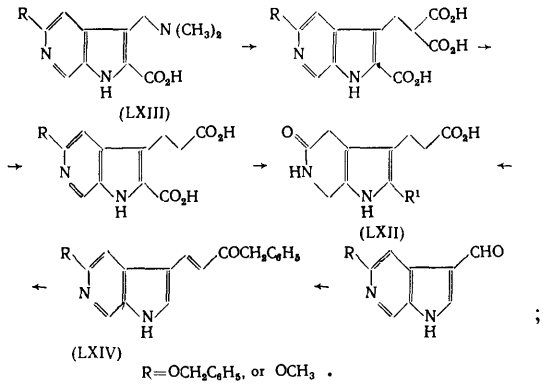


(LIX) (LX) (LXI)

Compounds of this type are of practical interest—as photosensitisers in colour photography[168-173].

A number of compounds have been synthesised from 3-formyl-6-azaindole[169], in particular its oxime, as well as 3-cyano-, 3-methyl-, 3-aminomethyl-, and 3-dimethylamino-6-azaindoles.

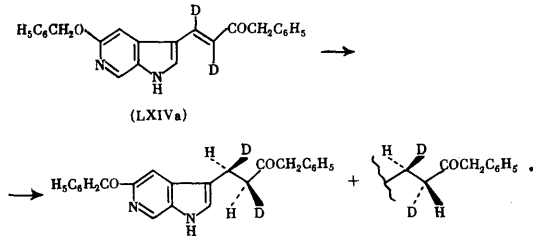
The lactams of porphobilinogen-2-carboxylic acids (LXII, R^1 = COOH) have been synthesised via the Mannich bases (LXIII) [17,18], introduced into the malonic ester synthesis and then subjected to familiar transformations in accordance with the scheme



(LXIII) (LXII) (LXIV)

R=$OCH_2C_6H_5$, or OCH_3 .

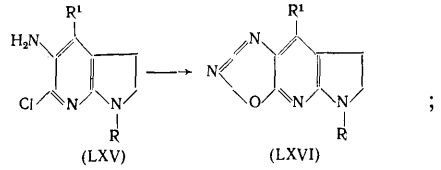
The reduction of the deuterated product (LXIVa) over a palladium catalyst gives rise to the racemate[19]. The separation of the optical isomers and their use in further synthesis yielded optically active lactams of porphobilinogens:



(LXIVa)

5. Synthesis of Condensed Heterocyclic Systems from 7-Azaindole Derivatives

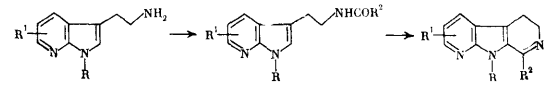
Derivatives of 7-azaindole have been used successfully in recent years to synthesise new more complex condensed systems. Thus the closure of the 1,2,3-oxadiazole ring has been achieved by the diazotisation of 5-amino-6-chloro-7-azaindoline (LXV) with formation of the 1,2,3-oxadiazolo[4,5-g]7-azaindoline system (LXVI) [151,174,175]:



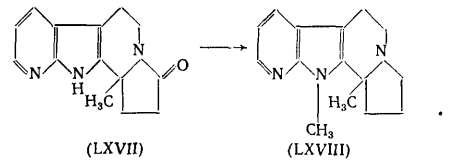
(LXV) (LXVI)

R and R^1 = H or alkyl.

The application of the Bischler–Napieralski and Pictet–Spengler reactions to 7-azatryptamines permitted the synthesis of derivatives of the new tricyclic system of 12-aza-β-carboline[176]:

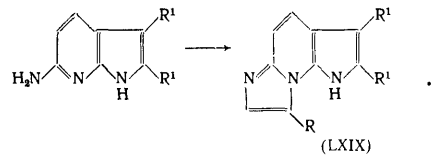


Cyclisation of 7-azatryptamine with laevulinic acid gave rise to the lactam (LXVII), which was converted into pyridopyrroloindolizine (LXVIII) by reduction and subsequent methylation[177,178]:



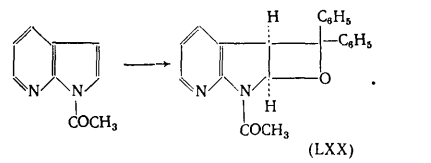
(LXVII) (LXVIII)

Derivatives of 1*H*-imidazo[1,2-*a*]pyrido[3,2-*e*]pyrrole (LXIX) have been obtained by condensing 6-amino-7-azaindoles with α-halogenocarbonyl compounds[179]:



(LXIX)

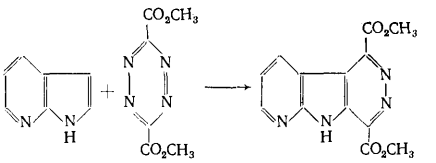
In contrast to furans and 2,3-dimethylthiophens, which interact with benzophenone under irradiation to form condensed oxetans, unsubstituted 7-azaindole, pyrrole, and imidazole do not react with benzophenone under these conditions[180]. This has been explained[180] by the quenching influence of the free electron pair of the pyrrole nitrogen atom on the excited ketone. Indeed, when a mixture of 1-acetyl-7-azaindole and benzophenone is irradiated, cycloaddition to the double bond of 7-azaindole and the formation of oxetano-7-azaindoline (LXX) in 4% yield are observed:



(LXX)

Condensed pyridazinoazaindoles (LXXI) have been obtained by the cycloaddition (of the type of the Diels–Alder reaction) of the tetrazine (LXXII) to the unsubstituted 7-azaindole, acting as the dienophile, with subsequent elimination of a

nitrogen molecule[181]:



(LXXII) (LXXI)

V. THE BIOLOGICAL PROPERTIES OF AZAINDOLE DERIVATIVES

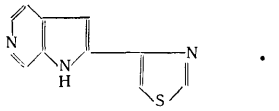
The range of studies of the biological activity of azaindole derivatives has significantly expanded in recent years, although the main information still concerns 7-azaindoles.

The high and varied biological activities of a wide variety of azaindole derivatives have been reported in the patent literature. It has been established[182] that 2,3-dimethyl-5-azaindole and its 1-glucopyranoside suppress the growth of the tumour cells of sarcoma-37 to the extent of 60–67% in experiments *in vivo* and at the same time exhibit a low toxicity. In experiments on sea urchins 4-methyl-1-phenyl-7-azatryptophan exhibited a cytotoxic activity[183].

(7-Azaindol-3-yl)alkylpiperazines showed a considerable psychotropic and cardiovascular effect[148,165]. Antidepressant properties have been found in a series of derivatives of azaindoles and their analogues[132,184,185]; 7-methyl-7-azaindole[132], which blocks certain effects of reserpine in experiments on mice, proved to be most active. Tryptamine-like properties have been found in 3-amino-methyl-4-methyl-1-phenyl-7-azaindole[147,186]; when 3-hydroxymethyl-4-methyl-1-phenyl-7-azaindole is administered to various animal species both internally and parenterally, it induces a state resembling narcosis[146].

A series of 7-azaindole derivatives, particularly 7-azaindole-3-acetoxime, exhibit a hypotensive activity[166,167,187,188]. There have also been reports of the vasoconstrictor activity of imidazolinylalkyl-7-azaindoles[131], the anti-inflammatory activity of 4-aminophenyl-5-azaindoles[86,157], the gonadotropic effect of 7-azatryptophan[189], the antiserotonine activity of 4-methyl-1-phenyl-7-azatryptamine[190,191], etc.

Chemotherapeutic research on laboratory animals revealed an activity of the 4-,5-,6, and 7-aza-analogous of thiabendazole, for example compound (LXXIII), as well as 2-phenyl-5-azaindole and 2-phenyl-6-azaindole against trichostrongylids[44]:



(LXXIII)

It has been shown that 7-azatryptophan does not exhibit a significant inhibiting activity on the development of *Heterodera trifolii*[192], while 7-azaindole to a large extent suppresses the formation of *Meloidogyne javanica* galls[193] and inhibits the stimulating effect of indole-2-carboxylic acid on the multiplication of *Aphelenchoides ritzema-bozi*[194].

One of the diastereoisomers of (1-*p*-chlorobenzyl-7-azaindol-3-yl)-2-piperidinylmethanol proved to be an effective antimalerial agent[133,134]. A study of the antifungal activity of coal tar led to the isolation of 2-isopropyl- and 2-isobutyl-7-azaindoles as active components[195]. 7-Azaindole and its condensed systems have been detected in tobacco smoke and tobacco[196]. The antimicrobial properties of 2-alkyl- and 2-alkenyl-7-azaindoles have been the cause of the incorporation of these compounds in the composition of cosmetics for the skin[197].

Numerous studies have been devoted to the involvement of 7-aza-analogues of tryptophan and its metabolites in biochemical processes in the cell[198–216]. The bacteriological synthesis[217–219] of *L*-7-azatryptophan by a whole series of bacterial and fungal strains from 7-azaindole has been reported. The similarity of the biological activities of 7-azaindole-3-acetic acid and indole-3-acetic acid (heteroauxin) has been confirmed[220]. A number of studies on the interrelations of 7-azatryptophan with plant objects have been carried out[221–225].

During the preparation of this review for the press, new data on the syntheses of isomeric azaindoles were published; substituted 4-azaindoles have been obtained from isoxazolylpyrrole[226] and enaminonitriles[227], derivatives of 5-azaindole (of the type of 3,7-dididesazaxanthine) have been obtained from pyrrole-2,3-dicarboxylic acid esters[228] and 2,3-disubstituted 6-azaindoles have been synthesised by the reduction of (3-nitro-4-pyridyl)dicarbonyl compounds[229]. A series of studies[230–236], which throw light on the "anomalous" course of the Fischer reaction, observed in the formation of azaindoles and associated with the homolytic dissociation of the N–N bond in hydrazones, have been carried out.

Physicochemical investigations of azaindoles dealt with the spectroscopic characteristics of substances of this class[237–239], the phototautomerism of 7-azaindole and its derivatives[240–242], the kinetics of deuterium exchange[243] and the nitration of isomeric azaindoles[244], etc[245]. The π- and σ-electron densities of the carbon atoms of isomeric azaindoles have been calculated, the results being used to estimate their capacities for electrophilic substitution reactions[246].

New data have been published on the behaviour of azaindoles under the conditions of electrophilic[247,248] and nucleophilic[249,250] attack. Studies have been continued on the synthesis of *N*-glycosylated azaindoles[251], and a cobalt complex of 7-azaindole has been obtained[252]; a series of compounds containing azaindole fragments proved to be of interest for photography[253–257].

The publication of studies on the biochemical and chemotherapeutic activities of azaindole derivatives has been continued[228,258–265]. Certain derivatives of 7-azaindoles exhibited an antiulcer activity[266] and inhibited the secretion of the gastric juice and the growth of malignant neoplasms[267].

REFERENCES

1. L.N.Yakhontov, Uspekhi Khim., **37**, 1258 (1968) [Russ.Chem.Rev., No.7 (1968)].
2. R.E.Willette, Adv.Heterocycl.Chem., **9**, 27 (1968).
3. M.F.Marshalkin and L.N.Yakhontov, Khim.Geterotsikl.Soed., 1576 (1972).
4. L.N.Yakhontov and M.F.Marshalkin, Tetrahedron Letters, 2807 (1975).
5. M.F.Marshalkin and L.N.Yakhontov, Uspekhi Khim., **42**, 1593 (1973)[Russ.Chem.Rev., No.8 (1973)].
6. L.N.Yakhontov, D.M.Krasnokutskaya, E.M.Peresleni, Yu.N.Sheinker, and M.V.Rubtsov, Tetrahedron, **22**, 3233 (1966).
7. L.N.Yakhontov, D.M.Krasnokutskaya, E.M.Peresleni, Yu.N.Sheinker, and M.V.Rubtsov, Dolk.Akad.Nauk SSSR, **172**, 118 (1967).
8. L.N.Yakhontov, D.M.Krasnokutskaya, E.M.Peresleni, Yu.N.Sheinker, and M.V.Rubtsov, Dokl.Akad.Nauk SSSR, **176**, 613 (1967).
9. E.M.Peresleni, L.N.Yakhontov, D.M.Krasnokutskaya, and Yu.N.Sheinker, Dokl.Akad.Nauk SSSR, **177**, 592 (1967).

10. E.M.Peresleni, M.Ya.Uritskaya, V.A.Loginova, Yu.N.Sheinker, and L.N.Yakhontov, Dokl.Akad.Nauk SSSR, **183**, 1102 (1968).
11. G.G.Dvoryantseva, T.N.Ul'yanova, Yu.N.Sheinker, and L.N.Yakhontov, Khim.Geterotsikl.Soed., 767 (1973).
12. G.G.Dvoryantseva, T.N.Ul'anova, N.P.Kostyuchenko, Yu.N.Sheinker, E.I.Lapan, and L.N.Yakhontov, Tetrahedron Letters, 2857 (1972).
13. G.G.Dvoryantseva, T.N.Ul'yanova, Yu.N.Sheinker, D.M.Krasnokutskaya, and L.N.Yakhontov, Khim. Geterotsikl.Soed., 1072 (1976).
14. R.Sulhadoinik, "Nucleoside Antibiotics", Wiley, New York, 1970, p.300.
15. M.N.Preobrazhenskaya, T.D.Miniker, V.F.Martynov, L.N.Yakhontov, N.P.Kostyuchenko, and D.M.Krasnokutskaya, Zhur.Org.Khim., **10**, 745 (1974).
16. M.N.Preobrazhenskaya, T.D.Miniker, V.S.Martynov, L.N.Yakhontov, and D.M.Krasnokutskaya, Zhur.Org. Khim., 10, 2449 (1974).
17. A.R.Battersby, D.A.Evans, K.H.Gibson, E.McDonald, and L.Nixon, J.Chem.Soc., Perkin Trans.I, 1546 (1973).
18. A.I.Scott, C.A.Towsend, K.Okada, and M.Kajiwara, J.Amer.Chem.Soc., **96**, 8054 (1974).
19. A.R.Battersby, E.McDonald, H.K.W.Wurziger, and K.J.James, Chem.Comm, 493 (1975).
20. B.Robinson, Chem.Rev., **69**, 227 (1969).
21. R.C.Elderfield (Editor), "Heterocyclic Compounds" (Translated into Russian), Inostr.Lit., Moscow, 1953, Vol.1, p.318.
22. A.H.Kelly and J.Parrick, Canad.J.Chem., **43**, 296 (1965).
23. P.A.Crooks and B.Robinson, Chem.Ind.(London) 547 (1967).
24. P.A.Crooks and B.Robinson, Canad.J.Chem., **47**, 2061 (1969).
25. A.H.Kelly and J.Parrick, J.Chem.Soc., (C) 303 (1970).
26. R.Herbert and D.G.Wibberley, J.Chem.Soc., (C) 1505 (1969).
27. E.Bisagni, C.Ducrocq, and A.Civier, Tetrahedron, **32**, 1383 (1976).
28. M.F.Marshalkin and L.N.Yakhontov, Khim.Geterotsikl.Soed., 652 (1972).
29. L.N.Yakhontov and M.F.Marshalkin, Khim.Geterotsikl.Soed., **1638** (1972).
30. L.N.Yakhontov, E.V.Pronina, B.V.Rozynov, and M.V.Rubtsov, Dokl.Akad.Nauk SSSR, **178**, 127 (1968).
31. L.N.Yakhontov and E.V.Pronina, Zhur.Org.Khim., **4**, 1675 (1968).
32. L.N.Yakhontov and E.V.Pronina, Khim.Geterotsikl. Soed., 1121 (1969).
33. L.N.Yakhontov, E.V.Pronina, and M.V.Rubtsov, Khim.Geterotsikl.Soed., 186 (1970).
34. L.N.Yakhontov, M.F.Marshalkin, and O.S.Anisimova, Khim.Geterotsikl.Soed., 508 (1972).
35. M.F.Marshalkin and L.N.Yakhontov, Khim.Geterotsikl.Soed., 1576 (1972).
36. L.N.Yakhontov, M.F.Marshalkin, and E.V.Pronina, Khim.Geterotsikl.Soed., 351 (1972).
37. L.N.Yakhontov, N.N.Suvorov, V.Ya.Kanterov, N.Ya.Podkhalyuzina, E.V.Pronina, N.E.Starostenko, and V.N.Shkil'kova, Khim.Geterotsikl.Soed., 656 (1972).
38. L.N.Yakhontov, N.N.Suvorov, V.Ya.Kanterov, N.Ya.Kanterov, N.Ya.Podkhalyuzina, N.E.Starostenko, and V.N.Shil'kova, Khim.Geterotsikl.Soed., 1146 (1972).
39. L.N.Yakhontov, R.G.Glushkov, E.V.Pronina, and V.G.Smirnova, Dokl.Akad.Nauk SSSR, **212**, 389 (1973).
40. R.G.Glushkov, L.N.Yakhontov, E.V.Pronina, and O.Yu.Magidson, Khim.Geterotsikl.Soed., 564 (1969).
41. I.I.Grandberg and N.G.Yaryshev, Khim.Geterotsikl. Soed., 1070 (1972).
42. I.I.Grandberg and N.G.Yaryshev, Khim.Geterotsikl. Soed., 1202 (1972).
43. R.R.Lorenz, B.F.Tullar, C.F.Koelsch, and S.Archer, J.Org.Chem.., **30**, 2531 (1965).
44. M.H.Fisher, G.J.Schwartzkopf, and D.R.Hoff, J.Medicin.Chem., **15**, 1168 (1972).
45. L.N.Yakhontov and V.A.Azimov, USSR P.253 068 (1968); Byul.Izobret., No.30, 30 (1969).
46. B.Frydman, S.J.Reil, J.Boned, and H.Rapôport, J.Org.Chem., **33**, 3762 (1968).
47. L.N.Yakhontov, V.A.Azimov, and E.I.Lapan, Tetrahedron Letters, 1909 (1969).
48. L.N.Yakhontov and V.A.Azimov, Dokl.Akad.Nauk SSSR, **192**, 583 (1970).
49. E.M.Peresleni, M.Ya.Uritskaya, V.A.Azimov, V.A.Loginova, T.F.Vlasova, Yu.N.Sheinker, and L.N.Yakhontov, Khim.Geterotsikl.Soed., 389 (1974).
50. M.N.Fisher and A.R.Matzuk, J.Heterocyclic Chem., **6**, 775 (1969).
51. B.Frydman, G.Buldain, and J.C.Repetto, J.Org. Chem., **38**, 1824 (1973).
52. B.A.J.Clark, M.M.S.El-Bakoush, and J.Parrick, J.Chem.Soc., Perkin Trans.I, 1531 (1974).
53. R.W.Daisley and J.R.Hanbali, Synthetic Comm, **5**, 53 (1975).
54. N.Finch, M.M.Robinson, and M.P.Valerio, J.Org. Chem., **37**, 51 (1972).
55. B.A.J.Clark, J.Parrick, P.J.West, and A.H.Kelly, J.Chem.Soc., (C) 498 (1970).
56. L.N.Yakhontov, M.Ya.Uritskaya, A.A.Prokopov, V.A.Loginova, and T.F.Vlasova, Khim.Geterotsikl. Soed., 1428 (1975).
57. A.A.Prokopov and L.N.Yakhontov, Khim.Geterotsikl. Soed., 1531 (1977).
58. A.A.Prokopov, L.F.Linberg, T.F.Vlasova, Yu.N.Sheinker, and L.N.Yakhontov, Khim.Geterotsikl.Soed., 492 (1978).
59. A.A.Prokopov and L.N.Yakhontov, Khim.Geterotsikl. Soed., 1135 (1977).
60. V.A.Azimov and L.N.Yakhontov, Khim.Geterotsikl. Soed., 1425 (1977).
61. A.A.Prokopov and L.N.Yakhontov, Khim.Geterotsikl. Soed., 86 (1979).
62. A.A.Prokopov and L.N.Yakhontov, Khim.Geterotsikl. Soed., 496 (1978).
63. L.N.Yakhontov, M.S.Sokolova, and M.V.Rubtsov, "Khimiya Geterotsiklicheskikh Soedinenii" (The Chemistry of Heterocyclic Compounds), Vol.1, "Azotsoderzhashchie Geterotsikly" (Nitrogen-Containing Heterocycles), Izd.Zinatne, Riga, 1967, p.455.
64. L.N.Yakhontov, M.S.Sokolova, and T.D.Pervacheva, Khim.Geterotsikl.Soed., 1546 (1970).
65. L.N.Yakhontov, M.S.Sokolova, and T.D.Pervacheva, Khim.Geterotsikl.Soed., 1122 (1970).
66. D.M.Krasnokutskaya and L.N.Yakhontov, Khim. Geterotsikl.Soed., 650 (1974).
67. L.N.Yakhontov, E.I.Lapan, and M.V.Rubtsov, Khim. Geterotsikl.Soed., 550 (1969).
68. L.N.Yakhontov, M.S.Sokolova, N.I.Koretskaya, K.A.Chkhikvadze, O.Yu.Magidson, and M.V.Rubtsov, Khim.Geterotsikl.Soed., 145 (1968).

69. E.I.Lapan and L.N.Yakhontov, Khim.Geterotsikl. Soed., 859 (1972).
70. L.N.Yakhontov and E.I.Lapan, Khim.Geterotsikl. Soed., 27 (1970).
71. L.N.Yakhontov and M.S.Sokolova, Khim.Geterotsikl. Soed., 1111 (1969).
72. Yu.I.Vainshtein, I.N.Palant, L.N.Yakhontov, D.M.Krasnokutskaya, and M.V.Rubtsov, Trudy Vses.Nauch.-Issled.Inst.Khim.Reaktvivov i Osobo Chistykh Khim.Veshchestv, **30**, 329 (1967).
73. Yu.I.Vainshtein, I.N.Palant, L.N.Yakhontov, D.M.Krasnokutskaya, and M.V.Rubtsov, Khim. Geterotsikl.Soed., 1106 (1969).
74. I.N.Palant, Yu.I.Vainshtein, L.N.Yakhontov, D.M.Krasnokutskaya, and M.M.Gol'din, Trudy Vses. Nauch.-Issled.Inst.Khim.Reaktvivov i Osobo Chistykh Khim.Veshchestv, **35**, 68 (1973).
75. I.N.Palant, Yu.I.Vainshtein, D.M.Krasnokutskaya, and L.N.Yakhontov, Khim.Geterotsikl.Soed., 773 (1973).
76. I.N.Palant, D.M.Krasnokutskaya, K.F.Turchin, O.S.Anisimova, Yu.I.Vainshtein, and L.N.Yakhontov, Khim.Geterotsikl.Soed., 1277 (1975).
77. I.N.Palant, Yu.I.Vainshtein, D.M.Krasnokutskaya, and L.N.Yakhontov, "Novosti Elektrokhimii Geterotsiklicheskikh Soedinenii.Tezisy Dokladov VIII Vsesoyuznogo Soveshchaniya po Elektrokhimii Organicheskikh Soedinenii, Riga, 1973" (Advances in the Electrochemistry of Heterocyclic Compounds. Abstracts of Reports of the VIIIth All-Union Conference on the Electrochemistry of Organic Compounds, Riga, 1973), p.42.
78. V.A.Azimov, D.M.Krasnokutskaya, I.N.Palant, and L.N.Yakhontov, Khim.Geterotsikl.Soed., 375 (1979).
79. L.V.Ektova, T.D.Miniker, I.V.Yartseva, and M.N.Preobrazhenskaya, Khim.Geterotsikl.Soed., 1083 (1977).
80. P.I.Abramenko, Zhur.Vses.Khim.Obshch.im.Mendeleeva, **18**, 715 (1973).
81. A.Brodrick and D.G.Wibberley, J.Chem.Soc., Perkin Trans.I, 1910 (1975).
82. W.Zimmermann, K.Eger, and H.J.Roth, Arch.Pharm. (Weinheim, Ger.); **309**, 597 (1976).
83. A.Z.Britten and W.G.Griffiths, Chem.Ind.,(London) 278 (1973),
84. French P.2 063 918 (1971); Chem.Abs., **76**, 126 961 (1972).
85. E.Bisagni, J.Bourzat, and J.Andre-Louisfert, Tetrahedron, **26**, 2087 (1970).
86. French P.2 174 746 (1973); Chem.Abs., **80**, 8 2933 (1974).
87. C.Ducrocq, E.Bisagni, J.M.Lhoste, J.Mispelter, and J.Defaye, Tetrahedron, **32**, 773 (1976).
88. F.Floy and A.Deryckere, Helv.Chim.Acta, **53**, 645, (1970).
89. S.W.Schneller and R.S.Hosmane, J.Heterocyclic Chem., **14**, 1291 (1977).
90. V.G.Granik, N.B.Marchenko, T.F.Vlasova, and R.G.Glushkov, Khim.Geterotsikl.Soed., 1509 (1976).
91. V.G.Granik, A.B.Grigor'ev, and M.K.Polievktov, Khim.Geterotsikl.Soed., 1523 (1977).
92. V.A.Azimov, V.G.Granik, R.G.Glushkov, and L.N.Yakhontov, Khim.Geterotsikl.Soed., 355 (1978).
93. M.Ogata, H.Matsumoto, and H.Kano, Tetrahedron, **25**, 5217 (1969).
94. US P.3 901 899 (1975); Chem.Abs., **83**, 193 079 (1975).
95. P.G.Gassma and Chin Ten Huang, J.Amer.Chem. Soc., **95**, 4453 (1973).
96. K.C.C.Bancroft, T.J.Ward, and K.Brown, J.Chem. Soc., Perkin Trans.I, 1852 (1974).
97. T.Kato and T.Niitsuma, J.Pharm.Soc.Japan, **92**, 1024 (1972); Ref.Zhur.Khim., 7Zb312 (1973).
98. B.A.J.Clark and J.Parrick, Tetrahedron, **30**, 475 (1974).
99. L.N.Yakhontov, M.Ya.Uritskaya, E.I.Lapan, and M.V.Rubtsov, Khim.Geterotsikl.Soed., 18 (1968).
100. L.N.Yakhontov, M.Ya.Uritskaya, V.A.Loginova, and M.V.R.Lubtsov, Khim.Geterotsikl.Soed., 456 (1968).
101. M.Ya.Uritskaya, V.A.Loginova, and L.N.Yakhontov, Khim.Geterotsikl.Soed., 1311 (1973).
102. A.La Manna, G.P.Bettinetti, V.Ghislandi, and P.P.Righetti, Boll.chim.farm., 112, 22 (1973).
103. T.Kauffmann and H.Fisher, Chem.Ber., **106**, 220 (1973).
104. V.G.Kartsev, P.B.Terent'ev, A.N.Kost, and M.F.Budyka, Khim.Geterotsikl.Soed., 1431 (1975).
105. L.N.Yakhontov, M.A.Portnov, V.A.Azimov, and E.I.Lapan, Zhur.Org.Khim., **5**, 956 (1969).
106. A.El-Anani, S.Clementi, A.R.Katrizky, and L.Yakhontov, J.Chem.Soc., Perkin Trans.II, 1072 (1973).
107. G.Favini and A.Gamba, J.Chim.Phys., **64**, 1443 (1967).
108. D.A.Bochvar, A.A.Bagatur'yants, A.V.Tutkevich, L.N.Yakhontov, M.Ya.Uritskaya, D.M.Krasnokutskaya, and M.V.Rubtsov, Izv.Akad.Nauk SSSR, Ser.Khim., 354 (1966).
109. D.A.Bochvar and A.A.Bagatur'yants, Teor.Eksper. Khim., **3**, 793 (1967).
110. D.A.Bochvar and A.A.Bagatur'yants, Teor.Eksper. Khim., **5**, 749 (1969).
111. P.J.Black, R.D.Brown, and M.L.Heffernan, Austral.J.Chem., **20**, 1305 (1967).
112. P.J.Black, R.D.Brown, and M.L.Heffernan, Austral. J.Chem., **20**, 1325 (1967).
113. G.G.Dvoryantseva, T.N.Ul'yanova, Yu.N.Sheinker, D.M.Krasnokutskaya, and L.N.Yakhontov, Khim. Geterotsikl.Soed., 76 (1976).
114. P.G.Riley and B.Robinson, Canad.J.Chem., **47**, 3257 (1969).
115. R.Herbert and D.G.Wibberley, J.Chem.Soc., B 459 (1970).
116. J.P.Saxena, Indian J.Chem., **5**, 73 (1967).
117. J.Elguero, C.Marzin, and M.E.Peek, Org.Magn. Reson., **7**, 445 (1975).
118. M.J.Toneby, J.Chromatog., **97**, 47 (1974).
119. L.N.Yakhontov, M.Ya.Uritskaya, and V.A.Loginova, USSR P.461 099 (1973); Byul.Izobret., No.7, 54 (1975).
120. L.N.Yakhontov, D.M.Krasnokutskaya, E.M.Peresleni, Yu.N.Sheinker, and M.V.Rubtsov, Dokl.Akad.Nauk SSSR, **176**, 613 (1967).
121. Yu.N.Sheinker, E.M.Peresleni, I.S.Rezchikova, and N.P.Zosimova, Dokl.Akad.Nauk SSSR, **192**, 1295 (1970).
122. C.A.Taylor, M.A.El-Bayoumi, and M.Kasha, Proc. Nat.Acad.Sci.U.S.A., **63**, 253 (1969).
123. V.I.Pechenaya and V.I.Danilov, Chem.Phys.Letters, **11**, 539 (1971).
124. K.C.Ingham, M.Abu-Elgheit, and M.A.El-Bayoumi, J.Amer.Chem.Soc., **93**, 5023 (1971).
125. K.C.Ingham and M.A.El-Bayoumi, J.Amer.Chem. Soc., **96**, 1674 (1974).
126. R.F.Hopmann, J.Phys.Chem., **78**, 2341 (1974).

127. M.A.El-Bayoumi, P.Avouris, and W.R.Ware, J. Chem.Phys., **62**, 2499 (1975).
128. M.A.El-Bayoumi, J.Phys.Chem., **80**, 2259 (1976).
129. L.Znojek, Acta Polon.Pharm., **24**, 121 (1967); Chem. Abs., **68**, 114 458 (1968).
130. US P.3 960 876 (1976); Chem.Abs., **85**, 177 390 (1976).
131. B.P.1 141 949 (1969); Chem.Abs., **70**, 68338 (1969).
132. US P.3 777 246 (1968); Chem.Abs., 11 7131 (1968).
133. A.J.Verbiscar, U.S.Clearinghouse Fed.Sci.Tech. Inform., AD 1969, AD-697 814; Chem.Abs., **72**, 90 338 (1970).
134. A.J.Verbiscar, J.Medium Chem., **15**, 149 (1972).
135. BRD Appl.2 306 001 (1973); Chem.Abs., **79**, 126 518 (1973).
136. B.A.J.Clark and J.Parrick, J.Chem.Soc., Perkin Trans.I, 2270 (1974).
137. R.J.Kline, L.F.Sytsma, and D.R.Shackie, Inorg. Nuclear Chem., Letters, **7**, 311 (1971).
138. R.W.Brookes and R.L.Martin, Austral.J.Chem., **28**, 1363 (1975).
139. R.W.Brookes and R.L.Martin, Inorg.Chem., **14**, 528 (1975).
140. C.Chavis, F.Dumont, G.Gosselin, and J.T.Imbach, Carbohydr.Res., **46**, 43 (1976).
141. A.V.Stetsenko and I.P.Kupchevskaya, Ukrain. Khim.Zhur., **38**, 503 (1972).
142. A.Ducruix, C.Riche, and C.Pascard, Tetrahedron Letters, 51 (1976).
143. L.N.Yakhontov, D.M.Krasnokutskaya, and M.V.Rubstov, "Khimiya Geterotsiklicheskikh Soedinenii" (The Chemistry of Heterocyclic Compounds), Vol.1, "Azotsodershashchie Geterotsikly" (Nitrogen-Containing Heterocycles), Izd.Zinatne, Riga, 1967, p. 450.
144. L.N.Yakhontov and V.A.Azimov, Khim.Geterotsikl. Soed., 32 (1970).
145. L.N.Yakhontov and E.I.Lapan, Khim.Geterotsikl. Soed., 1528 (1972).
146. M.Ya.Uritskaya, V.V.Vasil'eva, S.S.Liberman, and L.N.Yakhontov, Khim-Farm.Zhur., No.11, 8 (1973).
147. L.N.Yakhontov, S.S.Liberman, D.M.Krasnokutskaya, M.Ya.Uritskaya, V.A.Azimov, M.S.Sokolova, and L.N.Gerchikov, Khim-Farm.Zhur., No.11, 5 (1974).
148. US P.3 362 956 (1968); Chem.Abs., **69**, 10 467 (1969).
149. M.Schulz, H.Wegwart, and K.Both, Plaste Kant., **21**, 430 (1974); Chem.Abs., **81**, 170 340 (1974).
150. S.Okuda and M.Robison, J.Org.Chem., **24**, 1008 (1959).
151. D.M.Krasnokutskaya and L.N.Yakhontov, Symposium, "Khimiya i Farmakologiya Indol'nykh Soedinenii" (The Chemistry and Pharmacology of Indole Compounds), Izd.Shtiintsa, Kishinev, 1975, p.64.
152. D.M.Krasnokutskaya and L.N.Yakhontov, Khim. Geterotsikl.Soed., 380 (1977).
153. A.F.Pozharskii, V.V.Kuz'menko, V.A.Azimov, and L.N.Yakhontov, Khim.Geterotsikl.Soed., 1232 (1973).
154. L.N.Yakhontov, D.M.Krasnokutskaya, and A.N.Akalaev, Dokl.Akad.Nauk SSSR, **192**, 118 (1970).
155. L.N.Yakhontov, D.M.Krasnokutskaya, A.N.Akalaev, I.N.Palant, and Yu.I.Vainshtein, Khim.Geterotsikl. Soed., 789 (1971).
156. J.D.Bourzat and E.Bisaghi, J.Heterocyclic Chem., **10**, 511 (1973).
157. E.Bisagni, J.D.Bourzat, C.Labrid, P.Delort, and A.Le-Ridant, Chim.Theraphie, **8**, 559 (1973); Chem.Abs., **81**, 9617 (1974).
158. J.P.Marquet, L.Montagnier, J.Gruest, J.D.Bourzat, J.Andre-Louisfert, and E.Bisagni, Chim.Theraphie, **6**, 427 (1971); Chem.Abs., **76**, 126 924 (1972).
159. D.M.Krasnokutskaya, A.S.Morkovnik, B.A.Tertov, and L.N.Yakhontov, Khim.Geterotsikl.Soed., 1527 (1977).
160. M.Ya.Uritskaya, V.A.Loginova, and L.N.Yakhontov, Khim.Geterotsiki.Soed., 1370 (1973).
161. V.A.Azimov, M.Ya.Uritskaya, and L.N.Yakhontov, Khim.Farm.Zhur., No.11, 6 (1968).
162. B.Carnmalm, A.Misiorny, S.B.Ross, and N.E.Stjernstrom, Acta Pharm.Suec., **11**, 196 (1974); Chem.Abs., **81**, 37 512 (1974).
163. N.P.Kostyuchenko, K.G.Zhirnova, M.N.Preobrazhenskaya, Yu.N.Sheinker, and N.N.Suvorov, Zhur.Org. Khim., **8**, 2422 (1972).
164. A.LaManna, C.Caramella, U.Conte, V.Ghislandi, and G.P.Bettinetti, Boll.Chim.Farm., **112**, 12 (1973).
165. US P.3 511841 (1970); Chem.Abs., 73, 25 523 (1970).
166. South African P.02 787 (1975); Chem.Abs., **85**, 21 487 (1976).
167. BRD Appl.2 427 207 (1975); Chem.Abs., **82**, 156 360 (1975).
168. US P.3 687 675 (1972); Chem.Abs., **78**, 73 667 (1973).
169. US P.3 923 524 (1975); Chem.Abs., **85**, 64 803 (1976).
170. BRD Appl.2 047 383 (1971); Chem.Abs., **76**, 20 044 (1972).
171. BRD Appl.2 242 761 (1973); Chem.Abs., 79, 47 868 (1973).
172. BRD Appl.2 264 552 (1974); Chem.Abs., **81**, 19 229 (1974).
173. BRD Appl.2 363 216 (1974); Chem.Abs., 81, 113 650 (1974).
174. L.N.Yakhontov and D.M.Krasnokutskaya, USSR P.453 403; Byul.Izobret, No.46, 55 (1974).
175. D.M.Krasnokutskaya and L.N.Yakhontov, Khim. Geterotsikl.Soed., 380 (1977).
176. L.N.Yakhontov and D.M.Krasnokutskaya, Khim. Geterotsikl.Soed., 1550 (1970).
177. BRD Appl.2 321 520 (1973); Chem.Abs., **80**, 47 964 (1974).
178. US P.3 911 130 (1975); Chem.Abs., **84**, 59 426 (1976).
179. K.C.C.Bancroft, T.J.Ward, and K.Brown, J.Chem. Soc., Perkin Trans.I, 468 (1977).
180. T.Nacano and M.Santana, J.Heterocyclic Chem., 13, 585 (1976).
181. G.Seitz and T.Kaempchen, Arch.Pharm.(Weinheim, Ger.), **309**, 679 (1977); Chem.Abs., **86**, 29 734 (1977).
182. L.G.Brantsevich, N.S.Miroshnichenko, A.V.Stetsenko, A.T.Slabospitskaya, and V.V.Chekmacheva, Mikrobiol.Zhur.(Kiev), **37**, 635 (1975).
183. G.A.Buznikov, L.Rakic, T.M.Turpaev, and L.N.Markova, Exp.Cell Res., **86**, 317 (1974).
184. M.D.Mashkovskii, A.I.Polezhaeva, N.I.Andreeva, T.K.Trubitsyna, B.A.Medvedev, and L.F.Roshchina, Khim.Farm.Zhur., No.2, 38 (1978),
185. M.F.Marshalkin, A.I.Polezhaeva, M.D.Mashkovskii, and L.N.Yakhontov, Khim.Farm.Zhur., No.11, 11 (1973).
186. L.N.Yakhontov, S.S.Liberman, D.M.Krasnokutskaya, M.Ya.Uritskaya, V.A.Azimov, M.S.Sokolova, and L.N.Gerchikov, Khim.Farm.Zhur., No.11, 5 (1974).
187. M.R.Bell, J.O.Hoppe, H.E.Lape, D.Wood, A.Arnold, and W.H.Selberis, Experientia, **23**, 298 (1967).

188. H.E.Lape, J.O.Hoppe, M.R.Bell, D.Wood, W.H.Selberis, and A.Arnold, Arch.Int.Pharmacodyn. Ther., 171, 394 (1968); Chem.Abs., 68, 85 975 (1968).
189. H.S.Pitkow, R.H.Davis, A.Frank, P.Ward, and H.G.Hill, Libr.compend., 3, 601 (1975); Chem.Abs., 84, 54 802 (1976).
190. G.A.Buznikov, L.Rakich, and T.M.Turpaev, Zhur. Evol.Biokhim.Fiziol., 8, 478 (1972).
191. G.A.Buznikov, B.N.Manukhin, L.Rakich, T.M.Turpaev, A.A.Aroyan, P.R.Akopyan, N.F.Kucherova, T.R.Ovsepyan, and L.N.Yakhontov, Zhur.Evol. Biokhim.Fiziol., 12, 31 (1976).
192. B.Y.Endo, G.W.Schaeffer, Phytopathology, 57, 576 (1967).
193. J.Kochba and R.M.Samish, J.Amer.Soc.Hort.Sci., 97, 178 (1972); Chem.Abs., 77, 84 299 (1972).
194. J.M.Webster, Nematologica, 13, 256 (1967); Chem. Abs., 67, 63 168 (1967).
195. K.Tsuji, Yakugaku Zasshi, 96, 479 (1976); Chem. Abs., 85, 99 075 (1976).
196. I.Schmeltz and D.Hoffmann, Chem.Rev., 77, 295 (1977).
197. Japanese P.75 129 751 (1975); Chem.Abs., 84, 79 606 (1976).
198. R.D.Masteller and C.Yanofsky, J.Bacteriol., 105, 268 (1971).
199. G.J.Mitchison and M.Wilcox, Nature, New Biol., 246, 229 (1973).
200. M.Rabinovitz, A.Finkelman, R.L.Reagan, and T.R.Breitman, J.Bacteriol., 99, 336 (1969).
201. J.C.Kuhn, M.J.Pabst, and R.L.Somerville, J. Bacteriol., 112, 93 (1972); Chem.Abs., 78, 53 213 (1973).
202. W.F.Prouty and A.L.Goldberg, Nature, New Biol., 240, 147 (1972); Chem.Abs., 78, 69 039 (1973).
203. S.Schlesinger, J.Biol.Chem., 243, 3877 (1968); Chem.Abs., 69, 24 801 (1969).
204. B.S.Sharman and R.U.Haque, J.Gen.Microbiol., 77, 221 (1973).
205. T.Leboeuf-Trudeau, J.De Repentigny, R.M.Frenette, and S.Sonea, Canad.J.Microbiol., 15, 1 (1969).
206. S.Lariviere, M.Legars, and L.G.Mathieu, Canad.J. Comp.Med., 33, 98 (1969); Chem.Abs., 71, 120 744 (1969).
207. J.Janecek and J.Spizek, Foila Microbiol., 14, 529 (1969); Chem.Abs., 72, 75 898 (1970).
208. L.G.Mathieu and D.Legault-Hetu, Rev.Canad.Biol., 32, 11 (1973); Chem.Abs., 79, 13 948 (1973).
209. S.Barlati and O.Ciferri, J.Bacteriol., 101, 166 (1970).
210. J.Majerfeld, S.Barlati, and O.Ciferri, J.Bacteriol., 101, 350 (1970).
211. H.Rosenfeld and P.Feigelson, J.Bacteriol, 97, 697 (1969).
212. H.Rosenfeld and P.Feigelson, J.Bacteriol., 97, 705 (1969).
213. J.Ismande, Genetics, 75, 1 (1973).
214. P.T.Sullivan, M.V.Kester, and S.J.Norton, Biochem. Biophys.Acta, 293, 343 (1973).
215. P.Laban, P.Morelis, and C.R.Hebd, Seances Acad. Sci., Ser. D, 281, 671 (1975); Chem.Abs., 84, 13 035 (1976).
216. Japanese P.7 348 686 (1973); Chem.Abs., 79, 103 645 (1973).
217. Japanese P.7 391 281 (1973); Chem.Abs., 80, 131 685 (1974).
218. M.Wilcox, Anal.Biochem., 59, 436 (1974).
219. H.Y.T.Yang and N.H.Neff, Mol.Pharmacol., 12, 69 (1976).
220. P.E.Pilet and C.R.Hebd, Seances Acad.Sci., Sev. D, 273, 2253 (1971); Chem.Abs., 76, 95 687 (1972).
221. J.M.Widholm, Biochim.Biophys.Acta, 261, 52 (1972).
222. J.M.Widholm, Biochim.Biophys.Acta, 261, 44 (1972).
223. J.M.Widholm, Biochim.Biophys.Acta, 279, 48 (1972).
224. E.C.Cocking, J.B.Power, P.K.Evans, F.Safwat, E.M.Frearson, C.Hayward, S.F.Berry, and D.George, Plant Sci.Letters, 3, 341 (1974); Chem.Abs., 82, 28 689 (1975).
225. B.Sproessler and F.Lingens, Hoppe-Seyler's Z. Physiol.Chem., 351, 967 (1970); Chem.Abs., 73, 94 863 (1970).
226. E.Alello, G.Dattolo, G.Cirrincione, S.Plescia, and G.Daidone, J.Heterocyclic Chem., 15, 537 (1978).
227. T.Murata, T.Sugawara, and K.Ukawa, Chem.Pharm. Bull., 26, 3080 (1978).
228. S.W.Schneller, R.S.Hosmane, L.B.MacCartney, and D.A.Hessinger, J.Medicin.Chem., 21, 990 (1978).
229. A.A.Prokopov and L.N.Yakhontov, USSR P.687 075; Byul.Izobret, No.35, 107 (1979).
230. M.F.Marshalkin and L.N.Yakhontov, Zhur.Org. Khim., 14, 1729 (1978).
231. M.F.Marshalkin, V.A.Azimov, L.F.Linberg, and L.N.Yakhontov, Khim.Geterotsikl.Soed., 1120 (1978).
232. Yu.P.Kitaev and T.V.Troepol'skaya, Khim.Geterotsikl.Soed., 1011 (1978).
233. M.F.Marshalkin and L.N.Yakhontov, Khim.Geterotsikl.Soed., 1478 (1978).
234. M.F.Marshalkin, V.A.Azimov, and L.N.Yakhontov, Zhur.Org.Khim., 15, 442 (1979).
235. M.F.Marshalkin, V.A.Azimov, and L.N.Yakhontov, Zhur.Org.Khim., 15, 1781 (1979).
236. M.F.Marshalkin, V.A.Azimov, A.S.Gasparyants, and L.N.Yakhontov, Khim.Geterotsikl.Soed., 1279 (1979).
237. P.Staeglich and M.Zander, Z.Naturforsh., 31A, 1391 (1976); Chem.Abs., 86, 88 587 (1977).
238. B.A.J.Clark and J.Parrick, Org.Mass.Spectrom., 12, 421 (1977).
239. G.Moller and A.M.Nishimura, J.Phys.Chem., 81, 147 (1977).
240. P.Avouris, Li L.Yang, and M.A.El-Bayoumi, Photochem.Photobiol., 24, 211 (1976).
241. V.I.Danilov, L.G.Il'chenko, and V.I.Pechenaya, Dokl.Akad.Nauk Ukrain.SSR, Ser.A, 253 (1978).
242. M.A.El-Bayoumi, Report 1977, COO-2039-33, From Energy Res.Abstr., 3 (8) 1978, Abstr.No.19 319; Chem.Abs., 89, 67 804 (1978).
243. S.Clementi, S.Lepri, G.B.Sebastiani, S.Gronowitz, Ch.Westerlund, A.-B.Hörnfeldt, J.Chem.Soc. II, 861 (1978).
244. V.A.Azimov, A.A.Prokopov, I.S.Zhivotovskaya, M.K.Polievktov, and L.N.Yakhontov, Khim. Geterotsikl.Soed., 1489 (1979).
245. H.Nakamura and J.J.Pisano, J.Chromatog., 152, 167, (1978).
246. M.Ciureanu, Rev.Roum.Chim., 21, 1007 (1976).
247. M.Ya.Uritskaya, O.S.Anisimova, and L.N.Yakhontov, Khim.Geterotsikl.Soed.,80 (1979).
248. A.A.Prokopov and L.N.Yakhontov, Khim.Geterotsikl. Soed., 847 (1979).
249. S.W.Schneller and R.S.Hosmane, J.Org.Chem., 43, 4487 (1978).
250. S.W.Schneller and R.S.Hosmane, J.Heterocyclic Chem., 15, 325 (1978).

251. M.N.Preobrazhenskaya and T.D.Miniker, Nucleic Acid Chem., 749 (1978); Chem.Abs., **90**, 23 525 (1979).
252. F.A.Cotton, D.G.Lay, and M.Millar, Inorg.Chem.. 17, 186 (1978).
253. US P.3 984 248 (1976); Chem.Abs., **86**, 18 376 (1977).
254. US P.3 988 154 (1976); Chem.Abs., **86**, 180 677 (1977).
255. US P.3 988 156 (1976); Chem.Abs., **86**, 180 678 (1977).
256. US P.4 028 113 (1977); Chem.Abs., **87**, 54 536 (1977).
257. Canadian P.1 023 188 (1977); Chem.Abs., **89**, 14 803 (1978).
258. H.Bothe and G.Eisbrenner, Biochem.Physiol. Pflanz., 171, 323 (1977); Chem.Abs., **87**, 640 (1977).
259. J.Kochba and P.Spiegel-Roy, Z.Pflanzenphysiol., 81, 283 (1977); Chem.Abs., **86**, 101 853 (1977).
260. J.Kuhn, Antimicrob.Agents Chemother., 12, 322 (1977); Chem.Abs., **87**, 148 484 (1977).
261. D.N.Wheatley and M.S.Inglis, Exp.Cell Res., **107**, 191 (1977); Chem.Abs., **87**, 112 423 (1977).
262. H.Kende, M.Fukuyama-Dilworth, and R.Dezacks, Plant Growth Subst., Proc. VIII Int.Conf., 1973, p.675; Chem.Abs., **87**, 130 594 (1977).
263. T.Kosuge, K.Tsuji, K.Wakabayashi, T.Okamoto, K.Shudo, Y.Iitaka, A.Itai, T.Sugimura, T.Kawachi et al., Chem.Pharm.Bull., **26**, 611 (1978).
264. J.Williamson and T.J.Scott-Finnigan, Antimicrob. Agents Chemother., 13, 735 (1978); Chem.Abs., **89**, 85 214 (1978).
265. R.J.Payley, W.W.Fredricks, and O.H.Smith, J.Bacteriol., **136**, 219 (1978).
266. D.E.Beattie, R.Crossley, A.C.W.Curran, O.C.Hill, and A.E.Lawrence, J.Medicin.Chem., **20**, 718 (1977).
267. US P.4 029 667 (1977); Chem.Abs., **87**, 102 305 (1977).

Ordzhonikidze All-Union Institute
of Chemistry and Pharmacology,
Moscow

Translated from *Uspekhi Khimii*, 49, 848 - 878 (1980) U.D.C. 547.912.4.

Structure and Properties of Networks in Heat-resistant Polymers

A.A.Askadskii and Yu.S.Kochergin

Methods are discussed for obtaining networks in heat-resistant polymers, including cross-linking at terminal groups, the use of reactive oligomers together with heat-resistant polymers capable of interacting with them, polycyclotrimerisation, etc. The influence of the chemical structure of the network and the frequency of branch points has been traced on the dynamic mechanical properties of the polymers and also on the stress relaxation and creep under static conditions. Network parameters and strength properties are compared, and methods of controlling the mechanical properties of network systems possessing enhanced heat-resistance are discussed. A list of 75 references is included.

CONTENTS

I.	Introduction	445
II.	Influence of chemical structure on molecular mobility of networks	445
III.	Dynamic mechanical investigation of chemical cross-linking processes	448
IV.	Strength properties of networks	450
V.	Relaxation properties of networks under conditions of static contraint (stress relaxation and creep)	453

I. INTRODUCTION

The preparation and properties of heat-resistant polymers based on network systems have been the object of persistent attention by research workers. This is due to the great difficulties often encountered in producing articles from linear heat-resistant polymers, as a consequence of the high temperatures and pressures in their processing by the usual methods (hot extrusion, injection moulding) necessitated by the high softening points and great viscosities of the systems. However, the initial compounds for the preparation of network systems (oligomers of aromatic structure, mixtures of linear thermostable polymers with reactive oligomers) can easily be converted into a plastic state, and the required materials obtained from them by heat-treatment or other methods.

Several processes are now available for obtaining network systems based on heat-resistant polymers: oligomers containing aromatic rings and reactive terminal groups can be cross-linked; heat-resistant linear polymers containing reactive groups in the chain can be mixed with reactive oligomers, and the mixture then heat-treated; and oligomers containing aromatic units between reactive groups can undergo cyclotrimerisation. The chemical structure of the chain segments between branch points, of course, has a substantial influence on the properties of the heat-resistant network system; formation of a supermolecular structure at different stages of network formation is also important.

A vast amount of research work, summarised in a monograph[1], has been devoted to traditional network systems. The present Review is concerned with the structure and properties of network heat-resistant polymers. Such systems have the characteristic methods of preparation enumerated above (which, however, have much in common with methods for obtaining traditional networks) and exhibit specific effects of network structure on polymer properties. In the case of networks constructured of flexible macromolecules forming the internodal segments heat-resistance can be enhanced only by substantial increase in the density of cross-linking. However, the polymer material then loses its valuable qualities: brittleness, cracking, etc. appear. A high degree of cross-linking is not necessary to obtain heat-resistant materials based on rigid macromolecules, for the chemical structure of the internodal segments then has the greatest influence on properties. Furthermore, a feature of networks based on aromatic compounds is their capacity of order, evident in signs of crystallinity at high degrees of conversion.

II. INFLUENCE OF CHEMICAL STRUCTURE ON MOLECULAR MOBILITY OF NETWORKS

Heat-resistant polymers are extremely interesting materials for the investigation of relaxation transitions, since they exist in a vitreous state over wide temperature ranges, within which many transitions can be detected. Completely aromatic polymers provide unique opportunities for the study of molecular motions, in particular those responsible for transition ranges and relaxation effects. In ordinary linear aromatic polymers relaxation processes arise from rotational movements of chain segments and also of various polar radicals. In completely aromatic polymers the rotational mobility of the molecules is considerably restricted by resonance and steric effects (e.g. barriers to rotation due to *ortho*-substitution), so that mobilities other than rotational must be expected.

Great attention has recently been paid to the study of relaxation transitions in heat-resistant polymers[2-13]. Fundamental research on transitions in heat-resistant aromatic polymers[2] has involved study of the relaxation properties of poly(phenylquinoxalines) over the wide temperature range from −200 to 500 °C. Far less study has been made of the dynamic mechanical properties of network systems based on heat-resistant polymers. Most heat-resistant aromatic polymers can be cross-linked simply by holding isothermally at high temperatures. The density of cross-linking and hence the dynamic mechanical characteristics can be varied within wide limits by controlling the time and/or temperature of cross-linking.

Investigation of the influence of the previous thermal history on the dynamic characteristics of polyquinoxaline and poly(phenylene oxide) films has shown[2,5] that heating in helium at 400 °C gradually displaces the temperature dependence of the modulus of elasticity E' to higher temperatures, and shorter times of heating in air yield similar results. This change in modulus is explained[2,5] by pyrolytic cross-linking during heating in an inert atmosphere, which in air is accompanied by oxidation.

Linear poly-(2,2'-*p*-phenylene-6,6'-bis-3-phenylquinoxaline) has been cross-linked[14] by isothermal heating at 425–490 °C, with the kinetics monitored by the variation in the glass point T_{gl}. The influence of the molecular mass and nature of terminal groups on dynamic properties was examined in three specimens differing only in these characteristics. The apparent activation energy of cross-linking is independent of them and has the same value (60 kcal mole^{-1}) as the activation energy of thermal breakdown of the polymer (which was determined from measurements of the isothermal weight losses). However, the rate of change of the glass point resulting from heating at these temperatures is a function of both molecular mass and type of terminal groups. It was also observed that the isothermally cross-linked polymer undergoes a sharp decrease in mass at a higher temperature than its linear analogue, and leaves a larger carbon residue at 800 °C.

The same workers have investigated[15] the thermomechanical properties of poly(phenylimide-quinoxaline), which differs from the polyphenylenephenylquinoxaline only in the presence of an imide group in the chain. In the present case, unlike the former, no difference between rates of change of glass point is observed after specimens containing different terminal groups have been heated. Comparison of such rates in specimens of the two types of polymer showed that, despite the identical activation energies, formation of cross-links is far more intense in the polymeric imide derivatives. This implies an additional mechanism of formation of cross-links, probably involving opening of the imide ring.

The density of cross-linking can be varied also by introducing reactive side-groups. An investigation[16] of the mechanism of the hardening of linear poly(phenylenequinoxalines) containing and not containing such groups led to the conclusion that their presence promotes more rapid change in glass point. An accompanying kinetic examination of cross-linking in poly(phenylamide-quinoxalines) of high molecular mass showed that isothermal holding in nitrogen at temperatures from 380 to 420 °C produced an initial lowering of the glass point followed by a rise with increasing duration of heating. In some polymers of this type the fall in glass point during the initial stage of heating reached 16 deg. Such behaviour was attributed[16] to the superposition of two effects—random chain rupture and cross-linking—the former of which leads initially to a sharp decrease in mean molecular mass with a corresponding fall in glass point, whereas thermal cross-linking produces an almost linear rise in glass temperature. In polymers of low molecular mass random chain rupture has little effect on the glass point, change in which is due mainly to cross-linking. Therefore such polymers do not exhibit a minimum in the isothermal variation of glass point with time. It must be stressed that such minima have never been observed with poly (phenylenequinoxalines) or poly (phenylimide-quinoxalines), which possess greater resistance to chain rupture, so that cross-linking is dominant.

When isothermal heating is conducted above the glass point the time variation of the loss coefficient passes through a maximum. In all cases (heating below and above the glass point) an equilibrium state is established within a time depending on the hardening temperature. However, the resulting glass points do not remain the same, but rise significantly[16].

Comparison of the dynamic mechanical properties of hardened phenolic resins with those of poly(phenylenequinoxalines) showed[17] that not only the speed but also the absorption of sound is greater in the former, which is unexpected, since materials with a higher velocity of sound usually have lower absorption. It was therefore assumed[17] that some additional loss mechanism operates in phenolic resins. The absorption of sound depends significantly on the degree of hardening, and may serve for determination of the degree of cross-linking.

Oligo(phenylquinoxalines) containing vinyl terminal groups undergo thermal cross-linking far more readily than does the standard poly(phenylenequinoxaline) and form structures with a high frequency of cross-linking and high glass points[18]. On heat-treatment (in nitrogen at 350 °C) the glass point rises rapidly during the first 15 min, after which it remains almost unchanged.

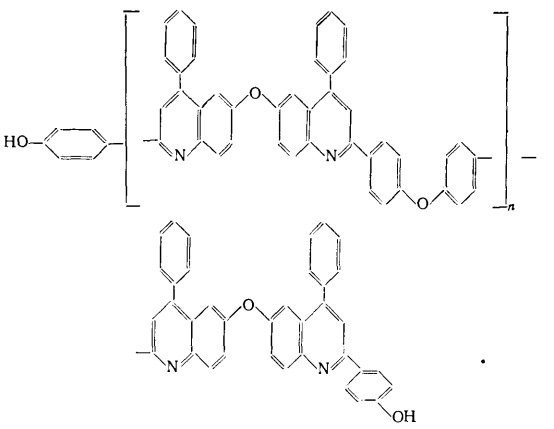
Oligo(phenylquinoxalines) containing acetylenic terminal groups are also used to form network heat-resistant polymers[19,20]. The oligomers dissolve well in organic solvents and have comparatively low softening temperatures. When such systems are heated at 200–300 °C they undergo cross-linking owing to polymerisation of the acetylenic groups; the process of cross-linking is extremely complicated and takes place by various mechanisms. Analysis of the influence of temperature and duration of hardening of oligo(phenylquinoxalines) on their properties must take into account the sharp rise in glass point on hardening, which slows down cross-linking. Thermogravimetric and mass-spectrometric examination of hardening of the oligomers and degradation of the hardened systems has shown[20] no evolution of volatile components in the temperature range of hardening (200–300 °C), and vacuum degradation beginning at 465 °C.

The cross-linking of poly(phenylene sulphide) when heated is assumed[21] to be accompanied by oligomerisation with increase in chain length. In air cross-linking is thought to be effected by oxygen bridges, but in an inert atmosphere through benzene rings and sulphide bridges. The cross-linking of poly(phenylene sulphide) by sulphur leads to a decrease in thermal stability, although the heat-resistance increases[22].

Several studies have been made[23–26] on the properties of thermostable polymers already cross-linked in course of preparation. Biphenylene units introduced into the macromolecular chain have been used[23] as hardening agents for polyquinolines. Cross-linking takes place without evolution of volatile products, but the resulting compounds possess enhanced heat-resistance. Hardening can be effected either thermally or in the presence of a rhodium catalyst, which appreciably lowers the temperature of cross-linking. Cross-linked poly(phenylquinoxalines) have been obtained[24] by introducing trisbenzyl into the reaction mixture. They have been used in the production of multicomponent materials containing graphite fibres.

Cross-linked polymers have been obtained[25] by the polycondensation of tetracarboxylic dianhydrides with polyfunctional amines. Under thermomechanical constraint these polymers behave similarly to other cross-linked systems that exhibit a rise in glass point with increase in concentration of the cross-linking agent.

Cross-linked polyphenylenes and poly(phenylquinolines) have been obtained[26] by the cyclotrimerisation of aryl cyanates. An example of the former is the condensation of di-*p*-acetylphenyl ether with di-*p*-amino-*m*-benzoylphenyl ether and *p*-hydroxyacetophenone to give the structure This prepolymer containing terminal hydroxyls was treated with excess of cyanogen bromide to convert it into the aromatic dicyanate, which was then transformed by heat-treatment into a cross-linked product. The temperature required for cross-linking rises with increase in the length of the segment between the cyanato-groups. Cross-linking raises significantly the glass point of the polymer (in relation to those of the prepolymers), although leaving it lower than for linear analogues (e.g. polyphenylene).



(I)

However, chemical cross-linking in heat-resistant polymers, which can be effected at relatively low temperatures (200–300 °C), yields materials having lower glass points (and hence lower operating temperatures) than have materials that have been thermally cross-linked at high temperatures[23, 24, 26]. Even with 100% content [sic] of cross-linking agent the materials exhibit thermoplasticity[24], but this is eliminated by additional heating at high temperatures (482–510 °C). Similar results have been obtained by the high-temperature afterhardening of compositions with lower contents (30–60%) of cross-linking agent.

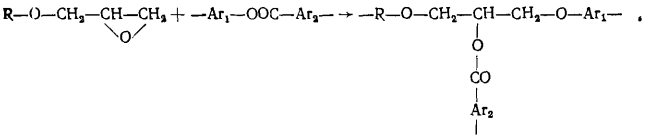
Calculated and experimental glass points for poly(phenylquinoxaline) have been compared[27, 28]. Formation of cross-links in this polymer by heat-treatment raises the glass point by 50–80 deg.

Investigation of the dynamic mechanical properties of polyamides has shown[29] that formation of a polymer network by irradiation[30] or chemical reaction[31] diminishes the mobility of the amorphous regions. As a consequence there is a loss of mechanical properties due to large amounts of the α-form. The glass transition of the polyamide is displaced to higher temperatures. The influence of density of cross-linking on local and segmental mobility of networks has been discussed in detail in the monograph[1].

The effect of isothermal heat-treatment of a polyimide on its dynamic mechanical properties has been studied[32, 33]. Heating at 500 °C raises the glass point from 350 to ~500 °C, whereas the relaxation transition in the vitreous state (with a maximum at ~150 °C) actually remains unchanged after heat-treatment. This suggests that here the density of cross-linking is sufficient to have an appreciable influence on the motion of the large chain segments involved in the glass transition but insufficient to affect the small-scale movements responsible for relaxation in the vitreous state.

An important achievement of the dynamic mechanical method for investigating relaxation transitions is to permit study not only of the properties of the final reaction products but also of the variation in such properties during the actual reaction. Recently several workers[34–39] have used measurements of dynamic mechanical properties to study the kinetics of hardening. Usually the phenomenon is investigated by estimating the degree of conversion of reactive groups by chemical analysis, infrared spectroscopy, or calorimetry. However, the sensitivity of these methods drops abruptly in the final stages of hardening (at high degrees of conversion) that generally are largely responsible for the optimum properties of cross-linked polymers.

The dynamic mechanical method has been used[39] to investigate the kinetics of the hardening of epoxy-polymers of heat-resistant aromatic systems. Such hardening is due to reaction of the epoxy-rings with ester links[40]. When a polyarylate serves as chemically active heat-resistant polymer, for example, its reaction with an epoxy-oligomer can be represented[41]:



The temperature at which reaction begins and the rate are significantly influenced by the chemical structure both of the epoxy-polymer and of the polyester. Reaction takes place also in the hardening of compositions containing traditional hardeners together with polyesters. The result is a polymer network possessing several interesting mechanical properties, as will be shown below.

A study has been made[39] of the influence of the composition of polymer networks on the temperature dependence of the modulus of eleasticity E' and tan δ. Fig. 1*a* illustrates the measured temperature dependence for a composition based on the polyarylate F-2 (a polyester of terephthalic acid and phenolphthalein)[42] and the cycloaliphatic epoxy-resin UP-612 (epoxide number 26–28) and containing various quantities of the hardener UP-607 (a polyanhydride of sebacic acid). Increase in the hardener concentration is accompanied by increase in the maximum values of tan δ, but a fall in the glass point, evidence of the plasticising effect of the aliphatic hardener. A sharp rise in tan δ, corresponding to softening of the system as a whole, occurs with all compositions in a similar temperature range. Fig. 1*a* shows also that introducing a larger quantity of hardener leads to formation of a more elastic network with a smaller modulus of elasticity. In order to assess the effect of the concentration of the epoxy-polymer on the temperature dependences, various quantities of UP-612 were introduced into a composition containing 50 parts by weight of UP-607 per 100 of F-2. Fig. 1*b* shows that tan δ_{max} increases with the concentration of the epoxy-polymer and that the corresponding temperature T_{max} rises. The slight increase can be attributed to the accompanying decrease in the proportion of the plasticising low-molecular hardener.

A characteristic feature of a polymer network formed by reaction between a polyarylate and an epoxy-polymer is a well defined difference in rigidity between cross-linked chains (polyarylate) and cross-linking bridges (epoxy-polymer). The network itself can be constructed in several ways—by formation of (i) an ordinary three-component network, (ii) so called interpenetrating networks as a consequence of the difference in reactivity between two macromolecular hardeners, and (iii) an intermediate system by partial interpenetration of networks accompanied by formation of chemical branch points—of which process (iii) is the most interesting. Interpenetrating networks form a complicated system[43–47] comprising two or more three-dimensional network polymers, not combined chemically but inseparable owing to the mechanical intertwining of chains consequent on the conditions of preparation. In the opinion of some workers[45] such systems must be regarded as a particular case of graft copolymers, in which the number of cross-links between macromolecules of each component far exceeds the number of grafts of one component on the other.

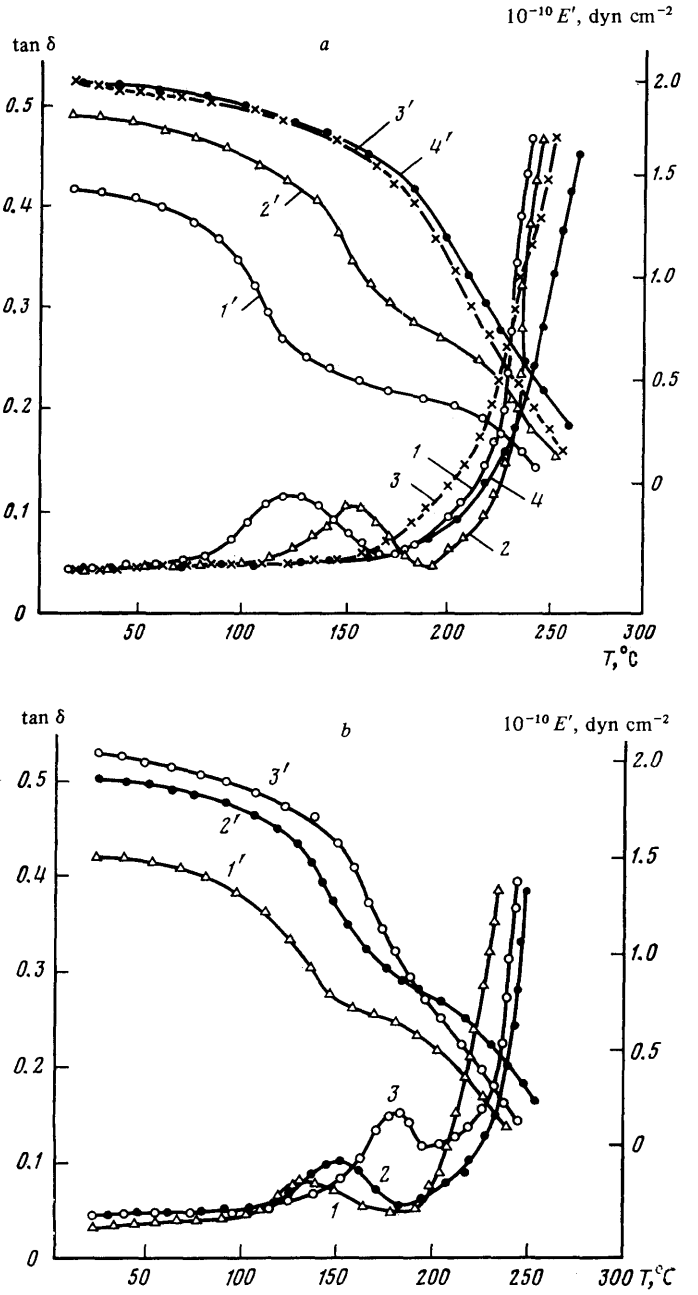


Figure 1. Temperature dependence of tan δ (unprimed curves) and E' (primed) for materials based on (parts by weight) 100 F-2: (*a*) with 100 UP-612 and different quantities of UP-607 hardener: 1,1′) 100; 2,2′) 50; 3,3′) 25; 4,4′) 0; (*b*) with 50 UP-607 and various quantities of UP-612: 1,1′) 50; 2,2′) 100; 3,3′) 150.

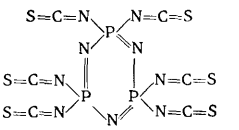
The synthesis of interpenetrating networks represents a new method for controlling the size and structure of different phase regions by varying the degree of cross-linking. Whereas many mechanical mixtures of polymers exhibit a tendency to form large (1–10 μm) phase regions, interpenetrating networks give a more uniform phase structure with smaller inhomogeneities. When the phase regions are very small (~100 Å), the classic concept of a sharp boundary separating two phases is inapplicable. A composite material having regions of ~100 Å is non-classical and varies continuously from point to point. In this case every local volume element makes its contribution to the glass point according to its composition and structure.

Materials comprising normally incompatible polymers forced into a single network possess a fairly broad region of high damping, which may cover the temperature range between the glass points of the individual components. Several vibration-absorbing materials having a wide (and controllable) useful temperature range for the damping of vibrations have been obtained[48–51] by preparing special compositions of interpenetrating networks, but they cannot be applied above ~100 °C. The temperature range of effective damping can be extended by the use of heat-resistant systems. In particular, a high-temperature vibration-absorbing material, exhibiting great absorption of mechanical energy over the range 160–220 °C, has been developed from networks of a polyarylate and epoxy-polymers[52,53].

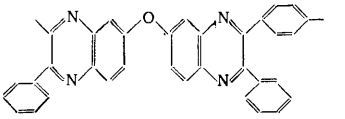
III. DYNAMIC MECHANICAL INVESTIGATION OF CHEMICAL CROSS-LINKING PROCESSES

Since hardening is a chemical reaction accompanied by conformational rearrangements of the polymer molecules, the dynamic mechanical method might be used to investigate not only the kinetics of hardening but also any solid-phase reaction in general. In this case, too, highly heat-resistant polymers provide unique opportunities for research. Indeed, owing to the degeneration of the relaxation transitions that are due to rotational mobility, and because of the high softening temperatures, heat-resistant polymers may have wide temperature ranges within which their intrinsic relaxation does not develop. This enables them to be used as matrices for the investigation of chemical changes in reactive substances introduced into them.

Chemical reactions of the relatively simple compound—hexaisothiocyanatocyclotriphosphazene



have been investigated[39] in a matrix of the poly(phenylquinoxaline)



Diffractograms obtained for the initial hexaisothiocyanate powder and for a film of the polymer modified with the former show that the crystalline hexaisothiocyanate undergoes complete amorphisation on introduction into the poly (phenylquinoxaline) matrix, which indicates excellent compatibility of the two compounds.

Application of the dynamic mechanical method to films containing different quantities of the hexaisothiocyanate shows (Fig.2) a sharp increase in tan δ with rise in temperature, to reach a maximum at ~150 °C. Such behaviour of the films on heating is due to softening of the system followed by chemical formation of a network by polymerisation

of the hexaisothiocyanate. A higher content of the latter corresponds, of course, to a more intense maximum in tan δ observed at the given temperature. With decrease in the hexaisothiocyanate content the maximum gradually degenerates, and is not observed at all for the initial poly (phenylquinoxaline).

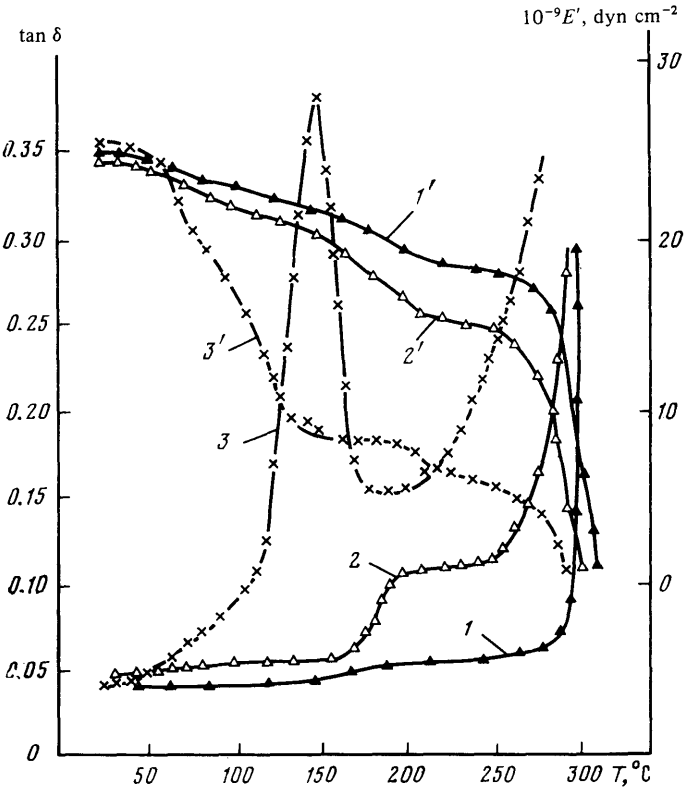


Figure 2. Temperature dependence of tan δ (unprimed curves) and E' (primed) for films obtained from mixtures of 100 parts by weight of poly(phenylquinoxaline) with different quantities of hexaisothiocyanatocyclotriphosphazene: 1,1') 1; 2,2') 10; 3,3') 50.

The characteristic temperature dependence of tan δ suggests[54] that by the dynamic mechanical method it is comparatively easy to study chemical processes occurring in the solid phase on heating: the sharp increase corresponds to the temperature range in which chemical reaction takes place; and the temperatures at which reaction begins, has its maximum rate, and in effect terminates can easily be determined (from respectively the start of the rise in tan δ, its maximum value, and the end of its decrease). The modulus of elasticity falls fairly sharply (which is to be expected of a system with great molecular mobility) in the temperature range in which the hexaisothiocyanate softens and formation of a network is only beginning. After reaction has proceeded sufficiently on heating to temperatures above that of maximum tan δ, the decrease in modulus of elasticity slows down. In this respect these systems differ in behaviour fundamentally from the usual linear and network polymers, which when heated pass from the solid (vitreous or crystalline) state to a hyperelastic or plastic state. In this case, too, a maximum is observed in the temperature dependence of tan δ, but the modulus of elasticity falls by a few orders of magnitude.

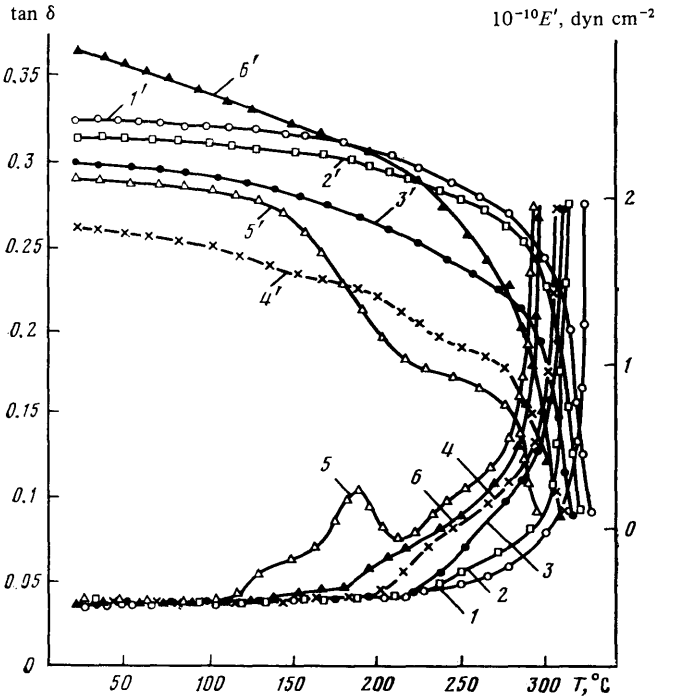


Figure 3. Temperature dependence of tan δ (unprimed curves) and E' (primed) for films, preheated at 180 °C for 30 h, of 100 parts by weight of poly(phenylquinoxaline) with different quantities of hexaisothiocyanatocyclotriphosphazene: 1,1') 1; 2,2') 10; 3,3') 25; 4,4') 50; 5,5') 100; 6,6') 100 additionally preheated at 280 °C for 4 h.

The dynamic mechanical results have been confirmed[54] by direct infrared-spectroscopic monitoring of the polymerisation of hexaisothiocyanatocyclotriphosphazene in a film of the poly(phenylquinoxaline). The variation in the characteristic absorption bands indicated both polymerisation of the hexaisothiocyanate with ring cleavage and reaction of isothiocyanato-groups with terminal amino-groups in the poly (phenylquinoxaline) to form thiourea links. The result is cross-linking of the polymer with a loss in solubility and a change in physicomechanical properties. This appears entirely probable, since ordinary poly(phenylquinoxalines) obtained from stoichiometric proportions of the reactants usually contain terminal amino-groups[55]. The hexaisothiocyanate is distinguished by great reactivity and readily interacts with compounds containing active hydrogen (amines, alcohols)[56].

Comparison of the results of infrared and thermomechanical spectroscopy on specimens that have been heated to different temperatures shows that heating lowers tan δ_{max} and shifts it slightly to higher temperatures. Heating at a relatively low temperature (120 °C) leads to some diminution in tan δ_{max}

in comparison with the initial specimen, but even when the temperature is raised only slightly (to 130–150 °C) the value decreases significantly, and at higher temperatures the maximum degnerates completely[54]. All this is consistent with the infrared results, and indicates a vigorous irreversible chemical reaction occurring in the range 140–160 °C. With rise in the temperature of preheating the sharp increase in tan δ following the maximum, which corresponds to softening of the specimens as a whole, takes place at increasingly high temperatures. This is evidence of the formation of a single network on opening of the phosphazotrien ring and interaction with the poly(phenylquinoxaline.)

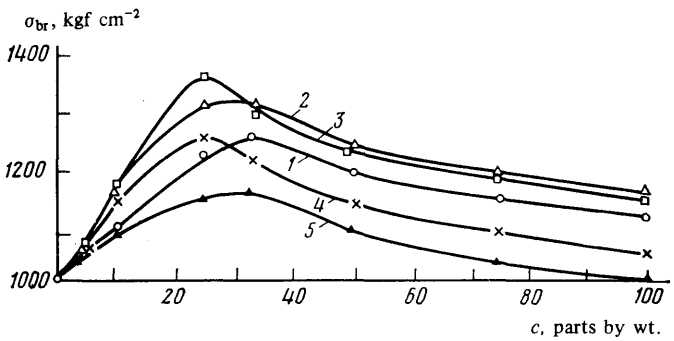


Figure 4. Effect of content c (parts by weight) of UP-612 on breaking strength σ_{br} of compositions, preheated at 200 °C for 20 h, of 100 F-2 with different quantities of UP-607: 1) 0; 2) 5; 3) 10; 4) 20; 5) 30.

Investigation of the effect of the hexaisothiocyanate concentration on the temperature dependence of tan δ for films heated at 180 °C for 30 h has shown (Fig.3) that, under otherwise similar conditions, the completeness of network formation depends on the quantity of hexaisothiocyanate added. When the latter is large (100 parts by weight) a well defined maximum is observed in tan δ with a peak at 180 °C; when the content is lowered (to 50 and below) the maximum degenerates almost completely, and the sharp rise in the temperature dependence occurs at ever higher temperatures. The presence of a clear maximum at 100 parts by weight indicates that under the above conditions (180 °C for 30 h) network formation is incomplete. Further heating of the specimen at 280 °C for 4 h results in complete disappearance of the maximum (Fig.3, curve *6*). This again confirms that the dynamic mechanical method permits the study even of extremely delicate chemical changes in the solid phase and reliable assessment of their completeness.

IV. STRENGTH PROPERTIES OF NETWORKS

Here we consider the changes in the strength and deformation properties of heat-resistant polymers accompanying formation of network systems and the influence of composition on the mechanical properties. It has been shown above that a network system can be obtained from an epoxy-polymer by the simultaneous introduction into the resin of a chemically active heat-resistant polymer of high molecular weight and traditional hardeners such as a polyanhydride of sebacic acid (UP-607) and tetrahydromethylphthalic anhydride. As a consequence of the presence of excess of the reactive polymer the portion thereof not involved in network formation remains as a free powder and serves as a filler. Such a chemically active macromolecular filler lowers significantly the specific gravity of the material, and produces sharp increases in thermal shock resistance and mechanical indices relative to a material containing an ordinary mineral filler[57]. Several compositions[58–61] have a density of 1.1 g cm^{-3}.

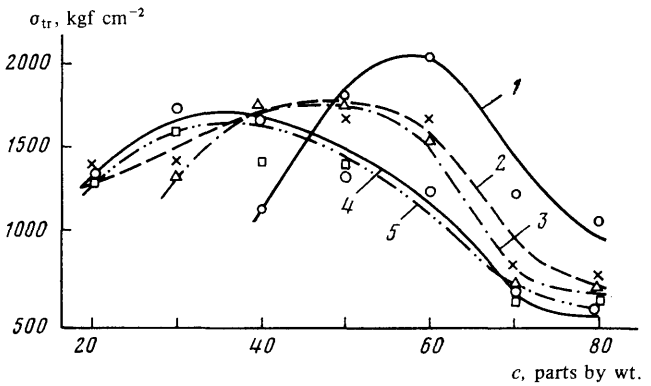


Figure 5. Dependence of transverse strength σ_{tr} on content c of UP-607 hardener for different contents of F-2 polyarylate: 1) 10; 2) 20; 3) 30; 4) 40; 5) 50.

Fig.4 shows the dependence[39] of the breaking stress σ_{br} of F-2 polyarylate network compositions containing various quantities of UP-607 hardener on the content of UP-612 polymer. All the curves pass through a maximum at a content of 25–33 parts by weight of the epoxy-polymer per 100 of the polyarylate. If the strenght of the polyarylate is 1020 kg cm^{-2}, the introduction of 33 parts by weight of UP-612 increases the breaking strength to 1260 kg cm^{-2} (curve *1*). Addition of a small quantity of the hardener (5–10 per 100 parts by weight of UP-612) produces a further improvement in strength properties (curves *2* and *3*). When the hardener content is increased to 20 parts by weight and above, the strength properties of the materials deteriorate (curves *4* and *5*). These compositions exhibit maximum specific elastic modulus at a UP-607 content of 40–60 parts by weight. Fig. 5 illustrates the variation in the transverse strength σ_{tr} for monolithic specimens of the same compositions[58]. The dependence of this property on the UP-607 content with various contents of F-2 polyarylate also passes through a maximum, at approximately 50% of UP-607.

It is noteworthy that the strength characteristics of the network systems exceed those of the polyarylate over very wide ranges of contents both of UP-607 and of F-2 polyarylate; this permits wide variation in the composition of the systems to obtain materials with other optimum mechanical properites, without fear of lowering the tensile strength[39,58]. In contrast to the above variation in breaking and transverse strengths, the compressive strength σ_c and the modulus of elasticity E' usually decrease monotonically with increase in the content of UP-607 hardener (Fig.6). Compositions containing a minimum quantity of UP-607 exhibit the highest values of these two properties, which is fully explicable,

since network formation by cross-linking with a more rigid system (F-2 polyarylate) will produce more rigid networks possessing a higher modulus of elasticity and greater static compressive strength. Introduction of a larger quantity of a flexible-chain oligomeric hardener will yield a more elastic network with a smaller modulus of elasticity and lower compressive strength. On the whole the mechanical properties on compression of networks based on heat-resistant polymers are quite high (Fig.6).

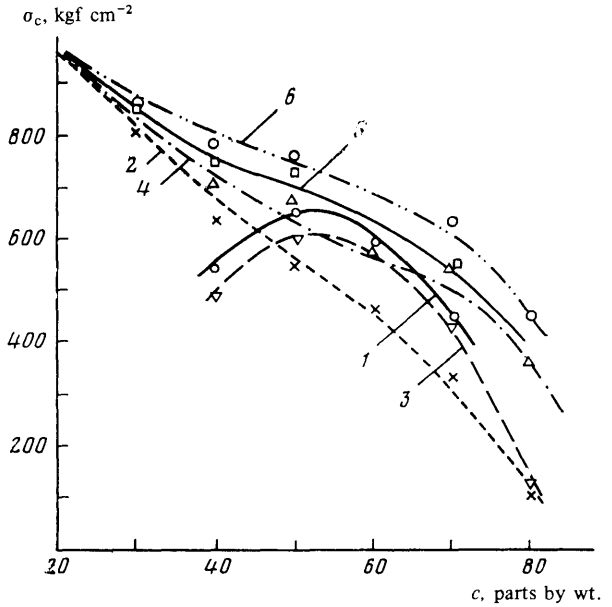


Figure 6. Dependence of compressive strength σ_c on content c of UP-607 hardener for different contents of F-2 polyarylate: 1) 10; 2) 20; 3) 0; 4) 30; 5) 40; 6) 50.

Data on mechanical properties have been obtained for other compostions based on UP-612 cycloaliphatic epoxy-polymer with UP-607 and tetrahydromethylphthalic anhydride as traditional hardeners and F-2 polyarylate, a polyimide of benzophenonetetracarboxylic acid and anilinephthalein, or an aromatic polyamide of terephthalic acid and anilinefluorene as chemically active macromolecular hardener–filler[61]. The results are essentially similar to those illustrated in Figs.5 and 6. Thus the introduction into compositions based on epoxy-polymers of chemically active aromatic polymers of high molecular weight, which act both as hardeners and as fillers, yields strong and light materials, capable of functioning over wide ranges of temperature and mechanical loadings.

Interesting results have been obtained[39] for the strength and deformation properties of a poly(phenylquinoxaline) alone and modified with a small quantity (20 parts by weight) of hexaisothiocyanatocyclotriphosphazene. Fig.7 shows that at low temperatures the modified polymer is slightly the stronger, but with rise in temperature loses strength more rapidly. At 150 °C, however, the decrease in breaking strength ceases owing to network formation, and at high temperatures (when this can be completed within the duration of the experiment) there may even be some increase in strength, with the modified specimen becoming stronger than the unmodified. At comparatively low temperatures the former breaks down at smaller deformations, but with rise in temperature to 220–230 °C the pattern reverses abruptly: at high temperatures the modified poly(phenylquinoxaline) exhibits extremely large (up to 200%) elongations at rupture, which is not usually characteristic of heat-resistant polymers. Hence the modification of poly(phenylquinoxaline) by the addition of a small quantity of hexaisothiocyanatocyclotriphosphazene tends to improve the deformability of the system at high temperatures.

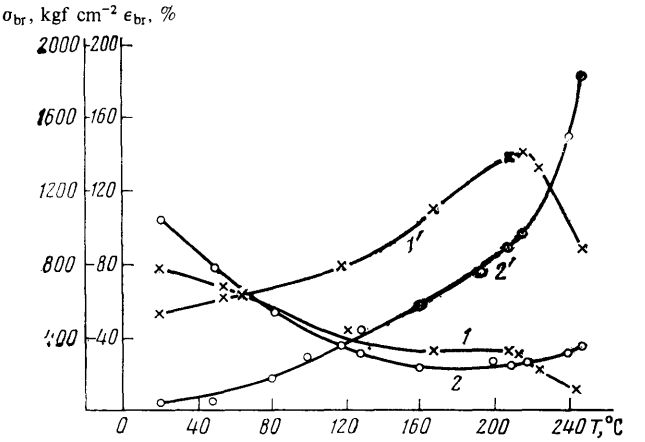


Figure 7. Effect of modification with hexaisothiocyanatocyclotriphosphazene temperature dependence of breaking strength σ_{br} and elongation at break ε_{br} for poly(phenylquinoxaline): 1) unmodified σ_{br}; 1') unmodified ε_{br}; 2) modified σ_{br}; 2') modified ε_{br}.

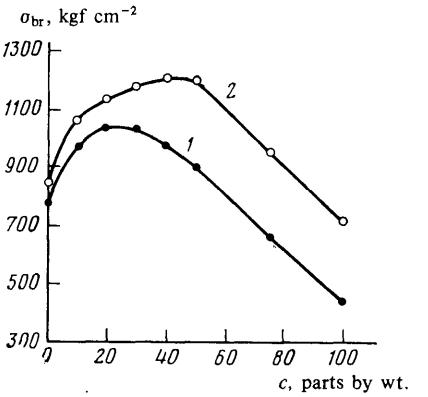
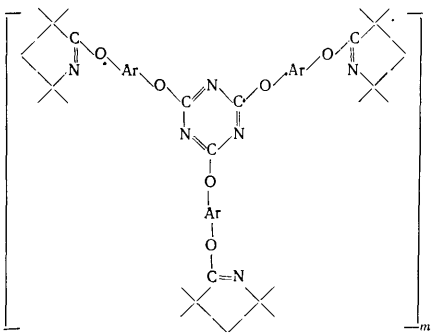


Figure 8. Dependence of breaking strength σ_{br} on content c of hexaisothiocyanatocyclotriphosphazene in modified poly(phenylquinoxaline) films: 1) initial; 2) after heating.

An increase in strength is produced[39] also by heating at 150 °C for 2 h poly(phenylquinoxaline) films modified with different quantities of hexaisothiocyanatocyclotriphosphazene (Fig.8). As already noted, this is due to the polymerisation of the hexaisothiocyanate occurring under these conditions, with formation of a network system. With such heat-treatment the strength of the initial poly(phenylquinoxaline) changes little (from 780 to 830 kg cm^{-2}), but an appreciable increase in breaking strength (to 1200 kg cm^{-2}) is produced at a higher temperature (280 °C for 10 h). The probable cause is formation of a network system by thermal cross-linking of the polymer molecules, but this is accompanied by a sharp decrease in deformability.

An interesting recent development in heat-resistant systems is investigation of the preparation and properties of networks formed by the polycyclotrimerisation of various arylene dicyanates[62,63] to give network aromatic polycyanates having the structure



This process is characterised by great selectivity and a quantitative yield of a highly cross-linked polycyanate. Hence the resulting network is very regular, and monolithic specimens are distinguished by improved properties in comparison with ordinary network polymers.

It is of interest to examine in greater detail the influence of the chemical structure of the initial dicyanic esters on the properties of the network polycyanates[64]. In the case of dinuclear aromatic dicyanates the nature of substituents attached to the central carbon atom has a significant effect on the properties of the networks. Table 1 shows the structure of the initial esters together with several parameters for the corresponding polycyanates. Since mechanical and other properties depdend also on the crystallinity of the specimens, Table 1 includes appropriate characteristics.

The first striking fact is that polymers of dicyanates containing identical small substituents attached to the central carbon atom (I–III in Table 1) have abnormally high resilience (23–25 kgf cm cm^{-2}). However, the presence of identical aromatic substituents attached to this atom (IV–VI), and also large planar groups (VII–IX), produces an appreciable diminution in resilience for moulded specimens of the polycyanates. In the latter cases, however, the transverse strength of the polycyanates is increased appreciably.

In the absence of a bonding sp^3 carbon atom between the benzene rings, as in the polycyanate (XII) from *pp'*-biphenylylene dicyanate, the resulting material has comparatively low specific resilience (6 kgf cm cm^{-2}). Diminishing the distance between branch points to single phenylene groups (polycyanates from *m*- and *p*-phenylene dicyanates) again produces a considerable improvement in resilience and transverse strength.

X-Ray examination indicates that most of the polycyanates obtained are amorphous polymers. In several cases, however, when identical small substituents (hydrogen, methyl) are attached to the central carbon atom, and also in polycyanates formed from dicyanic esters of resorcinol, quinol, and biphenyl-*pp'*-diol, slightly and moderately ordered structures are formed. Thus the presence of a rigid three-dimensional network in these polymers is not an obstacle to the appearance of ordered structures. A slightly ordered crystalline structure is observed also in the polycyanate from 10,10-diphenylanthr-9-one *pp'*-dicyanate, which contains large planar groups attached to the central carbon atom.

Table 1. Physical properties of polycyantes from dicyanic esters of various aromatic diols[64].

No.	Aromatic dicyanate*	Specific elastic modulus, kgf cm cm^{-2}	Transverse strength $10^{-3}\sigma_{tr}$, kgf cm^{-2}	Density (20 °C), g cm^{-3}	Mol. mass of chain unit	Volume of chain unit, A^3	Packing coeff. *K*	X-Ray results
(I)	$NCOC_6H_4—CH_2—C_6H_4OCN$	23	1.22	1.307	750.78	655.81	0.688	cryst., moderate order
(II)	$NCOC_6H_4—C(CH_3)_2—C_6H_4OCN$	25	1.40	1.235	834.95	769.63	0.686	amorphous, signs of cryst.
(III)	$NCOC_6H_4—C(CF_3)_2—C_6H_4OCN$	24	1.46	1.528	1158.80	858.79	0.682	amorphous
(IV)	$NCOC_6H_4—C(H)(C_6H_5)—C_6H_4OCN$	10	1.59	1.255	979.08	891.85	0.689	amorphous
(V)	$NCOC_6H_4—C(CH_3)(C_6H_5)—C_6H_4OCN$	17	1.85	1.229	1021.16	943.93	0.684	amorphous
(VI)	$NCOC_6H_4—C(C_6H_5)_2—C_6H_4OCN$	5	1.62	1.220	1207.37	1118.53	0.681	amorphous
(VII)	3,3-Di-*p*-cyanatophenylphthalide	6	2.02	1.322	1105.06	934.63	0.673	amorphous
(VIII)	9,9-Di-*p*-cyanatophenylfluorene	5	1.54	1.269	1207.37	1080.73	0.688	amorphous
(IX)	10,10-Di-*p*-cyanatophenylanthr-10-one	6	1.69	1.288	1285.36	1134.90	0.685	cryst. slight order
(X)	*m*-$NCOC_6H_4OCN$	18	1.92	1.414	480.41	388.33	0.688	amorphous, signs of cryst.
(XI)	*p*-$NCOC_6H_4OCN$	12	1.73	1.431	480.41	388.33	0.697	cryst., slight order
(XII)	$NCOC_6H_4—C_6H_4OCN$	6	1.47	1.319	708.70	615.13	0.689	cryst., moderate order

* With the exception of polymer (X) all the phenylene groups were *para*-substituted.

V. RELAXATION PROPERTIES OF NETWORKS UNDER CONDITIONS OF STATIC CONSTRAINT (STRESS RELAXATION AND CREEP)

Investigation of stress relaxation in heat-resistant aromatic polymers under both isothermal and non-isothermal conditions and study of the mechanical applicability of the systems under conditions of stress relaxation over wide ranges of temperature and deformation have been conducted for a relatively long time and have been quite widely discussed[65–68]. In the present Review, therefore, attention will be concentrated mainly on the most recent studies of static relaxation properties.

A detailed investigation of the relaxation properties of networks based on epoxy-oligomers and heat-resistant aromatic polymers[58–60] has enabled the influence of the chemical structure of the network on the heat-resistance to be identified and the boundaries of possible application of the materials to be determined. Both binary systems (epoxy-resin–aromatic polymer) and ternary systems (with addition of a hardener) have been studied. Relaxation properties have been examined under non-isothermal conditions with uniaxial compression by a method[68,69] permitting determination of the ranges of stress and temperature within which the polymer retains distinct hardness and can function as a structural material. The boundary of the operable region is drawn through the maxima of relaxation curves obtained with a linear temperature rise at a specified rate for compressed specimens whose deformation remains constant during an experiment.

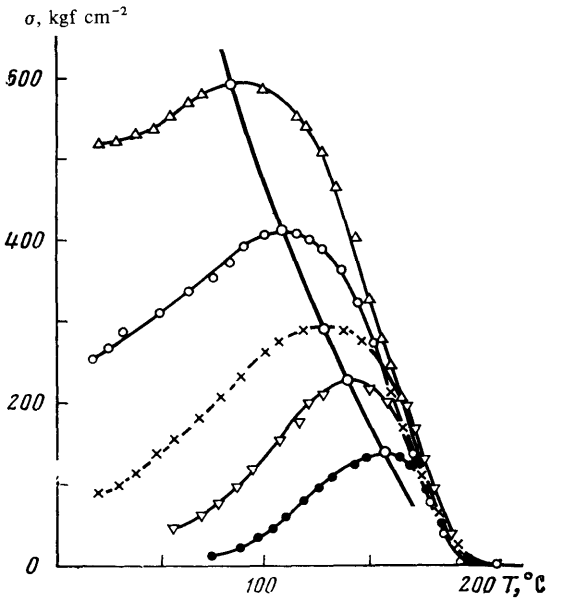


Figure 9. Region of applicability of composition containing (parts by weight) 100 UP-612 + 60 F-2.

Hardening an epoxy-oligomer with a chemically active aromatic polymer leads to a significant broadening of the region of mechanical applicability, with respect both to stress and especially to temperature. For example, the solid material formed by reaction between an epoxide and a polyarylate possesses far greater heat-resistance than do the usual hardened epoxy-resins. Such a material can be used at significantly higher temperatures than can an ordinary composition hardened with a traditional hardener.

A similar result has been obtained[58] for binary compositions containing UP-612 cycloaliphatic resin and F-2 polyarylate. The composition for which results are illustrated in Fig. 9 possesses the largest range of application, with respect to both temperature and stress, among all the solid compositions studied.

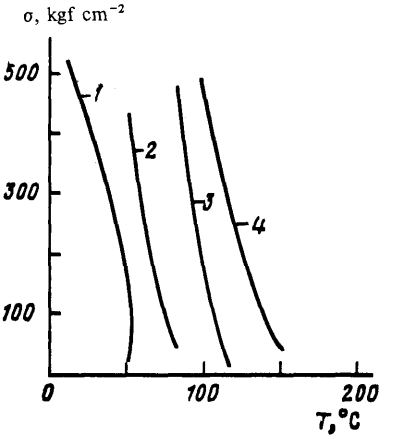


Figure 10. Curves bounding regions of applicability of various compositions (parts by weight): 1) 100 Ed-16 + 60 UP-607; 2) 100 ED-16 + 40 F-2; 3) 100 Ed-16 + 50 F-2; 4) 100 ED-16 + 60 F-2.

In order to trace the effect of the quantity of polyarylate on heat-resistance curves bounding the region of applicability have been obtained for a composition based on ED-16 epoxy-resin hardened with a polyanhydride of sebacic acid. With increase in the quantity of polyarylate these curves (Fig. 10) are regularly displaced to higher temperatures, and are situated substantially to the right of the curve for an ordinary solid composition. Thus introduction of a polyarylate into an epoxy-resin increases the heat-resistance of the composition, which may function at higher temperatures under greater loads.

As has already been noted, the introduction of a heat-resistant aromatic polymer into an epoxy-resin with the aim of obtaining a network does not prevent simultaneous use of a traditional hardener. Networks formed by the interaction of three components have special features. As example Fig. 11 shows the region of applicability of a solid composition comprising a polyarylate, ED-16 epoxy-oligomer, and a polyanhydride of sebacic acid as the traditional hardener. Introduction of a polyarylate into a ternary composition appears to give two regions of applicability, characterised respectively by (i) comparatively low temperatures and high stresses and (ii) high temperatures and low stresses. The region corresponding to high stresses remains approximately the same whether or not the heat-resistant polymer (polyarylate) is present: there is merely a slight

rise in the temperature limits. However, in the presence of the polyarylate the composition based on the epoxy-resin can withstand at high temperatures far larger loads than can the usual compositions. The height of the "loop" (i.e. the stress) then increases with the quantity of polyarylate added[58].

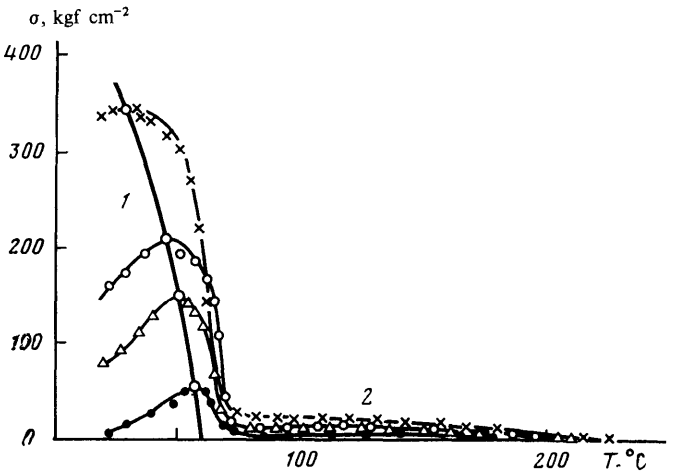


Figure 11. Region of applicability of composition comprising (parts by weight) 100 ED-16 + 40 UP-607 + 50 F-2.

These results have been attributed[58] to differences in flexibility among the chain segments between branch points in the network formed by hardening of an epoxy-resin with a mixture of a traditional hardener and a polyarylate. When such a network is heated in a stressed state for determination of the region of applicability, stress relaxation will occur primarily by the appearance of molecular mobility in the flexible chain segments of the epoxy-resin. Since these are present in every composition, acceleration of relaxation processes will develop, of course, at approximately the same temperatures in composite materials differing in composition. At high temperatures, however, at which stress relaxation is complete in the usual compositions, the presence of polyarylate fragments in the present case prevents complete relaxation right up to 220 °C: slight stress is retained in the material.

A similar result is obtained when other heat-resistant aromatic polymers are introduced into compositions based on epoxy-resins of diverse structure. Two regions of applicability are evident: the high-temperature region may extend to 300 °C; the low-temperature region (at high stresses) remains almost the same as in the absence of heat-resistant aromatic polymers[61].

Thus the investigation[58-61] has shown that solid compositions based on epoxy-resins can be obtained without the use of traditional hardeners by introducing into the resin chemically active heat-resistant polymers (polyarylates, aromatic polyamides, polyimides, etc.). Such a process produces a significant extension to higher temperatures of the region of mechanical applicability of the composition. Introduction of aromatic polymers into an epoxy-resin does not prevent use of ordinary hardeners, and the properties of the material can be controlled by varying the composition of such a ternary system[61].

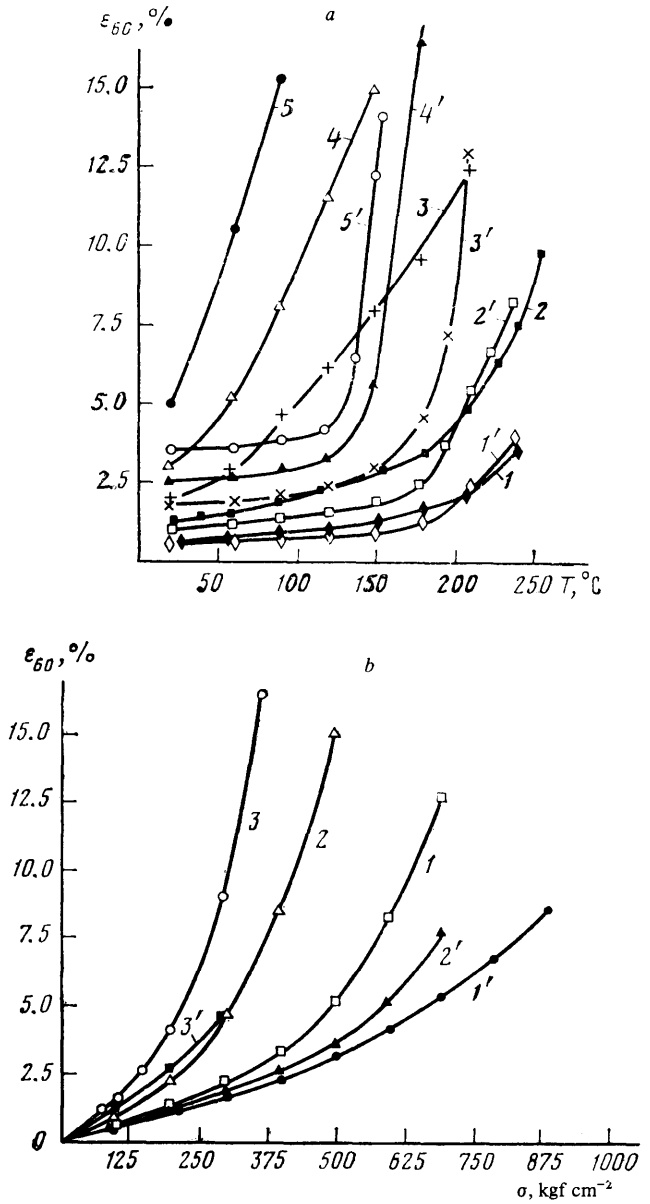


Figure 12. Dependence for initial and preheated polyarylate (respectively unprimed and primed curves) of deformation ε_{60} developed during 60 min of creep: (*a*) on temperature under stresses σ (kgf cm^{-2}): 1,1′) 100; 2,2′) 200; 3,3′) 300; 4,4′) 400; 5,5′) 500; (*b*) on stress at various temperatures *T* (°C): 1,1′) 20; 2,2′) 90; 3,3′) 150.

A considerable number of studies has been made on creep in network systems based on heat-resistant polymers. Such investigation is of fundamental interest, since it helps to reveal the limits of stress, temperature, and duration within

which deformation in the polymer material does not exceed a specified value. It may even be claimed that the study of creep is more importanat than the investigation of stress relaxation for assessing the mechanical applicability of polymer materials, since in most cases their working conditions tend to develop creep (with variable or constant loading and temperature). Measurements of creep must be made over all temperature and stress ranges possible for a given specimen in order completely to characterise the region of its applicability. The possible range of stresses is determined by the ability of the polymeric material to creep without disintegration; the possible temperature range is determined in the case of heat-resistant solid plastics by the glass point.

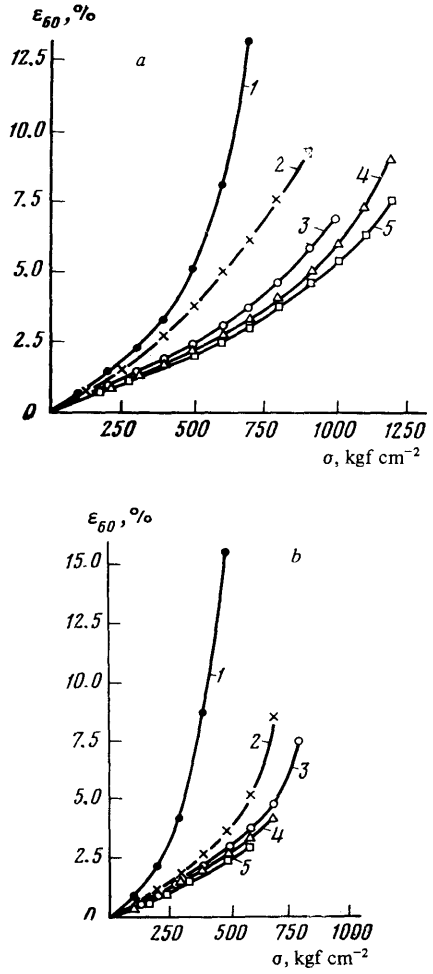


Figure 13. Dependence of ε_{60} on σ at (*a*) 20 °C and (*b*) 90 °C for 100 parts by weight of a polyarylate alone and in network systems containing various quantities of an epoxy-polymer: 1) 0; 2) 0 (preheated); 3) 10; 4) 20; 5) 33.

Detailed investigation of creep in the initial heat-resistant polymers and derived network systems[39,54,70] has shown that such polymers are characterised by very slight dependence of deformation on temperature over a very wide range. This experimental finding is illustrated by Fig.12, which shows the creep deformation ε_{60} developed during the process lasting 60 min for initial and heated polyarylates and for network systems. With various constant stresses the variation in ε_{60} is small over a fairly wide temperature range (depending on the stress), and only near the softening point does the creep begin to increase rapidly. This is especially characteristic of the heated polyarylate, which exhibits a far smaller tendency to creep than does the original specimen. Diffractograms[70] show that the reason for such behaviour is that the specimen becomes more ordered as a result of heating.

The influence of stress on creep is readily seen from Fig.12, in which is plotted the dependence of ε_{60} on mechanical stress at various constant temperatures. These curves show that the deformation increases appreciably with stress throughout its range, and here, too, a heated specimen exhibits far less tendency to creep than does the initial specimen.

Investigation[39,70] of the creep of film specimens containing various quantities of UP-612 epoxy-polymer and heated to form a cross-linked network of chemical bonds has revealed a generally smaller tendency of the network specimens to creep. In several cases the curves for the latter are almost horizontal lines: i.e. deformation does not develop with time. This result has considerable practical value, since undeformable materials, which do not change their shape with time under the influence of quite large stresses, can be obtained on the basis of networks of a polyarylate with an epoxy-polymer. A similar conclusion can be reached from a series of creep curves for initial and network specimens obtained under different mechanical stresses at a constant temperature[70].

To summarise the results and present them more vividly Fig.13*a* illustrates the stress dependence of ε_{60} (at 20 °C) for initial and heated polyarylate and for derived network specimens containing various quantities of UP-612. The network specimens exhibit a far smaller tendency to creep even than the heated polyarylate at the same stress throughout the range investigated. The best results are obtained with specimens containing 20–50 parts by weight of UP-612 per 100 of the polyarylate. The above tendency is maintained with rise in temperature, but the curves representing the stress dependence of ε_{60} are closer together (Fig.13*b*). This is entirely reasonable, since with rise in temperature the presence of a less heat-resistant material in the network should tend to increase creep, although, as noted above, network specimens undergo less deformation in all cases.

Thus the investigation of creep in an initial polyarylate and in network polymers based on the polyarylate and epoxy-polymers has shown that, as a consequence of the formation of a network of chemical bonds, heating diminishes substantially both the magnitude and the rate of creep. Almost complete cessation of the development of deformation with time under the influence of very large stresses can be achieved by varying the composition.

Fig.14 shows correlated logarithmic pliability curves plotted on the principle of temperature–time equivalence by displacement along time axis with $T_0 = 20$ °C selected as reference temperature. Three series of curves are included, representing respectively the behaviour under creep conditions of initial and heated polyarylate and of a network formed by interaction with UP-612 epoxy-polymer. Curves obtained at different constant stresses for initial and heated polyarylate specimens are evidently not superposable. The greater the applied stress, the greater the pliability. All this clearly indicates non-linear mechanical behaviour of

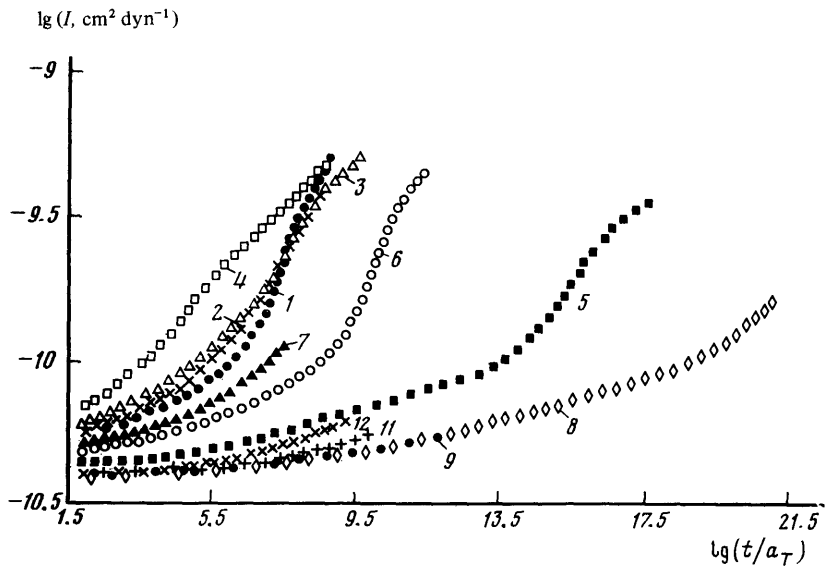


Figure 14. Correlated pliability curves (reference temperature $T_0 = 20$ °C) for initial and preheated polyarylates and a network polymer containing 33 parts by weight of an epoxy-polymer per 100 of the polyarylate, obtained under different stresses (kgf cm^{-2}): 1) polyarylate 200; 2) polyarylate 300; 3) polyarylate 400; 4) polyarylate 500; 5) preheated 200; 6) preheated 300; 7) preheated 400; 8) network 200; 9) network 300; 10) network 500; 11) network 600; 12) network 900.

polyarylates over wide ranges of stress and temperature. However, the network system exhibits quite different behaviour: the correlated curves practically coincide over a wide stress range, especially for short durations. Only at high stresses (600–900 kg cm^{-2}) do the curves begin to diverge towards an increase in pliability (at comparatively short durations). Another feature of the network system is lower pliability than for initial and heated polyarylate throughout the correlated curve.

Another feature of Fig.14 is that plots of $\lg I$ against $\lg (t/a_T)$ obtained for relatively small stresses, where I is the pliability, t the time, and a_T the displacement factor, consist of two segments having different slopes. The first is gently sloping, which indicates a low rate of creep within the given range of $\lg (t/a_T)$ values, corresponding to a definite range of comparatively low temperatures. The second segment has a greater slope, indicating compartively rapid creep. The principle of temperature–time equivalence can be used to determine the temperature range of the transition between these two sections of relatively slow and rapid creep. As has been established for a polyarylate, this temperature range, in which creep undergoes abrupt acceleration, coincides precisely with that in which stress relaxation is sharply accelerated.

Thus investigation of the creep of heat-resistant systems has yet again confirmed the advisability of subdividing the temperature range of the vitreous state into two subranges with different rates of relaxation. When polymeric materials are used under non-isothermal conditions, it must be borne in mind that a rapid increase in the rate of creep will be observed on passing from one subrange to the other, which may lead to an unacceptable change in shape of the material.

The course of the creep curves for the polymeric systems studied is well reproduced by the quantitative relation[71]

$$\varepsilon(t) = \sigma_0 I_\infty [1 - e^{-(t/\theta)^m}] + \frac{\sigma_0}{\eta} t,$$

where the product of the applied constant stress σ_0 and the equilibrium pliability I_∞ gives the equilibrium deformation $\varepsilon_0 = \sigma_0 I_\infty$, while θ is the time lag, m a constant characteristic of the material, and η the viscosity coefficient of the system. All the creep curves obtained for the initial F-2 polyarylate and its derived network systems have been calculated[70] by means of this equation from statistical least-squares processing of experimental results. The calculations show that the parameters m, θ, and η have a strong scatter, so that a regular temperature and stress dependence cannot be established. Only for the equilibrium pliability I_∞ is a smooth dependence observed.

A detailed investigation has been made[64] of the heat resistance of highly cross-linked polycyanates prepared from dicyanic esters of various aromatic diols. Fig.15 shows as example the temperature limits of the heat-resistance of several polycyanates as a function of the mechanical stress. A striking feature is the similarity between the non-isothermal stress-relaxation curves (broken) and curves bounding the region of applicability for highly cross-linked systems—polycyanates and linear heterochain polymers (with a polycarbonate as example).

Replacing an isopropylene by a fluorene group in the chain segments between branch points increases the heat-resistance of the polymer throughout the temperature and stress ranges investigated. An appreciable shift is also observed in the maximum temperature of applicability, at

which the stress in the specimen relaxes completely to zero. Replacing a *para*-substituted dinuclear dicyanate residue by a mononuclear *meta*-radical between the branch points in the polymer network lowers the heat-resistance of the polycyanate with respect both to temperature and to stress[64]. Introduction of a 1,2-carborane instead of a 9,9-fluorene bridge between the phenylene groups of the cyanate also lowers the heat-resistance of the polycyanates (Fig.15).

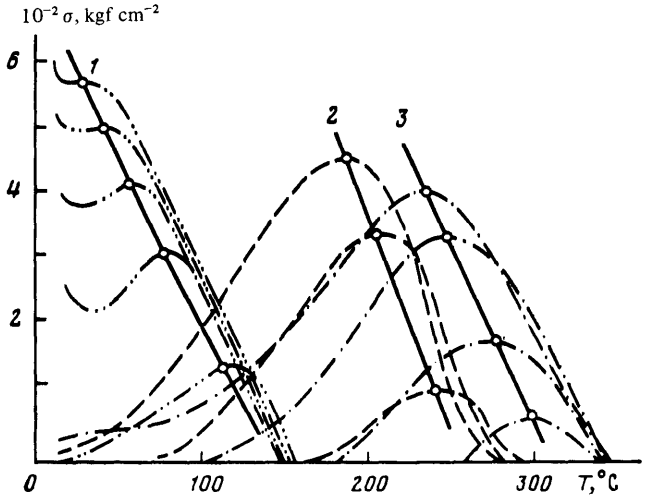
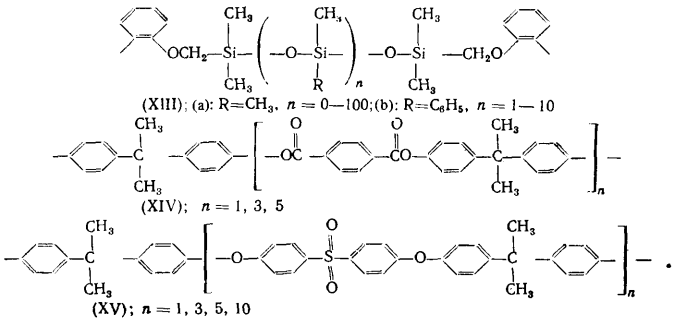


Figure 15. Regions of applicability of 1) a polycarbonate from 2,2-diphenylpropane-*pp'*-diol; 2) polycyanate (II); 3) polycyanate (VIII).

Thus the structure of the initial aromatic cyanate exerts a significant influence on the properties of the resulting polycyanates, although the latter are dense networks. Even small changes in the structure of the segments between branch points in such a dense network lead to appreciable changes in the properties of monolithic specimens of the polycyanates.

Still greater variation in properties can be achieved by varying the chemical nature of the segments between branch points in the dicyanates. Dicyanic esters of oligosiloxanes, oligo(arylene sulphoxides), and oligoarylates of various lengths have been used[72] as initial compounds for network formation. It is interesting that linear macromolecular analogues of these segments find wide application. The segments between the branch points[72] had the structures



Depending on the chemical structure and also on the number n of repeating units monolithic specimens of the network polycyanates had properties varying from rubberlike with large reversible deformation and a low modulus of elasticity to vitreous with a high modulus. Analysis of the equilibrium modulus in the rubberlike state showed that the distance between network branch points in the polycyanates corresponded almost exactly to the chain lengths in the initial oligocyanates, evidence of a process with high selectivity and a network with few defects. It is therefore possible to analyse the effect of the chemical structure of the internodal segments on the properties of the network polycyanates.

Table 2. Parameters in the Kohlrausch equation for network polymers.

n	Gel fraction, %	ε, %	E_∞ (kgf cm^{-2})	E_0 (kgf cm^{-2})	τ_p, min	k	$10^{-7}\eta$, P
Polymer (XIIIa)							
5	96	20	16.0	5.50	23	0.70	6.3
25	95	50	2.3	0.12	18	0.52	1.88
50	95	50	1.7	0.12	14	0.42	0.51
70	92	50	1.0	0.08	8	0.33	0.41
Polymer (XIV)							
1	96	30	19.3	9.17	32	0.83	$5.11\cdot10^9$
3	95	30	13.2	3.84	28	0.17	$6.03\cdot10^{10}$

The investigation[72] has shown that stress relaxation in the polycyanates is well described by the Kohlrausch equation with parameters depending very characteristically on the chemical structure of the network. Comparison of polycyanates based on oligosiloxanes and on oligoarylates with small values of n shows that such parameters as E_∞, E_0 and τ_p have closely similar values (Table 2). The main difference between these polymers lies in the fractional power of the time ($k = 0.70$ and 0.17) and in the viscosity ($\eta = 6.3 \times 10^7$ and 6.03×10^{10} P respectively). Such a substantial difference in the viscosities of the polymers is attributed to the chemical structure of the internodal segments. In the region of the hyperelastic state polymers with oligoarylate segments probably exhibit considerably greater intermolecular interaction and rigidity than do network polydimethylsiloxanes[72].

Comparison of the relaxation properties of polycyantes based on oligo(arylene sulphoxides) and on oligoarylates does not reveal such an important difference (at equal values of n). However, a network polycyanate based on the former type of oligomer has the larger relaxation modulus.

Great selectivity of the polycyclotrimerisation of arylene dicyanates, which governs many physical and chemical properties of the resulting polycyanates, distinguishes it favourably from that of other groups having multiple bonds (–N:C:O, –C:CH), which is accompanied by numerous side-reactions such as dimerisation, polymerisation in the chain, etc.[73,74]. As a consequence of the great selectivity of cyclotrimerisation of –O.C:N groups in arylene dicyanates and its nearly quantitative completion the resulting highly cross-linked polymers possess several properties marking them off from well known cross-linked polymers, e.g. greater specific resilience, which is not typical of highly cross-linked systems.

Under certain conditions several polycyanates form partly crystalline structures[72], which is probably also related to the regularity of their chemical structure, confirmed by calculations of the density of packing of macromolecules in the final monolithic polycyanates. The density of packing of the chain was assessed from the molecular packing coefficient defined by the formula

$$K = \frac{N_A \sum_i \Delta V_i}{M/d},$$

in which ΔV_i is the van der Waals volume of the ith atom in the repeating unit, M the molecular mass of the unit, d the density, and N_A Avogadro's number.

Calculations have shown[64] that packing coefficients for network polycyanates differing in aromatic structure lie in the range 0.673–0.697 (Table 1). The mean packing coefficient for monolithic specimens of linear polymers is 0.681. Hence network systems based on aromatic polycyanates exhibit as high a density of packing of macromolecules as do linear systems. When polysiloxane segments are introduced between network branch points, the packing coefficient decreases rapidly, especially with increase in chain length between these points[72]. This is a feature also of linear polydimethylsiloxanes.

The process of formation of the supermolecular structure of polycyanates at various stages of synthesis—from the initial monomer to a regular network with almost 100% conversion of functional groups—has been examined[75] in order to find the reasons for the improved mechanical indices (especially on impact). In the early stages the specimens were liquids, which were frozen down to −150 °C to fix the structure instantaneously after which relicas were sputtered at −190 °C. The initial monomer comprised finely crystalline structures, which on heating underwent changes as a consequence of polycyclotrimerisation. In the early stages of this reaction sharply bounded regions of globular structure, with globules of mean size 500 Å, appeared on the background of the characteristic structure of the monomer. With further polycyclotrimerisation the whole surface consisted of globules, whose size gradually diminished with increase in the degree of conversion of cyanato-groups. In the very last stage of polycyclotrimerisation fibrillar structures appeared. This may be the reason for the characteristic mechanical properties of aromatic polycyanates.

The relaxation properties also change with the degree of conversion (and hence the supermolecular structure). In the comparatively early stages the stress-relaxation curves shift to higher stress values (the modulus of eleasticity and the equilibrium modulus increase). In the later stages, however, these moduli begin to decrease (i.e. the rigidity of the specimen diminishes under otherwise similar geometrical conditions). Thus there exists a definite relation between the chemical structure of a polycyanate (its degree of conversion), the supermolecular structure, and its mechanical properties.

* * *

From our discussion of the structure and properties of networks based on heat-resistant polymers we may conclude that the most promising trends in this field are the synthesis of network systems from reactive oligomers of aromatic structure, including polycyclotrimerisation, and the production of networks by chemical reaction between oligomers such as epoxy-resins and heat-resistant aromatic polymers containing in the main chain groups capable of interacting with reactive groups in the oligomers. The properties of the resulting network systems can be controlled within wide limits by varying the chemical structure of the segments between and also the density of branch points in the network. In the Reviewers' opinion the greatest interest attaches to densely cross-linked polymers based on polycyanates, in which the networks are almost completely free from defects; the formation of these systems is accompanied by substantial change in the supermolecular structure at various stages of conversion, resulting in extremely ordered structures with clear signs of crystallinity at high conversions. In the future it may be of great interest to obtain highly crystalline network systems with interesting sets of properties.

It is also necessary to seek quantitative relations between the chemical structure, the topology of the network, and the set of mechanical properties. It is important to calculate the number of branch points in a network formed of aromatic segments. Since the mechanical (relaxation) behaviour of network systems having aliphatic and aromatic segments differs greatly, only a few values of the equilibrium modulus of elasticity may prove insufficient for such calculation.

There thus remains several unresolved questions in the recent study of the preparation and properties of network systems based on heat-resistant polymers, associated with controlling their properties by varying both chemical and network structures. In view of the rapid development of this field, interesting new results may be expected in the future.

REFERENCES

1. V.I.Irzhak, B.A.Rozenberg, and N.S.Enikolopyan, "Setchatye Polimery: Sintez, Struktura, Svoistva" (Network Polymers—Synthesis, Structure, Properties), Nauka, Moscow, 1979.
2. W.Wrasidlo, J.Polymer Sci., A2, **9**, 1603 (1971).
3. W.Wrasidlo, J.Macromol.Sci., **6**, 559 (1972).
4. J.K.Stille, J.F.Wolfe, S.O.Norris, and W.Wrasidlo, Polymer Preprints, 17, 41 (1976).
5. W.Wrasidlo, New Ind.Appl.Adv.Mater.Tech., **19**, 120 (1974).
6. W.Wrasidlo, S.O.Norris, J.F.Wolfe, T.Katto, and J.K.Stille, Macromolecules, **9**, 512 (1976).
7. W.Wrasidlo, Macromolecules, **4**, 642 (1971).
8. R.M.Ikeda, Polymer Letters, **4**, 353 (1966).
9. W.Wrasidlo and J.M.Augl, J.Polymer Sci., **B7**, 281 (1969).
10. W.Wrasidlo and J.M.Augl, J.Polymer Sci., **A1**, 7, 3393 (1969).
11. T.Lim, V.Frosini, V.Zeleckas, D.Morrow, and J.A.Sauer, Polymer Eng.Sci., **13**, 51 (1973).
12. M.I.Bessonov, N.P.Kuznetsov, N.A.Adrova, and F.S.Florinskii, Vysokomol.Soed., **16A**, 2093 (1974).
13. F.N.Nurmukhametov, Candidate's Thesis, Institute of Hetero-organic Compounds of the USSR Academy of Sciences, Moscow, 1975.
14. J.M.Augl and H.J.Booth, J.Polymer Sci., **A1**, 11, 2179 (1973).
15. J.M.Augl and H.J.Booth, J.Polymer Sci., **11**, 2195 (1973).
16. J.M.Augl, J.V.Duffy, and S.E.Wentworth, J.Polymer Sci., **A1**, **12**, 1023 (1974).
17. B.Hartman, J.Appl.Polymer Sci., **19**, 3421 (1975).
18. S.E.Wentworth and D.P.Macaione, J.Polymer Sci., **A1**, **14**, 1301 (1974) [sic].
19. F.L.Hedberg and F.E.Arnold, Polymer Preprints, 18, No.1, 826 (1977).

20. R.F.Kovar, F.L.Ehlers, and E.Arnold, J.Polymer Sci., **A1**, **15**, 1081 (1977).
21. R.T.Hawkins, Macromolecules, **9**, 189 (1976).
22. B.Hortling, Makromol.Chem., **178**, 2185 (1977).
23. J.Garapon and J.K.Stile, Macromolecules, **10**, 627 (1977).
24. R.F.Rafter and E.S.Harrison, Polymer Eng.Sci., **16**, 318 (1976).
25. P.Delvigs, Polymer Eng.Sci., **16**, 323 (1976).
26. J.K.Stille, R.G.Nelb, and S.O.Norris, Macromolecules, **9**, 516 (1976).
27. R.Becker and H.Raubach, Faserforsch.Textiltech., **26**, 406 (1975).
28. R.Becker and H.Raubach, Faserforsch.Textiltech., **26**, 51 (1975).
29. E.Simunkova, J.Zelinger, V.Kubanek, and V.Kraličeк, J.Appl.Polymer Sci., 17, 1387 (1973).
30. B.L.Tsetlin and S.R.Rafikov, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 1411 (1957).
31. V.Zilvar and J.Boukal, Kunststoffe, **59**, 313 (1969).
32. J.K.Gillham and H.C.Gillham, Polymer Eng.Sci., **13**, 2141 (1973).
33. J.K.Gillham, K.D.Hallock, and S.J.Stadnicki, J. Appl.Polymer Sci., **19**, 2595 (1975).
34. P.G.Babajevsky and J.K.Gillham, J.Appl.Polymer Sci., 17, 2067 (1973).
35. G.C.Papanicolaou, S.A.Paipetis, and P.S.Theocaris, J.Appl.Polymer,Sci., **20**, 903 (1976).
36. J.K.Gillham, J.Macromol.Sci., **B9**, 219 (1974).
37. E.Köhnlein, Kunststoffe, **65**, 583 (1975).
38. H.E.Bair, M.Matsuo, W.A.Salmon, and T.K.Kwei, Macromolecules, **5**, 114 (1972).
39. Yu.S.Kochergin, Candidate's Thesis, Institute of Hetero-organic Compounds of the USSR Academy of Sciences, Moscow, 1977.
40. L.I.Komarova, S.N.Salazkin, V.V.Korshak, S.V. Vinogradova, V.I.Nikolaichik, E.E.Zaborovskaya, and I.A.Bulgakova, Vysokomol.Soed., **16B**, 718 (1974).
41. L.I.Komarova, I.A.Bulgakova, S.N.Salazkin, Ya.S. Vygodskii, M.I.Malanii, V.V.Korshak, and S.V.Vinogradova, Polymer Letters, **14**, 179 (1976).
42. S.N.Salazkin, Candidate's Thesis, Mendeleev Moscow Institute of Chemical Technology, Moscow, 1965.
43. L.H.Sperling and D.W.Friedman, J.Polymer Sci., **A2**, 425 (1969).
44. L.M.Sergeeva and Yu.S.Lipatov, Uspekhi Khim., **45**, 138 (1976) [Russ.Chem.Rev., No.1 (1976)].
45. L.H.Sperling, T.A.Manson, and C.M.Yenwo, Polymer Preprints, **14**, 958 (1973).
46. V.Huelck, D.A.Thomas, and L.H.Sperling, Macromolecules, **5**, 348 (1972).
47. S.C.Kim, D.Klempner, K.C.Frisch, H.L.Frisch, and H.Chiradello, Polymer Eng.Sci., **15**, 339 (1975).
48. J.A.Grates, D.A.Thomas, E.C.Hickey, and L.H. Sperling, J.Appl.Polymer Sci., **19**, 1731 (1975).
49. H.Mizumachi and Y.Ogata, J.Adhes.Soc.Japan, 12, 2 (1976).
50. L.H.Sperling, T.W.Chiu, R.G.Gramlich, and D.A. Thomas, J.Paint Technol., **46**, 47 (1974).
51. L.H.Sperling and D.A.Thomas, US P.3833404 (1974); C.A., **83**, (62087 f) (1975).
52. A.A.Askadskii, G.M.Avilova, Ya.S.Vygodskii, Yu.S. Kochergin, Yu.I.Matveev, S.N.Salazkin, G.L.Slonimskii, and B.D.Tartakovskii, USSR P.534483 (1974); Byull.Izobr., No.41, 73 (1976).
53. A.A.Askadskii, G.M.Avilova, Yu.S.Kochergin, Yu.I.Matveev, G.L.Slonimskii, and B.D.Tartakovskii, in "Materialy Seminara, 'Vibropogloshchayushchie Materialy i Pokrytiya i ikh Primenenie v Promyshlennosti'" (Proceedings of a Seminar on "Vibration-absorbing Materials and Coatings and their Application in Industry", Leningrad, 1976, p.4.
54. Yu.S.Kochergin, A.P.Travnikova, A.A.Askadskii, E.S.Krongauz, G.L.Slonimskii, and V.V.Korshak, Vysokomol.Soed., **20A**, 839 (1978).
55. J.M.Augl, J.Polymer Sci., **A1**, 2403 (1972).
56. R.J.A.Otto and L.F.Audrieth, J.Amer.Chem.Soc., **80**, 5894 (1958).
57. L.N.Belkina, Voprosy Radioelektroniki, Ser.Obshchetekh., No.12, 169 (1973).
58. A.A.Askadskii, L.N.Belkina, L.I.Komarova, V.V.Korshak, S.N.Salazkin, Ya.S.Vygodskii, G.L.Slonimskii, and S.V.Vinogradova, Vysokomol.Soed., **22A**, 1347 (1980).
59. A.A.Askadskii, V.V.Korshak, and L.N.Belkina, Voprosy Radioelektroniki, Ser.Obshchetekh., No.12, 129 (1975).
60. A.A.Askadskii, V.V.Korshak, and L.N.Belkina, Voprosy Radioelektroniki, Ser.Obshchetekh., No.12, 138 (1975).
61. L.N.Belkina, Candidate's Thesis, Mendeleev Moscow Institute of Chemical Technology, Moscow, 1977.
62. W.A.Pankratow, W.W.Korschak, S.W.Winogradowa, and A.G.Putschin, Plaste und Kautschuk, **20**, 481 (1973).
63. S.V.Vinogradova, V.A.Pankratov, A.G.Puchin, and V.V.Korshak, Izv.Akad.Nauk SSSR, Ser.Khim., 837 (1971).
64. V.V.Korshak, V.A.Pankratov, A.A.Askadskii, A.G.Puchin, and S.V.Vinogradova, Vysokomol.Soed., **16A**, 981 (1974).
65. V.I.Pavlov, A.A.Askadskii, and G.L.Slonimskii, Vysokomol.Soed., **9A**, 385 (1967).
66. G.L.Slonimskii, A.A.Askadskii, and A.I.Mzhel'skii, Vysokomol.Soed., **12A**, 1161 (1970).
67. A.A.Askadskii, "Fiziko-khimiya Poliarilatov" (Physical Chemistry of Polyarylates), Khimiya, Moscow, 1968.
68. A.A.Askadskii, "Deformatsiya Polimerov" (Deformation of Polymers), Khimiya, Moscow, 1973.
69. G.L.Slonimskii and A.A.Askadskii, Mekhanika Polimerov, No.1, 36 (1965).
70. Yu.S.Kochergin, A.A.Askadskii, S.N.Salazkin, I.A.Bulgakova, V.F.Alekseev, S.V.Vinogradova, G.L.Slonimskii, and V.V.Korshak, Vysokomol.Soed., **20A**, 880 (1978).
71. A.A.Askadskii, V.G.Dashevskii, and Yu.S.Kochergin, Vysokomol.Soed., **19B**, 500 (1977).
72. V.A.Pankratov, A.A.Askadskii, M.M.Patsuriya, Yu.S.Kochergin, S.V.Vinogradova, G.L.Slonimskii, and V.V.Korshak, Vysokomol.Soed., **19A**, 142 (1977).
73. H.Kitano and F.Tanimoto, J.Japan Chem., **25**, 58, 135, 232 (1971).
74. L.G.Grigor'eva, V.A.Sergeev, V.K.Shitikov, and V.V.Korshak, Izv.Akad.Nauk SSSR, Ser.Khim., 1488 (1973).
75. V.V.Korshak, G.L.Slonimskii, V.A.Pankratov, S.V. Vinogradova, A.A.Askadskii, E.S.Obolonkova, E.M. Belavtseva, and K.A.Bychko, Dokl.Akad.Nauk SSSR, **221**, 621 (1975).

Institute of Hetero-organic
Compounds, USSR Academy of
Sciences, Moscow

Translated from *Uspekhi Khimii*, 49, 879-902 (1980) U.D.C. 543.544.8

Chemospecific (Covalent) Chromatography of Biopolymers

V.I.Lozinskii and S.V.Rogozhin

The literature on the applications of one of the modern methods for the isolation and thorough purification of biopolymers —chemospecific (covalent) chromatography based on the chemical interaction of substances in solution and the chromatographic carrier—is reviewed.
The bibliography includes 164 references.

CONTENTS

I. Introduction 460
II. General scheme for the process. Terminology 460
III. Chemical principles of the method 461
IV. Carriers for the chromatographic process 464
V. Applications of chemospecific chromatography 466
VI. Certain methodological problems of the chromatographic process 468

I. INTRODUCTION

Modern biochemical methods make it possible to isolate in a pure state from a wide variety of sources and to investigate the structure, properties, and the mechanism of action of virtually all classes of biopolymers present in the tissue and liquids of organisms even in extremely low amounts. However, the schemes developed for the isolation and purification of the required substance are sometimes too cumbersome and laborious. The success of new not unduly laborious but much more effective methods such as biospecific (affinity) chromatography, affinity electrophoresis, etc. is not therefore surprising. They have significantly simplified and reduced the cost (which is also important) of the processes involving the isolation and purification of peptides, proteins, enzymes, nucleic acids, etc.

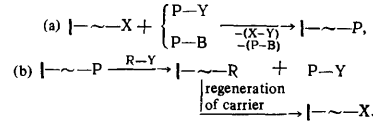
As will be shown below, there exist at the same time a number of problems which are difficult and sometimes simply impossible to solve on the basis of the physical properties of the substances alone or the principles of biological activity, since they require the "chemical involvement" of particular functional groups of the biomolecules. The processes in the isolation and purification of natural products, based on reversible chemical reactions between an insoluble carrier and the substances to be isolated, have come to be referred to as "covalent chromatography".

This review describes the main achievements of this method for the separation of substances and its applications and discusses some of its specific problems.

II. GENERAL SCHEME FOR THE PROCESS. TERMINOLOGY

"Covalent chromatography" is a comparatively new method for the isolation and purification of biopolymers. The first publication in this field refers to 1963 [1] and in the subsequent ten years only a few studies appeared[2-8]; subsequently, starting from 1973, interest in this method increased appreciably and the main bulk of the publications took place in the last five years. It is noteworthy that there are virtually no reviews of the method in the literature.

The general scheme for covalent chromatography includes the following sequence of operations†:



A mixture of biopolymers, one or several components of which are the required products of the separation (indicated by P–Y in the scheme above), is brought into contact with an insoluble carrier having a chemically active "anchor" group X capable of reacting selectively solely with group Y; this results in the immobilisaton of material carrying accessible Y residues and the products which have not been bound covalently (P–B) are washed off. The carrier–biomolecule covalent bond (hence the name of the method—covalent chromatography) is stable in the absence of a specific reagent (R–Y), but readily decomposes when such a reagent is introduced into the system in the next, deimmobilisation stage (b), as a result of which the required product of the separation passes to the solution. The carrier is regenerated as far as possible and is used again.

Several names have been proposed for the scheme given above: "covalent affinity chromatography"[7,8], "covalent chromatography"[9], and "reversible immobilisation"[10]. A more exact name for the method would probably be "chemospecific chromatography", which reflects the main ideas of the process—specific reversible chemical interaction of substances with an insoluble carrier. In the description below we shall therefore adhere to the terminology proposed here.

† Here and henceforth the symbol | denotes the matrix of the chemospecific carrier and the symbol ~ denotes an intermediate group ("spacer").

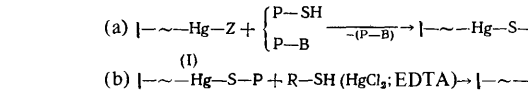
III. CHEMICAL PRINCIPLES OF THE METHOD

Since the main bulk of the publications in this field refer to studies on proteins and peptides, it is necessary to examine at the beginning the problem of which functional groups of protein molecules and which reversible chemical reactions involving them are used in the chemospecific chromatography (CSC) of proteins.

In the first place such groups must include the sulphydryl groups of the cysteine residues which form part of the composition of particular proteins. Whereas other groups (amino-, hydroxy-, phenoxy-, carboxy-, etc.) are present in other biopolymers (nucleic acids, polysaccharides) as well as proteins, the mercapto- and disulphide groups are almost exclusively a specific chemical feature of proteins as a class of biological macromolecules[11]. Numerous proteins with accessible SH groups are now known and the involvement of cysteine residues in enzyme catalysis by many enzymes (for example thiol proteases, creatine kinases, 3-phosphoglyceraldehyde dehydrogenases, etc.[12]) has been demonstrated. Reversible modifying agents for the mercapto-groups of proteins have also been thoroughly investigated[13]. It is not therefore surprising that reversible immobilisation via the SH groups of proteins was first used[1] for CSC and the majority of the publications on this method are in fact devoted to the isolation and purification of thiol-containing proteins and peptides on various carriers.

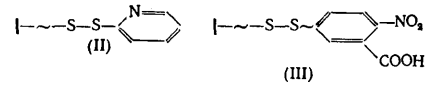
However, reactions other than those with SH groups can be used in the CSC of biopolymers. This has been demonstrated in a number of instances which will be discussed in detail below. Here one must emphasise that, in principle, it is possible to use the reversible reactions of any accessible groups in biomolecules subject to the only stipulation that the reactions must be highly specific and must occur under fairly mild conditions which do not decompose the biomolecules themselves or the carriers. Preliminary information concerning the effect of the low-molecular-weight reagent, whose insoluble analogue is to be employed, is therefore always necessary, i.e. CSC is based on data obtained in studies on the chemical modification of biopolymers. Thus this type of chromatography can also be regarded as the reversible modification of the functional groups of biological macromolecules by insoluble reagents.

As regards chemical processes involving SH groups, the formation reactions of either mercaptide (Hg—S), or disulphide (S—S), or thioester (CO—S) bonds have been used for CSC. The covalent bond between the mercury atom of the insoluble carrier and the mercapto-group of the protein or the peptide can be ruptured under mild conditions by low-molecular-weight thiols, soluble mercury salts, or complexones such as ethylenediaminetetra-acetic acid (EDTA):[1]

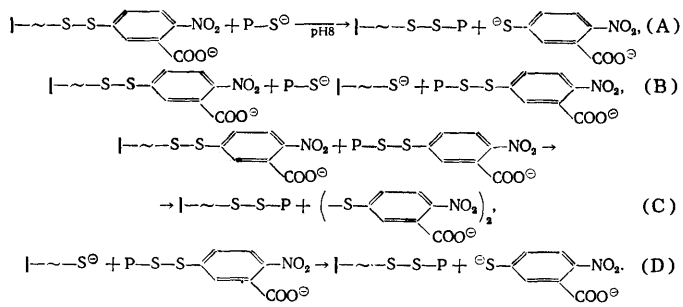


However, one should bear in mind that mercury-containing carriers must be used with a fair amount of caution, since the slow elution of the metal (partial decomposition of the carrier during manipulations and gradual hydrolysis of the carrier–ligand bonds), which always occurs, contaminates the protein, which is particularly undesirable if the biopolymer being isolated is to be introduced into some kind of organism. Furthermore, mercury carriers can retain also non-thiol proteins if the latter have intensely complex-forming groups capable of being incorporated in the coordination sphere around the mercury atom, which interferes with the isolation of the SH-products.

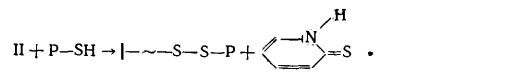
For CSC based on thiol–disulphide exchange reactions, insoluble analogues of reagents for SH groups have been used as the anchor groups of the carriers: di-(2-pyridyl)-disulphide (II) [14] and 5,5′-dithiobis-(2-nitrobenzoic acid) (III):[15]



The disulphide linkages of such carriers are activated by the electron-accepting effect of the aromatic system and readily enter into thiol–disulphide exchange reactions with the sulphydryl groups of the proteins. It has been noted[16] that, for carriers of type (III), the main reaction (A) via the CSC mechanism may be accompanied by other processes—(B), (C), and (D):



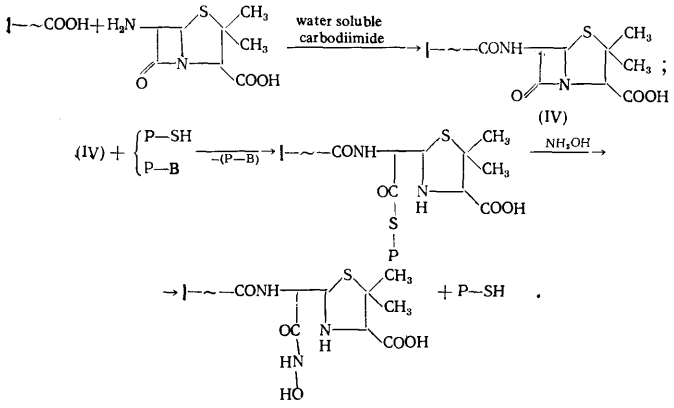
Such multiplicity of thiol–disulphide exchange reactions is missing in studies with carriers of type (II) containing dipyridyl disulphide active groups, since the 2-mercaptopyridine isolated immediately isomerises to 2-thiopyridone, which no longer takes part in the exchange processes and the reaction equilibrium is almost wholly displaced to the right[9,17,18]:



The deimmobilisation of the SH-protein occurs in the presence of an excess of a low-molecular-weight thiol (cysteine, 2-mercaptoethanol, and dithiothreitol).

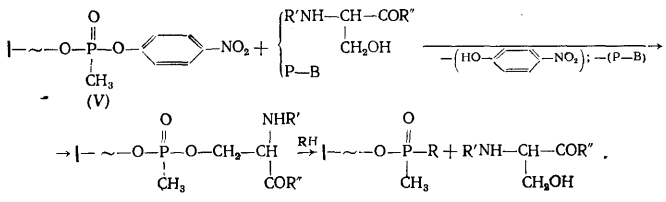
An interesting version of CSC has been achieved in the study of the penicillin-binding components of the membranes of *B. subtilis*[8,19,20]. As shown previously[21], these protein components are acylated by penicillin via the SH groups of the cysteine residues and the resulting thioester linkages can be ruptured either by hydroxylamine, or thiols, or hydrogen peroxide. A chromatographic process, carried out on carrier (IV) with immobilised 6-aminopennicillanic acid

(6-APA), has been developed on the basis of these data:



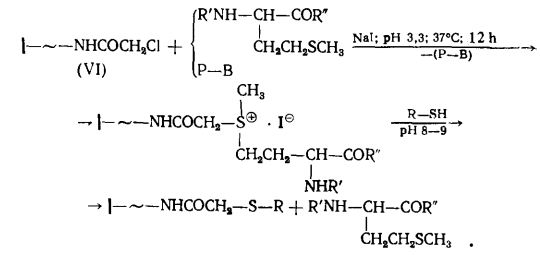
The above scheme is to some extent tentative, since the conditions governing the condensation of 6-APA with the COOH-carrier, quoted by the authors[8], do not exclude the formation in succession of several 6-APA molecules, linked by amide bonds, on the insoluble phase. It is therefore difficult to say which particular type of carrier is truly involved in the process—with monomeric or oligomeric penicillin. Another factor is important—this type of chemochromatographic approach can apparently prove useful in the study of the mechanism of the interaction of various medicinal drugs with cell components, since the formation of stable covalent ligand–protein bonds makes it possible to wash off thoroughly all the remaining substances and then to isolate the ligand receptors alone and to investigate them separately.

As already mentioned above, the CSC scheme need not be applied solely to SH-proteins. The reversible phosphorylation of the OH group of the serine residues has been used[7,22] in the isolation of enzymes containing this aminoacid at the active centre (acetylcholinesterase, α-chymotrypsin):



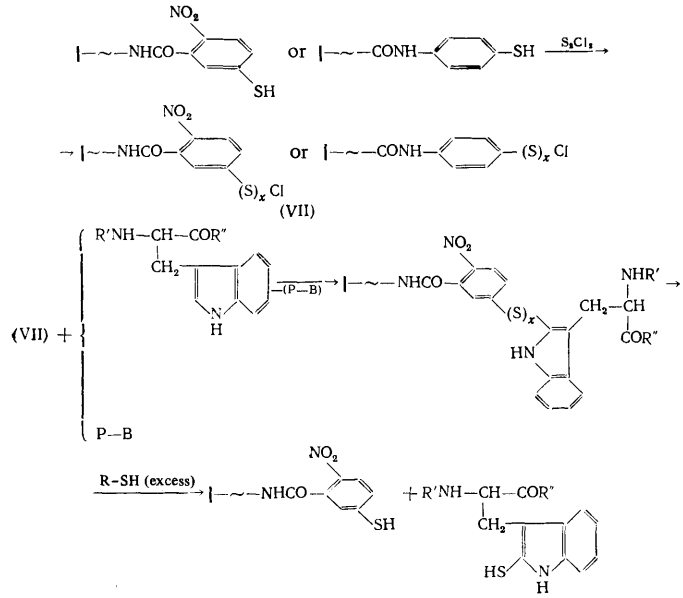
Here RH = 2-(hydroxyiminomethyl)-1-methylpyridinium iodide, 1,1′-trimethylenebis-(4-hydroxyiminomethyl)pyridinium dibromide, or hydroxylamine and R′ and R″ are polypeptide chains. The presence of serine in an activated form is apparently an essential condition for reaction with a carrier of type (V), since a protein not belonging to the class of serine enzymes but containing serine in its composition (serum albumin) is not retained by the carrier.

The formation of sulphonium derivatives on interaction of the thioester group of the methionine residue with α-halogeno-acids in an acid medium and their subsequent decomposition with low-molecular-weight thiols has been used recently[23] in CSC involving methionine residues:



It is necessary that the methionine residue is not a C-terminal aminoacid, since otherwise it is converted into a homoserine residue and the protein or peptide is not fixed on the carrier. One should note that the fairly severe conditions required for the immobilisation of methionine-containing substances probably limit the applicability of this scheme to relatively stable proteins. For peptides, it is apparently not so significant if they do not contain labile linkages of the type Asp–pro.[24] There are also some doubts about the stability of the material of the carrier under the fixation conditions. Furthermore, the above scheme does not provide for the regeneration of the carrier.

The ability of sulphenyl chloride[25] and sulphur monochloride[26] to modify the tryptophan residues at the 2-position of the indole ring has been used[27] for the chemospecific isolation of tryptophan-containing compounds:



Ultimately the tryptophan residue is modified—an SH group appears in the indole ring. The introduction of this group, which is convenient for further modification, will apparently prove useful also in the study of the role of Trp residues in enzyme molecules. Since carriers of type (VII) bind covalently also mercapto-groups, it follows that, when it is necessary to carry out the process via the tryptophan residues alone, one must block appropriately the SH groups of the cysteine.

Table 1. Carriers for the chemospecific chromatography of biopolymers.

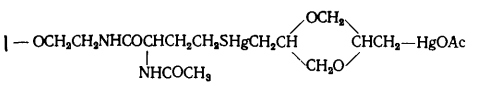
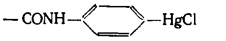
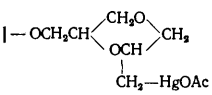
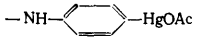
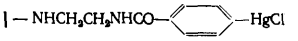
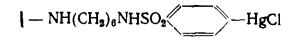
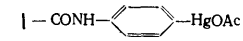
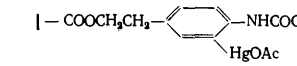
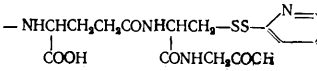
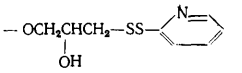
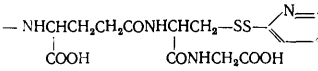
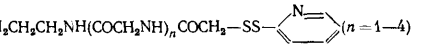
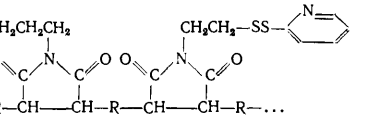
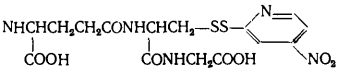
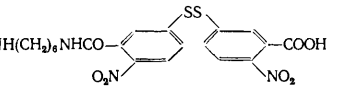
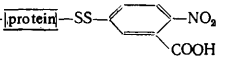
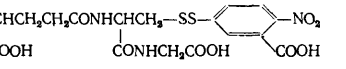
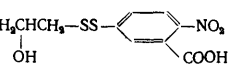
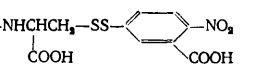
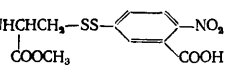
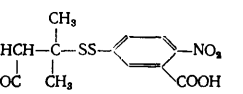
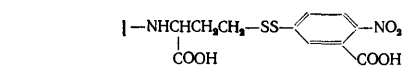
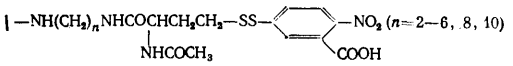
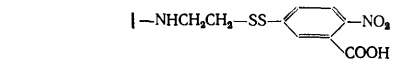
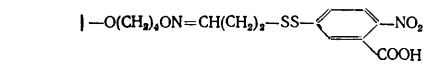
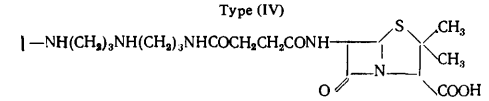
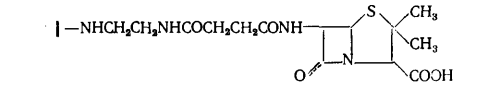
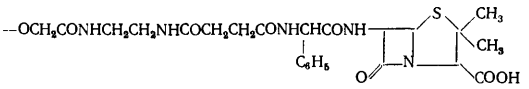
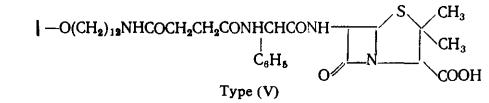
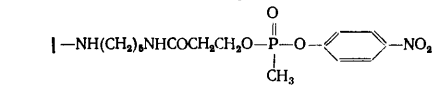
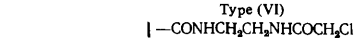
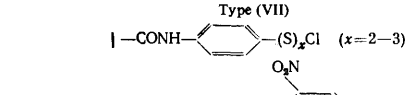
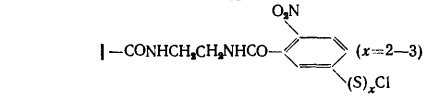
No.	Matrix	Chemospecific group with spacer	Capacity with respect to active groups	Refs.
		Type (I)		
1	Sephadex G-25		0.15 mmole g^{-1}	1
2*	Maleic anhydride–ethylene copolymer cross-linked by hexamethylenediamine		1.62 μmole g^{-1}	3
3	Cellulose		0.2—0.7 mmole g^{-1}	5
4	Sepharose 4B		0.2—0.5 mmole ml^{-1}	6
5	Ditto		0.2—1.2 μmole ml^{-1}	36, 82
6	»		1.2 μmole ml^{-1}	110
7a	Hydroxyalkyl methacrylate gel (Spheron)		0.03—0,10 mmole ml^{-1}	72
7b	Ditto		0,02—0,20 mmole ml^{-1}	72
		Type (II)		
8	Sepharose 4B		0.6—1.0 μmole ml^{-1}	9
9	Ditto		20 μmole ml^{-1}	42
10	Sepharose CL 4B		3.9 μmole ml^{-1}	41
11	Macroporous silica (Silochrome)		40 μmole g^{-1}	48—51
12	Ditto		10—20 μmole g^{-1}	51
13**	»		up to 160 μmole ml^{-1}	50,145
14	Sepharose 4B		3—10 μmole ml^{-1}	111
		Type (III)		
15	Sepharose 4B		0.14 mmole g^{-1}***	16
16****	Ditto		0.2—0.3 μmole ml^{-1}	83
17	»		0.95 μmole ml^{-1}	84
18	»		5.1 μmole ml^{-1}	33
19	»		0.048 μmole ml^{-1}	33
20	»		0.063 μmole ml^{-1}	33
21	»		0.033 μmole ml^{-1}	33

Table 1 (con'd).

No.	Matrix	Chemospecific group with spacer	Capacity with respect to active groups	Refs.
22	Sepharose 4B		0.19 μmole ml^{-1}	33
23	Ditto		—	59
24	»		0.045 μmole ml^{-1}	85
25	Cellulose		—	112
		Type (IV)		
26	Sepharose 4B		—	8
27	Ditto		—	8
28	»		—	113
29	Cellulose		—	114
		Type (V)		
30	Sepharose 4B		0.2-1.0 μmole ml^{-1}	7
		Type (VI)		
31	Cross-linked polyacrylamide		0.77 mmole g^{-1}***	22
		Type (VII)		
32	Cross-linked polyacrylamide		0.8 mmole g^{-1}***	27
33	Ditto		—	27

*Carrier exhibits an appreciable non-specific sorption with respect to the main proteins.
**The substituent R = *N*-vinylpyrrolidinone, ethyl vinyl ether, styrene, or ethylene.
***The capacity is quoted with respect to the dry weight of the carrier.
****The protein consists of the light κ-type immunoglobulin chain.

There have also been studies where a modified version of CSC, in which the anchor groups X were introduced into the biopolymer while the Y groups were contained in the carrier, has been used. For example, an SH-protein was treated with dipyridyl disulphide, the excess reagent was removed by gel filtration, the protein was hydrolysed by a proteolytic enzyme, and the solution of the resulting peptides was passed through a column with a carrier containing mercapto-groups[28]. In studies with polynucleotides both isolation of the mercapto-derivatives of nucleic acids on an Hg-carrier[29] and, conversely, the isolation of mercurated RNA and DNA on an SH-carrier have been used[30-32].

The choice of a chemical pathway for a chromatographic process is largely dictated by the specific conditions of each concrete problem. It is of course impossible to reach an unambiguous conclusion as to which version is best (with the anchor group on the carrier or on the biopolymer). One can only note that, from the standpoint of the stability of the carrier (in the case of insoluble thiol phases), preference should be given to chemosorbents with a protected SH group—in this form it is subject to much less risk of oxidation. The lower effectiveness of the fixation of the dithio-2-nitrobenzoate derivative of the protein on an SH-carrier compared with the reaction of an SH-protein and a type (III) carrier has also been demonstrated[33].

IV. CARRIERS FOR THE CHROMATOGRAPHIC PROCESS

Like any chromatographic process, chemospecific chromatography imposes requirements on the carrier: (1) chemical, physical, mechanical, and biological stabilities; (2) sufficient permeability to macromolecules ensuring their free approach to the active groups of the carrier; (3) hydrophilic properties of the carrier, permitting experiments in an aqueous medium; (4) homogeneity of shape—preferred use of

carriers in the form of spherical beads of identical size; (5) commercial availability of the material of the carrier matrix and as far as possible its low cost.

Apart from these properties of the matrices, which are generally speaking the same for all chromatographic processes involving biopolymers and which have been discussed in fair detail in specialist literature (see, for example, Klyashchitskii and Shapot[34] and Berezin et al.[35]), carriers with functional groups capable of undergoing readily reactions for the addition of anchor groups are necessary in CSC.

Table 1, which summarises the literature data for the carriers used in CSC, shows that chemosorbents based on agarose gels, which have proved useful for affinity chromatography and the immobilisation of biopolymers, have been used in most cases. Agarose matrices are available commercially, exhibit a non-specific sorption, and methods for the introduction of various groups into such carriers have been thoroughly developed[36–38]. However, such carriers are not free from a number of disadvantages either: namely their mechanical strength is low, the structure of the polysaccharide matrix breaks down under the influence of organic solvents and temperatures above 50–60 °C, and the rate of flow of the liquids through the column containing the gel is rather low even when a small excess pressure is applied, the carrier is subject to microbial infection, and, finally, it is fairly expensive. Cross-linked agarose gels of the type of Sepharose-CL,[39,40] which have improved physicomechanical properties, will probably prove very useful in this process, as shown[41] by the application of a chemosorbent based on this Sepharose derivative (No.10, Table 1). A similar cross-linked agarose carrier (Nos.9 and 18, Table 1) has been obtained[42] by treating a polysaccharide matrix with epichlorohydrin (for the introduction of epoxy-groups). However, since the degree of cross-linking was not controlled and the formation of cross-links in the gel was a concomitant process in the formation of the active groups on the carrier, it is not clear to what extent such cross linking took place.

Carriers based on cross-linked polyacrylamide gels have also been used in CSC (Nos.31–33, Table 1). They have been employed in studies with proteins of low molecular weight and peptides. Here the very matrix imposes limitations—biopolymers with high molecular weights (in excess of 100 000 for Bio-Gel P-100 and above 300 000 for Bio-Gel P-200, on the basis of which chemosorbents have been prepared[23,27]) cannot penetrate[43] into the particles of the swollen gel. Furthermore, the mechanical strength of weakly cross-linked polyacrylamide matrices is likewise low.

In recent years carriers on an inorganic base have been used increasingly in the immobilisation of various biologically active compounds[44,45] and also for the specific isolation of enzymes[46] and gene fragments[47] with the aid of affinity chromatography. Materials such as porous glass, macroporous silicas, metals, metal oxides, ceramics, etc. have a high mechanical strength and standardised characteristics, are resistant to microbial infection, and are readily available; any chaotropic agents, high salt concentrations, and organic solvents can be used in experiments with them.

We obtained[48–51] a number of carriers for the CSC of proteins and peptides (Nos.11–13, Table 1) on the basis of a macroporous silica—silochrome[52]. Carriers containing a polymer grafted to an inorganic surface (No.13, Table 1) (R = ethyl vinyl ether, *N*-vinylpyrrolidinone, etc.) are characterised by a non-specific sorption of proteins and an improved stability of the matrix in alkaline media, in addition to an ehanced capacity with respect to dipyridyl disulphide groups. We believe that inorganic carriers whose surface is coated by a hydrophilic polymer are promising for studies on biopolymeric phases, since they combine the useful physicomechanical properties of inorganic matrices with adsorption passivity (when a collect choice is made) of the polymer coating. The preparation and use of combined carriers of this type have been described in a number of publications on the immobilisation[53,54] and affinity chromatography[55–57] of enzymes.

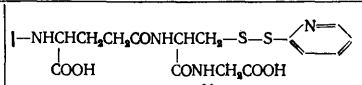
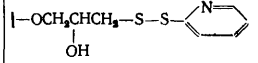
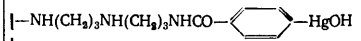
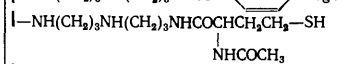
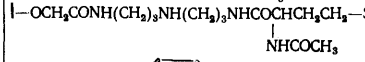
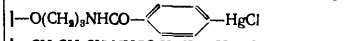
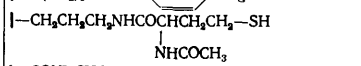
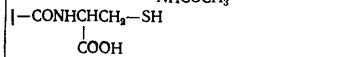
In the study of the properties of the carriers used, much attention has been devoted recently to the investigation of the influence of the distance of the immobilised affine ligand from the matrix on the efficiency of the chromatographic process and on the possibility of non-specific interactions. Such interactions (hydrophobic, electrostatic, sorption, etc.) usually interfere with the main procedure and its is therefore always desirable to eliminate them as far as possible. Summarising the results of these studies, one may conclude that the lengthening groups—the so called spacers—should undoubtedly by hydrophilic, simply because long polymethylene systems interact appreciably with the hydrophobic sections of protein molecules, as shown clearly, for example, by O'Carra et al.[58] Or, at least under the conditions employed (ionic strength of the solution, pH of the medium, and temperature), hydrophobic interactions should be minimal, which, however, must always be demonstrated in preliminary control experiments. It is also better if the spacer contains no ionogenic groups. Otherwise, there is, firstly, a superposition of ion exchange and, secondly, carriers of the gel type, containing charged groups, undergo an appreciable change in their volume and hence also there is a change in the size of the gel pores as the composition of the buffer is altered.

Although ionogenic groups do not in fact enter into the composition of the proposed spacer, the chosen chain of the chemical transformations for the immobilisation of the ligand frequently permits side reactions, which may "unexpectedly" give rise to an undesirable effect. For example, if the very popular method involving the attachment of amines to BrCN-activated agarose[37] is used, reactions via both NH_2 and SH groups can occur in the case of aminothiols[17]. This entails a decrease of the capacity of the carrier with respect to the mercapto-groups and introduces unnecessary ionogenic amino-groups. As regards the size of the spacer, the literature data are fairly contradictory. It is most likely that the optimum length is determined by the substance to be isolated and purified and by its structure and properties. It has been noted[34] that an unduly long spacer is relatively ineffective owing to its conformational bending, conversion into a helix, etc.

In CSC the influence of the length and structure of the spacer have so far been studied inadequately, although there are certain interesting data. Thus investigation of the kinetics of the deimmobilisation of lipoamide dehydrogenase with type (III) carriers (No.23, Table 1) established[59] that the enzyme dissolves under the influence of a reducing agent faster the longer the spacer, i.e. the approach of the cleaving agent to the covalent carrier–enzyme linkage is sterically facilitated. The chemical structure of the spacer near the active group is also important. It has been shown[33] that a carrier with the dithio-2-nitrobenzoate group at a quaternary carbon atom (No.21, Table 1) reacts to a very insignificant extent with SH-proteins—the shielding influence of the substituents has an effect, whereas branching at the next carbon atom of the main chain (Nos.17–20, Table 1) virtually no longer hinders the fixation of the protein. Thus, in the synthesis of active groups on carriers, it is necessary to take into account all the factors discussed above.

A number of carriers for CSC are now manufactured by certain companies. Table 2 presents the characteristics of

Table 2. Commercial carriers for chemospecific chromatography.

No.	Manufacturing company	Name of product	Matrix	Chemispecific group with spacer	Capacity with respect to active groups
1	Pharmacia Fine Chemicals (Sweden)	Activated Thiol-Sepharose	Sepharose 4B		1.0 μmole ml^{-1}
2	Ditto	Thiopropyl-Sepharose	Sepharose 6B		20 μmole ml^{-1}
3	Serva (Western Germany)	Servachrom-A-Hg	agarose		—
4	Ditto	Servachrom-A-SH	"		—
5	Bio-Rad Laboratories (USA)	Affi-Gel 401	"		6.0 μmole ml^{-1}
6	Ditto	Affi-Gel 501	"		3.0 μmole ml^{-1}
7	Pierce (USA)	Thiol/CPG	porous glass (d_{pore} = 550 A)		30 μmole g^{-1}
8	Koch-Light Ltd. (England)	Enzacryl-Polythiol	cross-linked polyacrylamide		—
9	Sigma (USA)	Cysteamine-agarose	agarose		0.1 μmole ml^{-1}
10	Ditto	*L*-Cysteine-agarose	"		2-10 μmole ml^{-1}

these chemosorbents based on the data supplied by the manufacturing companies (according to the 1977–1978 catalogues). Also included is information about certain commercially available SH-carriers, since they can be converted into derivatives with activated thiol functions by familiar reactions. However, one should note that all these carriers are fairly expensive, so that the development and practical employment of cheaper chemosorbents is an urgent problem whose solution will greatly extend the application of the CSC method not only in the laboratory but possibly also in biotechnology.

V. APPLICATIONS OF CHEMOSPECIFIC CHROMATOGRAPHY

The trends in studies on the CSC of biopolymers and the applications of this interesting highly selective method for the thorough purification of substances have now become clearly established. As already mentioned, most of the published data refer to studies with proteins or peptides. The use of CSC for the isolation of polynucleotides[30], gene fragments[29, 31,32], and low-molecular-weight cofactors[60] has been reported. Problems involving the isolation and purification of biopolymers, which have been solved with the aid of CSC, can be classified as follows.

1. Separation into fractions based on the chemical composition (for example, the separation of proteins with accessible SH groups from all the remaining mixture components).
2. Isolation of individual proteins and enzymes and isolation of isoenzymes.
3. Separation of chemically non-identical sub-units of oligomeric proteins.
4. Chemospecific isolation of peptides containing aminoacids with reactive side chains.
5. Purification of synthetic peptides.
6. Elimination of non-protein substances from proteins.
7. Isolation of modified nucleic acids and gene fragments.

Reversible immobilisation has also been used in the chemical modification of an enzyme temporarily fixed on an insoluble carrier followed by its dissolution[41,61]. This approach[41] makes it possible to avoid intermolecular cross-links if it is necessary to modify groups in the protein molecule in an isolated form by means of a bifunctional reagent.

Table 3 present a compilation of data on specific substances whose isolation or purification have been achieved with the aid of CSC. One should bear in mind that the chemospecific purification stage is hardly ever used in isolation. If there are simple methods for the preliminary fractionation and concentration of the desired product, then it is undoubtedly desirable to use them; this applies particularly to the removal of low-molecular-weight components, since they may contain substances which either interfere with the chemical fixation of the biopolymer on the carrier or are capable of cleaving the covalent carrier–biopolymer bond formed.

Table 3. Isolation and purification of biopolymers with the aid of CSC.

Substance isolated and purified	Source of biopolymer	Carrier		Refs.
		type	No. in Table 1	
1. Separation into fractions according to chemical composition				
SH-Protein fraction	rat liver homogenate	(I)	1	1
SH-Containing DNA nucleoproteins	rat liver cell nuclei	(I)	1	2
F3 histone fraction	calf thymus	(I)	5	82,86
Separation of SH-proteins from acid prolylcarboxypeptidase	ox adenohypophysis	(I)	6*	88
Band 3 polypeptide fraction	human erythrocyte membranes	(II)	1*	87
Penicillin-binding protein fraction	*B. subtilis* membranes	(IV)	26,27	8,19,20
Penicillin-binding proteins	*Salmonella typhimurium*	(IV)	28	113
2. Isolation of individual proteins and enzymes				
Haemoglobin albumin, human blood sera, glyceraldehyde-3-phosphate dehydrogenase, aldolase	separation of artificial mixture	(I)	1	1
Aldolase	rat muscle	(I)	1	1
Thiolated bovine γ-globulin	—	(I)	3	5
Mercaptopapain	preparation	(I)	4	6,89
"	"	(II)	8	9,17,18
"	"	(II)	9	115
"	dried papain latex	(II)	8	9,17,18
Mercaptoficin	*Ficus glabrata*	(I)	4	96
"	"	(II)	8	97
Cathepsin B_1	human liver	(I)	4	90
Ditto	ox spleen	(I)	4	91,92
Cathepsin B_2	ditto	(I)	4	92
Cathepsin H	human liver lysosomes	(I)	4	102
Cathepsin N	ox spleen	(I)	4	116
Streptococcal protease	—	(I)	4	93
Clostripain	*Clostridium*	(I)	4	103
SH-Protease	green bean plants	(I)	7	72
SH-Protease	*Phaseolus vulgaris*	(I)	7	104
SH-Protease of blood-sucking insects	*Phodnius prolixus*	(I)	4	117
Dipeptidylaminopeptidase I	ox spleen	(I)	4	118
L-pyrrolidonecarboxypeptidase	*B. amyloliquefaciens*	(I)	5	119
Thiolsubtilisin	—	(I)	4	68
Thioltrypsin	—	(I)	4	69
Oestradiol 17β-dehydrogenase	—	(I)	5	94
S-Adenosyl-L-methionine decarboxylase	rat liver	(I)	5	95
Ditto	sea urchin eggs	(I)	5	95
Creatine phosphokinase	chicken breast muscle	(I)	5	98
Ditto	human skeletal muscle	(I)	5	99
Cysteine-containing histone	calf thymus	(I)	5	100
ARE-histone	ditto	(I)	5	101
Factor XIII of blood clotting system	human blood plasma	(I)	6*	67
Ditto	human thrombocytes	(I)	6*	67
5-Methylthioadenosine nucleosidase	human placenta	(I)	6	120
Pyridoxamine(pyridoxin)-5-phosphate oxidase	baker's yeast	(I)	6*	121
Choline acetyltransferase	*Drosophila melanogaster*	(I)	5	122
"	mouse brain	(I)	5	123
Selenoprotein of the glycine reductase complex	*Clostridium sticklandii*	(I)	6*	124
Metallothionein	rat liver	SH–	–	125
Mercaptoalbumin	ox blood serum	(II)	8	105
"	ditto	(III)	15	16
Urease	*Canavalia ensiformis*	(II)	8	63,106
"	ditto	(II)	9	107
Collagen of type III	human and calf skin	(II)	1*	108
Phospholipase A_2	human blood plasma	(II)	1*	62
Ornithine decarboxylase	rat liver	(II)	1*	126
γ-Glutamylcyclotransferase	ditto	(II)	1*	127
Metallothionein	rat liver polysomes	(II)	1*	128
Copper-binding metallothionein	human liver	(II)	2*	129
Ferredoxin	*Lactuca sativa*	(II)	2*	130
α_1-Antitrypsin	human blood plasma	(III)	16	83,109
α_1-Antitrypsins of types M, S, and Z	ditto	(III)	16	131
Blood plasma SH-proteins (separated)	ditto	(III)	16–22	33
Human prealbumin	blood plasma	(III)	17	84
Ox prealbumin	ditto	(III)	17	132
F_1-ATPase	pig heart mitochondria	(III)	15	133
D-Alanine carboxypeptidase	*B. subtilis* membranes	(IV)	26,27	8,19,20
DD-Carboxypeptidase	*Proteus mirabilis* membranes	(IV)	29	114
Acetylcholinesterase	electric organ of the eel	(V)	30	7,22
α-Chymotrypsin	preparation	(V)	30	7,22

Table 3 (cont'd).

Substance isolated and purified	Carrier		Refs.
	type	No. in Table 1	
3. Separation of non-identical subunits of oligomeric proteins			
SH-subunit of lombricine kinase	(I)	4	64
SH-subunit of yeast phenylalanyl-tRNA synthetase	(I)	4	65
SH-subunit of the calf lens alpha crystallin	(I)	4	134
a-Subunit of factor XIII of the blood clotting system	(I)	6*	67
κ-Casein and α_S-casein	(II)	1*	66
β-Chain of ox haemoglobin	(II)	11	49
4. Chemospecific isolation of peptides			
Cysteine-containing peptides of the pepsin insulin hydrolysate	(I)	2	4
Cysteine-containing peptide of the trypsin hydrolysate of the SH-subunit of lombricine kinase	(I)	4	64
Cysteine-containing peptides of the trypsin hydrolysate of "Tu" factor for the elongation of the polypeptide chain	(I)	5	71
Cysteine-containing peptide of the chymotrypsin hydrolysate of human blood serum albumin	(I)	7	72
Cysteine-containing peptide of the BrCN-hydrolysate of yeast 3-phosphoglycerate kinase	(I)	4	135
Cysteine-containing peptides of pepsin hydrolysates: of hake muscle parvalbumin, ox serum albumin, and human ceruloplasmin	(II)	1*	74
Cysteine-containing peptides obtained by different types of hydrolysis of the β-chain of ox haemoglobin	(II)	11	49
Cysteine-containing peptides of chicken heart cytoplasmic aspartate aminotransferase	(II)	1*	76–78
Cysteine-containing peptides of di-2-pyridyl disulphide derivatives of albumin and ribonuclease	SH–	–	28
Cysteine-containing peptide of the BrCN-hydrolysate of ox serum albumin	(III)	15	16
Methione-containing peptides of the trypsin hydrolysate of lysozyme	(VI)	31	23
Tryptophan-containing peptides of the trypsin hydrolysates of glucagon and human blood serum albumin	(VII)	33	27
5. Purification of synthetic peptides			
Synthetic peptides of the 111–124 sequence of ribonuclease and the 1–37 sequence of histone H4	(I)	5	79
Synthetic peptide of the 33–48 sequence of allergen M	(II)	2*	73,136
Cbz-Trp-Ala	(VII)	33	27
6. Elimination of non-protein substances from proteins			
Elimination of residual cell components from the overall protein of baker's yeast	(II)	11	80
Elimination of non-protein impurities from reduced lysozyne	(II)	11	48
Elimination of surfactants and lipid-like compounds from proteins	(II)	11	81
7. Isolation of modified nucleic acids and gene fragments			
2-Thiouracil-containing RNA	(I)	6*	29
6-Thioguanosine-containing RNA	(I)	3	137
Mercurated RNA from different sources (chemical mercuration)	SH–	–	30–32, 138–141
Mercuriuridine-containing RNA	SH–	–	142
Mercurated RNA (chemical mercuration)	SH–	–	30,138,143
8. Isolation of cofactors			
Flavin-adenine dinucleotide	(I)	4	60
Coenzyme A from *Sarcina lutea*	(I)	4	60

*The number refers to Table 2.

The combination of CSC with other selective methods yields satisfactory results when it is necessary to obtain, for example, a particularly pure and active enzyme preparation. Thus, in the isolation of phospholipase A_2 from human blood serum[62], several preliminary purification stages were followed by the consecutive application of three affinity columns: chromatography on concanavaline A-Sepharose—for the isolation of glycoproteins, which included also the required phospholipase; chromatography on a column with immobilised antiserum and γ-immunoglobulin (in the fraction of which activity was detected) for the separation of immunoglobulin; and finally CSC on an activated thiol-Sepharose (No.1, Table 2). This yielded an enzyme with more than a 10 000-fold

degree of purification. The above example refers to the isolation of a protein present in the initial material in extremely low amounts. On the other hand, when the required product is one of the main components (for example, papain in dried papain latex[9]), it can be isolated with the aid of CSC fairly simply and rapidly using a minimum number of stages. This is particularly convenient for the thorough purification of commercial protein preparations. For example, the isolation of mercaptopapain from a commercial papain[9,17] or the isolation of highly active urease from a commercial preparation of this enzyme[63] have been achieved rapidly and effectively on chemospecific carriers, while the isolation of the SH-components alone of the above proteins by the usual methods is laborious and leads to considerable losses of valuable enzyme material.

It has been shown that it is possible to separate rapidly non-identical subunits of oligomeric proteins with the aid of chemospecific sorbents, when some subunits contain and others do not contain reactive aminoacid residues. The SH-subunit of lombricine kinase[64], the α-subunit of yeast phenylalanyl-tRNA synthetase[65], κ-casein and αS-casein from whole casein[66], the β-chain of bovine haemoglobin[49], and the *a*-subunit of factor XIII of the blood clotting system[67] have been isolated in this way. In the last case the SH-*a*-subunit, immobilised reversibly on an Hg-carrier (No.6, Table 2), was used also to investigate its non-covalent interactions with the *b*-subunit.

In the study of the properties of "unusual" proteolytic enzymes—thiolsubtilisin[68] and thioltrypsin[69], obtained by the chemical transformation of the serine residue of the active centre into a cysteine residue by the method of Photaki and Bardakos[70]—CSC made it possible to isolate in a single stage the active modified protein.

The chemospecific isolation of substances in the determination of the primary sequence in proteins and particularly high-molecular-weight proteins, where the separation of complex peptide mixtures based on the differences between the charges, molecular sizes, hydrophobic properties, etc. frequently becomes relatively ineffective, gives rise to interesting prospects. There exist two versions of the chemospecific extraction of peptides for further structural studies. The first involves the interaction of the active carrier with the mixture of peptides obtained enzymatically or by chemical hydrolysis. Depending on the type of carrier and the amino-acid composition of the protein fragments, the reaction with the corresponding side groups of the peptides can proceed: the mercapto-group of cysteine[4,16,64,71-73], the thioester group of methionine[23], and the indole ring system of tryptophan[27]. After washing away the unreacted material, the peptides fixed covalently on the chemosorbent are dissolved by treatment with an appropriate cleaving agent.

The second method involves the fragmentation (enzymatic or chemical) of the reversibly immobilised protein directly on the carrier[49,74-78]. The carriers on an inorganic base (No.11, Table 1), which we proposed[48], proved useful in this instance[49], because the matrix consisting of macroporous silicon dioxide (silochrome) is stable under the conditions of different types of treatment of immobilised polypeptide chains such as pepsinolysis, trypsinolysis, cleavage with bromocyanogen, rupture of aspartyl–proline bonds (pH 2.2, 37 °C, 36 h), as well as the solid-state version of the determination of the peptide sequence by the Edman method. The fragmentation of the reversibly immobilised enzyme simplifies the isolation and identification of the peptides containing functionally important (essential) chemical groups in the active centres, provided that it is possible to select conditions ensuring the covalent fixation of only such groups of the active centre on the chemosorbent.

Generally speaking, it is not difficult to envisage the chemical separation of peptides on a series of carriers which selectively extract from the mixture the peptide (or peptides) containing a specific trifunctional aminoacid.

One of the problems in the solid-phase peptide synthesis is the elimination from a peptide with a specified sequence of the so-called "false" peptides, which are formed in the course of the synthesis mainly in consequence of the failure of the reactions to reach completion at various stages of the multi-stage process. A procedure has been proposed[79] for the isolation of the desired peptide by CSC. The essential feature of the method is that, after the completion of the synthesis of the required sequence, the peptide is augmented by the Cys–Met fragment (either consecutively, one residue at a time, or by adding the dipeptide at once) and then all the peptides obtained are separated from the insoluble support with simultaneous removal of the protective groups (for example, by treatment with HF). The treatment of this sum total of peptides by a sorbent chemospecific in relation to the SH groups removes the Cys–Met peptides from solution. All the remaining products are washed off. Peptides are removed from the chemosorbent by a low-molecular-weight thiol, the excess reductant being eliminated by gel filtration. Next follows the cleavage of the N-terminal dipeptide with bromocyanogen and repeated gel filtration. As a result, it is possible to separate many "false" peptides, particularly those whose chain growth was arrested during the synthesis for various reasons (*N*-acylation, the formation of a pyroglutamic derivative, the inaccessibility of the growing chain to the reactants in consequence of steric hindrance, etc.). Synthetic peptides on an Hg-containing carrier[79] and on a dipyridyl disulphide carrier[73] have been purified in this way. Clearly peptides containing methionine residues in the main sequence cannot be isolated in this way; in this case it is necessary to employ another selectively cleaved terminal fragment.

It has been shown recently[80,81] that CSC can be used for the elimination of non-protein substances from proteins and peptides. A carrier on an inorganic base has been used, which made it possible to use solvents and concentrated urea solutions to wash surfactants and lipid-like compounds out of the temporarily immobilised protein[81].

VI. CERTAIN METHODOLOGICAL PROBLEMS OF THE CHROMATOGRAPHIC PROCESS

When the two main stages of CSC, namely (a) covalent fixation of substances from solution on the carrier followed by (b) their deimmobilisation are carried out, it is necessary to remember that chemical reactions, at least those on the carriers known hitherto, do not take place instantaneously—a certain amount of time is required to complete the reactions. The stream of liquid through the material of the packing in the column must not therefore be very rapid, particularly in the column version of the process; the use of recirculation gives rise to satisfactory results in stage (a). There are few literature data for the gradient supply of the cleaving agent for the removal of the immobilised biomolecules from carriers. Nevertheless this deimmobilisation procedure apparently greatly improves the resolving capacity of the method as a whole.

Elution with stepwise changes in the strength of the cleaving agent has been used already in the first studies on CSC.[1,2] A model mixture of SH-proteins (mercaptoalbumin, glyceraldehyde-3-phosphate dehydrogenase, haemoglobin, and aldolase) have been separated by this method on a mercury-containing carrier (No.1, Table 1).[1] In order to rupture the mercaptide carrier–protein bonds, a reducing

agent (mercaptoethanol or dithiothreitol) was applied to the column, ensuring a linear concentration gradient, which made it possible to separate the required SH compound (factor XIII in the blood clotting system) from other thiol proteins linked to the chemosorbent, "by virtue of their different reactivities with respect to the cleaving agent"[67]. Strictly speaking, this version of the process actually constitutes a chromatographic separation of the substances and not simply a sequence of two operations: chemospecific sorption and desorption. It may be hoped that the separation of biopolymers by CSC using a cleaving agent gradient will be employed on an increasing scale.

Our data[80] show that the presence of a reductant concentration gradient in experiments with carriers of type (II) makes it possible to wash the protein off the insoluble phase with the minimum amount of the low-molecular-weight thiol required for this purpose, which greatly diminishes the risk of the intramolecular disulphide bonds of the protein itself being affected.

One should note a disadvantage which is encountered when carriers of types (II) and (II) are used. When the SH-containing product, initially fixed on the insoluble phase, is removed with a thiol, it is difficult to detect the biopolymer at the outlet from the column, since the residual "unused" active groups of the carrier are also cleaved by the reductant and are washed off together with the required products, which makes the ultraviolet detection of the eluted protein or peptide with the aid of the usual flow-type photometers virtually impossible owing to the intense absorption by 2-thiopyridone or 2-nitro-5-thiobenzoate. It is therefore necessary to analyse the material by some other method (for example by the gel electrophoresis of the fractions, by measuring, whenever possible, the enzyme activity, by chromatography—for peptides, etc.). It is thought that, at least for proteins and polypeptides, this disadvantage can be eliminated by employing a membrane eluate concentrator (model CEC1, Amicon, Holland) beyond the column, which cuts off the low-molecular-weight substances in the stream. The only important factor is that the change in the salt composition of the buffer occurring under these conditions does not cause a sharp impairment of the solubility of the biopolymers.

Finally we come to the last remark concerning experiments with SH-biopolymers or sulphur-containing carriers; it is always necessary to use deaerated buffer solutions; likewise it is extremely undesirable that even traces of heavy metal ions should be present. In order to bind such ions, EDTA is therefore usually introduced into the solution. These precautions guarantee the stability of the mercapto- and disulphide groups in the test compounds.

---o0o---

In conclusion one should note that chemospecific chromatography has now found an honourable place among other highly selective methods for the isolation and purification of biologically active compounds; it is developing vigorously, is being improved, and is being applied on an increasing scale to a wide variety of test objects.

During the preparation of the review for publication, reports have been published, describing the syntheses of certain chemosorbents[144-148] belonging to types (I)–(IV) described above and the isolation by the CSC method of peptides[149], proteins[144,145,148-161], nucleic acids[147,162], and fragments of membranes[163], as well as studies of certain methodological problems of the process[157,164].

REFERENCES

1. L.Eldjarn and E.Jellum, Acta Chem.Scand., **17**, 2610 (1963).
2. E.Jellum and L.Eldjarn, Biochim.Biophys.Acta, **100**, 144 (1965).
3. I.E.Liener, Arch.Biochem.Biophys., **121**, 67 (1967).
4. I.E.Liener and L.-P.Chao, Analyt.Biochem., **25**, 317 (1968).
5. J.R.Shainoff, J.Immunol., **100**, 187 (1968).
6. L.A.A.Sluyterman and J.Wijdenes, Biochim.Biophys. Acta, **200**, 593 (1970).
7. Y.Ashani and I.B.Wilson, Biochim.Biophys.Acta, **276**, 317 (1972).
8. P.M.Blumberg and J.L.Strominger, Proc.Nat.Acad.Sci. U.S.A., **69**, 3751 (1972).
9. K.Brocklehurst, J.Carlsson, M.P.J.Kierstan, and E.M.Crook, Biochem.J., **133**, 573 (1973).
10. J.Carlsson, R.Axén, and T.Unge, Europ.J.Biochem., **59**, 567 (1975).
11. Yu.M.Torchinskii, "Sera v Belkakh" (Sulphur in Proteins), Izd.Nauka, Moscow, 1977.
12. Yu.M.Torchinskii, "Sera v Belkakh" (Sulphur in Proteins), Izd.Nauka, Moscow, 1977, p.157.
13. Yu.M.Torchinskii, "Sera v Belkakh" (Sulphur in Proteins), Izd.Nauka, Moscow, 1977, p.118.
14. D.R.Grassetti and J.F.Murray, Arch.Biochem.Biophys., **119**, 41 (1967).
15. G.L.Ellman, Biochem.Biophys., **82**, 70 (1959).
16. L.J.Lin and J.F.Foster, Analyt.Biochem., **63**, 485 (1975).
17. K.Brocklehurst, J.Carlsson, M.P.J.Kierstan, and E.M.Crook, Meth.Enzymol., **34B**, 531 (1974).
18. J.Carlsson, Protides Biol.Fluides, **23**, 537 (1976).
19. P.M.Blumberg, Fed.Proc., **32**, 482 (1973).
20. P.M.Blumberg and J.L.Strominger, Meth.Enzymol., **34B**, 401 (1974).
21. P.J.Lawrencse and J.L.Strominger, J.Biol.Chem., **245**, 3653 (1970).
22. H.F.Voss, Y.Ashani, and I.B.Wilson, Meth.Enzymol., **34B**, 581 (1974).
23. Y.Shechter, M.Rubinstein, and A.Patchornik, Biochemistry, **16**, 1424 (1977).
24. D.Piszkiewicz, M.London, and E.L.Smith, Biochem. Biophys.Res.Comm., **40**, 1173 (1970).
25. E.Scoffone, A.Fontana, and R.Rocchi, Biochemistry, 7, 971 (1968).
26. T.Wieland, O.Weinberg, and W.Dilger, Annalen, **592**, 69 (1955).
27. M.Rubinstein, Y.Schechter, and A.Patchornik, Biochem.Biophys.Res.Comm., **70**, 1257 (1976).
28. A.Svenson, J.Carlsson, and D.Eaker, FEBS Letters, **73**, 171 (1977).
29. M.Ono and M.Kawakami, J.Biochem., **81**, 1247 (1977).
30. R.M.K.Dale and D.C.Ward, Biochemistry, **14**, 2458 (1974).
31. M.M.Smith and R.C.C.Huang, Proc.Nat.Acad.Sci. U.S.A., **73**, 775 (1976).
32. G.F.Crouse, E.J.B.Fodor, and P.Doty, Proc.Nat.Acad. Sci.U.S.A., **73**, 1564 (1976).
33. C.-B.Laurell, E.Thulin, and R.P.Bywater, Analyt. Biochem., **81**, 336 (1977).
34. B.A.Klyashchitskii and V.S.Shapot, Uspekhi Biol. Khim., **17**, 234 (1976).
35. I.V.Berezin, V.K.Antonov, and K.Martinek (Editors), "Immobilizovannye Fermenty" (Immobilised Enzymes), Izd.Moskov.Gos.Univ., Moscow, **1976**, Vol.1, p.68.
36. R.Axén, J.Porath, and S.Ernbäck, Nature, **214**, 1302 (1967).

37. P.Cuatrecasas, J.Biol.Chem., **245**, 3059 (1970).
38. Affinity Chromatography. Principles and Methods, "Pharmacia Fine Chemicals", Uppsala, Sweden, 1977.
39. T.Låås, Protides Biol.Fluids, **23**, 495 (1976).
40. Sepharose-CL for gel filtration and affinity chromatography, "Pharmacia Fine Chemicals", Uppsala, Sweden, 1975.
41. G.P.Royer, S.i.Ikeda, and K.Aso, FEBS Letters, **80**, 89 (1977).
42. R.Axén, H.Drevin, and J.Carlsson, Acta Chem.Scand., **B29**, 471 (1975).
43. H.Determann, "Gel Chromatography" (Translated into Russian), Izd.Mir, Moscow, 1970, p.52.
44. H.H.Weetall, Analyt.Chem., **46**, 602A (1974).
45. G.Baum and M.Lynn, Process Biochem., **10**, 14 (1975).
46. H.H.Weetall and A.M.Filbert, Meth.Enzymol., **34B**, 59 (1974).
47. K.G.Skryabin, T.V.Venkstern, V.N.Zaharyev, V.P.Varlamov, S.V.Rogozhin, and A.A.Bayev, Z.physiol.Chem., **357**, 337 (1976).
48. V.I.Lozinskii, B.Yu.Zaslavskii, Yu.A.Davidovich, and S.V.Rogozhin, USSR P.540 870 (1975); Byul.Izobret., No.48, 72 (1976).
49. Ts.A.Egorov, M.I.Shakhparonov, Yu.A.Davidovich, V.I.Lozinskii, B.Yu.Zaslavskii, and S.V.Rogozhin, Bioorg.Khim., **3**, 1111 (1977).
50. V.I.Lozinskii, A.V.Il'ina, Yu.A.Davidovich, and S.V.Rogozhin, Symposium, "II Vsesoyuznaya Konferentsiya po Metodam Polucheniya i Analiza Biokhimicheskikh Preparatov, g.Olanie, 1977" (The IInd All-Union Conference on the Methods for Obtaining and Analysis of Biochemical Preparations, Olaine, 1977), p.105.
51. V.I.Lozinskii, I.G.Tsoi, Yu.A.Davidovich, and S.V.Rogozhin, Izv.Akad.Nauk SSSR, Ser.Khim., 1358 (1979).
52. N.K.Bebris, A.V.Kiselev, and Yu.S.Nikitin, Kolloid. Zhur., **29**, 326 (1967).
53. G.P.Royer, Chem.Technol., **4**, 694 (1974).
54. G.P.Royer, G.M.Green, and B.K.Sinha, J.Macromol. Chem., **A10**, 289 (1976).
55. V.P.Varlamov, G.E.Bannikova, A.V.Vlasov, B.E.Gadas, B.L.Tsetlin, and S.V.Rogozhin, Symposium, "II Vsesoyuznoe Simpozium po Polucheniyu i Primeneniyu Immobilizovannykh Fermentov, g.Abovyan, 1977" (The IInd All-Union Symposium on the Preparation and Applications of Immobilised Enzymes, Abovyan, 1977), p.1.
56. G.P.Royer, F.A.Liberatore, G.M.Green, W.E.Schwartz, and W.E.Meyers, Polymer Preprints, **16**, 76 (1975).
57. P.A.Anderson and L.Jervis, Biochem.Soc.Trans., **5**, 728 (1977).
58. P.O'Carra, S.Barry, and T.Griffin, FEBS Letters, **43**, 169 (1974).
59. C.R.Lowe, Europ.J.Biochem., **76**, 411 (1977).
60. Y.Matuo, R.Sano, T.Tosa, and I.Chibata, Analyt. Biochem., **68**, 349 (1975).
61. S.-i.Ikeda and S.Fukui, Biochem.Biophys.Res.Comm., **52**, 482 (1973).
62. R.Scherer, W.Huber-Friedberg, A.Salem, and G.Ruchenstroth-Bauer, Z.physiol.Chem., **357**, 897 (1976).
63. R.Norris and K.Brocklehurst, Biochem.J., **159**, 245 (1976).
64. E.Der-Terrossian, L.-A.Pradel, R.Kassab, and G.Desvages, Europ.J.Biochem., **45**, 243 (1974).
65. A.Murayama, J.P.Raffin, P.Remy, and J.P.Ebel, FEBS Letters, **53**, 23 (1975).
66. H.Nijhuis and H.Klostermeyer, Milchwissenschaft, **30**, 531 (1975).
67. J.McDonagh, W.C.Waggoner, E.G.Hamilton, B.Hindenach, and R.P.McDonagh, Biochim.Biophys.Acta, **446**, 345 (1976).
68. L.Polgàr, Acta Biochim.et Biophys.Acad.Sci.Hung., **11**, 81 (1976).
69. H.Yokosawa, S.Ojima, and S.Ishii, J.Biochem., **82**, 869 (1977).
70. J.Photaki and V.Bardakos, J.Amer.Chem.Soc., **87**, 3489 (1965).
71. S.Nakamura, K.-i.Arai, K.Takahashi, and Y.Kaziro, Biochem.Biophys.Res.Comm., **66**, 1069 (1975).
72. J.Turkovà, S.Vavreinovà, M.Krivàkovà, and J.Čoupek, Biochim.Biophys.Acta, **386**, 503 (1975).
73. "Thiopropyl-Sepharose 6B", "Pharmacia Fine Chemicals", Uppsala, Sweden, 1977.
74. T.A.Egorov, A.Svenson, L.Rydén, and J.Carlsson, Proc.Nat.Acad.Sci.U.S.A., **72**, 3029 (1975).
75. Ts.A.Egorov, M.I.Shakhparonov, and S.V.Rogozhin, Symposium, "Sovetsko-Amerikanskii Simpozium po Khimii i Fizike Belka, Riga, 1976" (The Soviet-American Symposium on the Chemistry and Physics of Proteins, Riga, 1976), p.59.
76. T.V.Demidkina, M.I.Shakhparonov, Ts.A.Egorov, and Yu.M.Torchinskii, Symposium, "IV Vsesoyuznyi Simpozium po Khimii Belkov i Peptidov, Minsk, 1977" (The IVth All-Union Symposium on the Chemistry of Proteins and Peptides, Minsk, 1977), p.100.
77. Ts.A.Egorov, M.I.Shakhparonov, and I.V.Nazimov, Symposium, "IV Vsesoyuznyi Simpozium po Khimii Belkov i Peptidov, Minsk, 1977" (The IVth All-Union Symposium on the Chemistry of Proteins and Peptides, Minsk, 1977), p.34.
78. Ts.A.Egorov, M.I.Shakhparonov, T.V.Demidkina, and Yu.M.Torchinskii, Biokhimiya, **42**, 2253 (1977).
79. D.E.Krieger, B.W.Erickson, and R.B.Merrifield, Proc. Nat.Acad.Sci.U.S.A., **73**, 3160 (1976).
80. V.I.Lozinskii, B.Yu.Zaslavskii, Yu.A.Davidovich, and S.V.Rogozhin, USSR P.533 631 (1975); Byul.Isobret., No.40, 70 (1976).
81. V.I.Lozinskii, Yu.A.Davidovich, B.Yu.Zaslavskii, Ts.A.Egorov, and S.V.Rogozhin, Biokhimiya, **43**, 257 (1978).
82. A.Ruiz-Carrillo and V.G.Allfrey, Arch.Biochem.Biophys., **154**, 185 (1973).
83. C.-B.Laurell, J.Pierce, U.Persson, and E.Thulin, Europ.J.Biochem., **57**, 107 (1975).
84. G.Fex, C.-B.Laurell, and E.Thulin, Europ.J.Biochem., **75**, 181 (1977).
85. W.W.-C.Chan and K.Mosbach, Biochemistry, **15**, 4215 (1976).
86. A.Ruiz-Carrillo, Meth.Enzymol., **34B**, 547 (1974).
87. A.Kahlenberg and C.Walker, Analyt.Biochem., **74**, 337 (1976).
88. L.P.Alekseenko and V.N.Orekhovich, Bioorg.Khim., **3**, 1387 (1977).
89. L.A.A.Sluyterman and J.Wijdenes, Meth.Enzymol., **34B**, 544 (1974).
90. A.J.Barrett, Biochem.J., **131**, 809 (1973).
91. H.Keilovà and V.Tomàsek, FEBS Letters, **29**, 335 (1973).
92. K.Otto and H.Riesenkönig, Biochim.Biophys.Acta, **379**, 462 (1975).
93. A.A.Kortt and T.Yu.Liu, Biochemistry, **12**, 320 (1973).
94. J.C.Nicolas, Meth.Enzymol., **34B**, 552 (1974).
95. C.-A.Manen and D.H.Russell, Biochemistry, **13**, 4729 (1974).

96. C.D.Anderson and P.L.Hall, Analyt.Biochem., **60**, 417 (1974).
97. J.P.G.Malthouse and K.Brocklehurst, Biochem.J., **159**, 221 (1976).
98. R.J.Boegman, FEBS Letters, **53**, 99 (1975).
99. V.Madelian and W.A.Warren, Analyt.Biochem., **64**, 517 (1975).
100. K.Ishikawa and K.Iwai, J.Biochem., **77**, 391 (1975).
101. J.Bode and K.G.Wagner, Biochem.Biophys.Res. Comm., **62**, 868 (1975).
102. H.Kirschke, J.Langner, B.Wiederanders, S.Ansorge, P.Bohley, and H.Hanson, Acta Biol.Med.Germ., **36**, 185 (1977).
103. I.Ermöd and B.Keil, FEBS Letters, **77**, 51 (1977).
104. S.Vavreinovà and J.Turkovà, Biochim.Biophys.Acta, **403**, 506 (1975).
105. J.Carlsson and A.Svenson, FEBS Letters, **42**, 183 (1974).
106. J.Carlsson, R.Axén, K.Brocklehurst, and E.M.Crook, Europ.J.Biochem., **44**, 189 (1974).
107. J.Carlsson, I.Olsson, R.Axén, and H.Drevin, Acta Chem.Scand., **B30**, 180 (1976).
108. B.C.Sykes, FEBS Letters, **61**, 180 (1976).
109. C.-B.Laurell, Protides Biol.Fluids, **23**, 359 (1976).
110. R.Porta, C.Esposito, and G.Della Pietra, Int.J.Biochem., **8**, 347 (1977).
111. J.Grunwald and L.J.Berliner, Biochim.Biophys.Acta, **523**, 53 (1978).
112. A.A.Nedospasov and R.M.Khomutov, "Tezisy Vsesoyuznoi Konferentsii po Metodam Polucheniya Vysokoochishchennykh Fermentov, Vil'nyus, 1978" (Abstracts of the All-Union Conference on Methods for the Preparation of Highly Purified Enzymes, Vilna, 1978), p.89.
113. S.T.Shepherd, H.A.Chase, and P.E.Reynolds, Europ. J.Biochem., **78**, 521 (1977).
114. H.H.Martin, W.Schilf, and C.Maskos, Europ.J.Biochem., **76**, 585 (1976).
115. T.Stuchbury, M.Shipton, R.Norris, J.P.G.Malthouse, K.Brocklehurst, J.A.L.Herbert, and H.Suschitzky, Biochem.J., **151**, 417 (1975).
116. A.Ducastaing and D.J.Etherington, Biochem.Soc.Trans., **6**, 938 (1978).
117. E.S.Garcia, J.A.Guimarâes, and J.L.Prado, Arch. Biochem.Biophys., **188**, 315 (1978).
118. R.M.Metrione, Biochim.Biophys.Acta, **526**, 531 (1978).
119. D.Tsuru, K.Fujiwaka, and K.Kado, J.Biochem., **84**, 467 (1978).
120. G.Cacciapuoti, A.Oliva, and V.Zappia, Int.J.Biochem., **9**, 35 (1978).
121. T.Tsuge, K.Sen-Maru, and K.Ohashi, FEBS Letters, **93**, 331 (1978).
122. W.J.Driskell, B.H.Weber, and E.Roberts, J.Neurochem., **30**, 1135 (1978).
123. L.-P.Chao, Neurochem.Res., **3**, 549 (1978).
124. J.E.Cone, R.M.Del Rio, and T.C.Stadtman, J.Biol. Chem., **252**, 5337 (1977).
125. S.G.Shapiro, K.S.Squibb, L.A.Markowitz, and R.J.Cousins, Biochem.J., **175**, 833 (1978).
126. M.F.Obenrader and W.F.Prouty, J.Biol.Chem., **252**, 2860 (1977).
127. N.Taniguchi and A.Meister, J.Biol.Chem., **253**, 1799 (1978).
128. K.S.Squibb and R.J.Cousins, Biochem.Biophys.Res. Comm., **75**, 806 (1977).
129. L.Rydén and H.F.Deutsch, J.Biol.Chem., **253**, 519 (1978).
130. A.de la Torre, A.Chueca, and J.L.Gorgé, Phytochemistry, **17**, 35 (1978).
131. J.-O.Jeppsson, C.-B.Laurell, and M.Fagerhol, Europ. J.Biochem., **83**, 143 (1978).
132. G.Fez and R.Lindgren, Biochim.Biophys.Acta, **493**, 410 (1977).
133. C.Godinot, A.DiPietro, B.Blanchy, F.Penin, and D.C.Gautheron, J.Bioenerg.Biomembr., **9**, 255 (1977).
134. K.Malinowski and W.Manski, Immunochemistry, **14**, 603 (1977).
135. A.Fattoum, C.Roustan, J.Feinberg, G.Desvages, and C.-A.Pradel, Europ.J.Biochem., **82**, 161 (1978).
136. G.Lindeberg, J.Tengborn, H.Bennich, and U.Ragnarsson, J.Chromatogr., **156**, 366 (1978).
137. W.T.Melvin and H.M.Keir, Biochem.J., **168**, 595 (1977).
138. R.M.K.Dale, E.Martin, D.C.Livingston, and D.C.Ward, Biochemistry, **14**, 2447 (1974).
139. H.Biessmann, R.A.Gjerset, D.Lewy, and B.J.McCarthy, Biochemistry, **15**, 4356 (1976).
140. A.R.Thomason and F.M.Rottman, Anal.Biochem., **89**, 501 (1978).
141. D.J.Goss and L.J.Parkhurst, J.Biol.Chem., **253**, 7804 (1978).
142. H.C.Towle, J.-J.Tsai, S.Y.Tsai, and B.W.O'Malley, J.Biol.Chem., **252**, 2396 (1977).
143. G.P.Georgiev, Yu.A.Illyin, A.P.Ryskov, N.A.Tchurikov, G.N.Yenikolopov, V.A.Gvozdev, and E.A.Ananiev, Science, **195**, 394 (1977).
144. J.Coyette, J.-M.Ghuysen, and R.Fontana, Europ.J. Biochem., **88**, 297 (1978).
145. A.V.Il'ina, V.I.Lozinskii, Yu.A.Davidovich, and S.V.Rogozhin, USSR P.687 081 (1977); Byul.Izobret., No.35, 109 (1979).
146. V.I.Lozinskii and S.V.Rogozhin, Symposium, "I Vsesoyuznyi Simpozium po Molekulyarnoi Zhidkostnoi Khromatografii, g.Dzerzhinsk, 1979" (The Ist All-Union Symposium on Molecular Liquid Chromatography, Dzerzhinsk, 1979), p.13.
147. W.T.Melvin and H.M.Keir, Analyt.Biochem., **92**, 324 (1979).
148. H.Horitsu, Y.Banno, S.Kimura, H.Shimizu, and M.Tomoyeda, Agric.Biol.Chem., **43**, 663 (1979).
149. M.Fukuda, Y.Eshdat, G.Tarone, and V.T.Marchesi, J.Biol.Chem., **253**, 2419 (1978).
150. H.Singh and G.Kalnitsky, J.Biol.Chem., **253**, 4319 (1978).
151. C.-B.Laurell, J.Chromatog., **159**, 25 (1978).
152. L.Polgár and P.Halász, Europ.J.Biochem., **88**, 513 (1978).
153. N.Ninamiura and K.T.Yasunobu, Biochem.Pharmacol., **27**, 2737 (1978).
154. K.Hosoi, S.Kobayashi, and T.Ueda, Biochem.Biophys. Res.Comm., **85**, 558 (1978).
155. I.R.Cottingham and C.I.Ragan, Biochem.Soc.Trans., **6**, 1307 (1978).
156. J.H.Keen and W.B.Jakoby, Analyt.Biochem., **90**, 136 (1978).
157. E.Noguchi, M.Nishikimi, and K.Yagi, Analyt.Biochem., **91**, 367 (1978).
158. P.D.Chantler and W.B.Gratzer, Analyt.Biochem., **91**, 626 (1978).
159. J.Carlsson, Hindustan, Antibiot.Bull., **20**, 105 (1976–1978).
160. D.Prigent, C.Geoffroy, and J.E.Alouf, Compt.rend., Ser.D, **287**, 951 (1978).
161. M.Shipton and K.Brocklehurst, Biochem.J., **171**, 385 (1978).

162. D.J.Goss and L.J.Parkhurst, J.Biol.Chem., **253**, 7804 (1978).
163. Y.Eshdat and A.Prujansky-Jakobovits, FEBS Letters, **101**, 43 (1979).
164. J.Lasch and R.Koelsch, Europ.J.Biochem., **82**, 181 (1978).

Institute of Organoelemental Compounds,
USSR Academy of Sciences, Moscow

Translated from *Uspekhi Khimii*, **49**, 903-930 (1980) U.D.C. 543.544

Reproducibility of Retention and Identification Data in Gas-Liquid Chromatography

A.N.Korol'

The elementary sorption processes taking place in a chromatographic column are discussed. The reasons for the lack of reproducibility of retention data in GLC are analysed. The basic requirements for a chromatographic apparatus capable of giving high-precision retention data are formulated, and conditions suitable for the measurement of retention quantities for identification are recommended. 243 references.

CONTENTS

I.	Introduction	473
II.	Solubility in the stationary phase	474
III.	The solid carrier - stationary phase interface	474
IV.	Adsorption at the liquid - gas interface	476
V.	Effect of changes in experimental conditions on the retention volume	476
VI.	Methods of presenting retention data for identification	479

I. INTRODUCTION

Gas chromatography was developed as a method of quantitative microanalysis of complex mixtures. In the early stages of its development the retention volume V_g was used[1-3] as the basic parameter for identifying the components of complex mixtures. However it was found that discrepancies in the measured values of V_g between different laboratories could be as high as 10–15%, and this led Adlard and coworkers[4] to recommend the use of the more reproducible Kovats retention indices for identification. Even this recommendation failed to solve the identification problem, because retention indices (I) measured in different laboratories were found to vary by 0.7 to 7.9 units, corresponding to an error of 1.6–12% in the measurement of retention volume. These discrepancies have focussed attention on the reasons for the unsatisfactory reproducibility of retention data obtained in different laboratories.

Careful studies of the sorption mechanism under GLC conditions have shown[5,6] that the retention data are affected not only by the gas–liquid separation coefficient K_l, but also by adsorption at interfaces and by the extent of curvature of the sorption isotherms: as a result, the retention data are a function of the amount of stationary phase deposited on the carrier (w_l) and of the sample size (q_S), i.e. of parameters which do not appear explicitly in the classical expression for calculating retention data. These conclusions raised doubts on the validity of retention data as a source of qualitative GLC information: in particular, it was stressed[7] that only in the most favourable circumstances can retention data be used to specify the order in which components will emerge from a column.

Yet the increasing precision of the measurement of retention data and the simplicity of the procedure are very attractive features of the use of these quantities for identification. The basic reasons for the lack of reproducibility of retention data measured in different laboratories have been investigated fairly fully, but the results have not yet been critically discussed in review articles, and therefore it is difficult at present to standardise methods of determining retention data †. This review aims to analyse the reasons underlying the lack of reproducibility of retention quantities, to assist the standardisation of experimental conditions, and to examine possible ways of presenting retention data for identification.

The general equation relating to net retention volume V_N to the parameters of the sorbent is[8]

$$V_N = \sum_i^k \frac{\partial V_N}{\partial V_i} V_i + \sum_j^m \frac{\partial V_N}{\partial S_j} S_j, \qquad (1)$$

where V_i is the volume of the i-th type (or state) of stationary phase, and S_j is the surface area of the j-th type of interface of the sorbent. Usually, with $w_l > 0{,}5\%$, the stationary phase on the surface of the solid carrier is present as a capillary liquid (index "c") or as an adsorbed layer (index "a")[9]. The following types of interface can be identified on the sorbent: solid carrier–stationary phase (index sl), capillary liquid–gas (index clg), and adsorbed liquid layer–gas (index alg). If all the distribution coefficients are constant Eqn.(1) can be written

$$V_N = K_{cl}V_{cl} + K_{al}V_{al} + K_{sl}S_{sl} + K_{clg}S_{clg} + K_{alg}S_{alg}, \qquad (2)$$

† The use of retention data for identification is discussed in the following recently published books: M.S.Vigdergauz, L.V.Semenchenko, V.A.Ezrets, and Yu.N.Bogoslovskii, "Kachestvennyi Gazokhromatograficheskii Analiz" (Qualitative Gas-chromatographic Analysis), Izd.Nauka, Moscow, 1978; Yu.N.Bogoslovskii, B.I.Anvaer, and M.S.Vigdergauz, "Spravochnik Khromatograficheskikh Velichin Uderzhivaniya" (Handbook of Chromatographic Retention Quantities), Izd.Standarty, Moscow, 1978; M.S.Vigdergauz, "Raschety v Gazovoi Khromatografii" (Calculations in Gas Chromatography), Izd.Khimiya, Moscow, 1978.

where K are the distribution coefficients of the sorbate between phases. With most of the sorbents commonly used in GLC ($w_l = 10-15\%$) over 90% of the stationary phase is in the form of a capillary liquid[9]: the contribution of the other four terms on the right-hand side of Eqn.(2) varies with the amount of stationary phase and with the nature of the carrier, and this is one of the main reasons for the lack of reproducibility of retention data between laboratories.

II. SOLUBILITY IN THE STATIONARY PHASE

When the stationary phase is first added to the carrier an adsorbed layer of liquid is formed: in the case of white diatomaceous carriers the formation of this layer is complete at $w_l = 0.3\%$, as shown by the existence of an optimum amount of modifier on the surface of the carrier[10-12]. Further additions of liquid phase produce two simultaneous effects: an increase in the thickness of the adsorbed layer, and the filling of the pores of the carrier by the "capillary liquid". The properties of the adsorbed layer of liquid are affected by the presence of the carrier surface, and they differ from those of the pure (or of the capillary) liquid, as shown by a decrease in the vapour pressure of the liquid[13,14]. There are reports[15] of differences in properties between the capillary and the pure liquid, though the theoretical analysis[16] suggests that substantial differences can be expected only for high-molecular stationary phases. The phase equilibrium constants for the pure and the capillary liquid (sorbates and sorbents of different polarity) have been found to be the same within experimental error (~1%).[4,17-20].

The effect of the carrier surface on the properties of the adsorbed liquid layer is discussed in Refs.21–26. It is found[27] that 5 monolayers of water and 10 monolayers of nitrogen are adsorbed on titanium dioxide. The effect of the solid surface on the properties of the adsorbed liquid can be detected at distances of up to 100 Å.[24] The upper temperature limit for the use of an adsorbed layer of stationary phase is found[28-31] to be higher in capillary columns than in packed columns. The thermodynamic properties of adsorbed and capillary liquids were found to be different[32,33], and an increase in density of a liquid in the adsorbed layer has been demonstrated by direct measurements[34]. Detailed studies[35-41] of the properties of layers of stationary phase adsorbed on diatomaceous carriers, silica gel, and graphite have established that the melting point of the compound increases by 4– K upon adsorption.

The retention volume (referred to the stability in the stationary phase, V_{Nl}) can be expressed as

$$V_{Nl} = K_{al}V_{al} + K_{cl}V_{cl};$$

and therefore, since $V_l = V_{al} + V_{cl}$, we can write

$$V_{Nl} = K_{cl}(V_l - V_{al}) + K_{al}V_{al}.$$

If the measurement is carried out at a sufficiently large value of w_l (such that only V_{Cl} is affected in changes in w_l) we can extrapolate the plot of V_{Nl} against V_l to $V_l = 0$ and obtain the extrapolated value V_N^{ext}:

$$V_N^{ext} = V_{al}(K_{al} - K_{cl}).$$

Evidently, $V_N^{ext} = 0$ for $K_{al} = K_{cl}$. It has been found experimentally[25] that $V_N^{ext} < 0$, i.e. $K_{cl} > K_{al}$.

Let us examine the case of a sorbate whose solubility depends on its concentration in solution. Liquid solutions usually have isotherms of the anti-Langmuir type[42-44], the only exceptions being solutions in which the activity coefficient is much less than unity[45]. The concentration dependence of the activity coefficient γ for non-electrolyte solutions is given by the Margules equation[46]

$$\ln\gamma = (1-x^2)\ln\gamma^{\infty},$$

where γ^{∞} is the activity coefficient of the solution at infinite dilution, and x is the mole fraction of solute. We can also use the Krichevskii equation[47], which is expressed in terms of the distribution coefficients $\tilde{K} = p/x$:

$$RT\ln\tilde{K} = RT\ln\tilde{K}^{\infty} - A_1x(2-x),$$

where A_1 is the concentration solubility coefficient and p is the vapour pressure in Torr. Replacing the parameter $\tilde{K}$ by the chromatographic distribution coefficient K_l, which characterises the ratio of the bulk concentrations, we obtain the equation

$$RT\ln K_l = RT\ln K_l^{\infty} + A_2x(2-x),$$

from which it follows that K_l increases with the concentration of the solution. A_2 is also a concentration coefficient. The concentration coefficients increase with the difference in polarity between the stationary phase and the sorbate[48]. It has been shown[20,49] that K_l varies with the concentration of the solution even if the solution obeys Henry's law: concentration-independent K_l values are found only in some solutions showing negative deviations from Raoult's law.

Thus, with a few exceptions, K_l is a function of the concentration of the solution, and therefore V_N also varies accordingly. Concentration effects are particularly strong in the chromatography of polar substances on non-polar stationary phases, as shown also by the molar heats of dissolution[20,50].

Differences in properties between the adsorbed and the capillary liquid are most conveniently revealed by comparing V_N values measured in capillary and in packed column (note that the adsorbed layer of liquid is more substantial in a capillary column than in a packed column). This type of comparison has shown[51-53] that the Kovats indices for hydrocarbons, their chloro-substituted derivatives, ketones, esters, alcohols, nitro compounds, and nitriles in squalane are identical for the two types of column, though the reproducibility of the retention data is unsatisfactory in the case of polar sorbates[52]. When polar stationary phases are used some differences between the retention data in capillary and in packed columns are observed[53].

III. THE SOLID CARRIER–STATIONARY PHASE INTERFACE

Though inertness towards adsorption is one of the main requirements for a chromatographic carrier, this requirement is never fully satisfied because all surfaces have an adsorption potential. Quantitative allowance for the effect of the carrier on the retention data was first made by Keller and Stewart[54], and the effect is discussed in detail in Refs.55–57. If adsorption at the *sl* interface is predominant the parameter V_N is given by the equation[58]

$$V_N/V_l = K_l\frac{K_{sl}S_{sl}}{V_l}. \qquad (3)$$

Extrapolation of plots of V_N/V_l against $1/V_l$ to $1/V_l = 0$ gives the constant K_l and the contribution of interfacial adsorption to V_N. A reference point method had been proposed[8] for calculating the adsorption contribution to V_N, but its precision is not high[59].

The effect of adsorption on V_N is especially marked when non-polar stationary phases are used to separate polar sorbates, and in this case it is very important to choose the carrier correctly. White and pink diatomaceous carriers have

different adsorption activities. Replacement of a pink carrier by a white carrier was found[60] to lower the adsorption contribution to V_N 2.5–3-fold. The lowest adsorption activity towards polar compounds is found in silanised white diatomites, which yield the most inert carriers (HP type) after heat treatment. A good example of such a carrier is Chromation N Super. The adsorption activity of diatomaceous carriers decreases in the following sequence of sorbates: amines > n-alcohols > iso-alcohols > carbonyl compounds > nitriles > nitro compounds > ethers > chloro-hyrocarbons > aromatic hydrocarbons > olefins > saturated hydrocarbons.

V_N for polar sorbates in non-polar sorbents is significantly affected by the nature of the carrier surface, and therefore the reproducibility of retention data in these systems can be problematic, since neither adsorbents nor carriers have fully reproducible properties. Evans and Smith[61] prepared a squalane and dinonyl phthalate sorbent with three different batches of silanised Chromosorb G: the retention indices for polar sorbates on these sorbents failed to show any differences arising from the different adsorption activities of the solid carriers. The effect of differences in the carrier on the retention data has been studied also by other workers[62–67].

Teflon has been recommended[68–70] as the ideal inert carrier, with the smallest possible adsorption effects: however, later work[61,71,72] revealed a high adsorption activity in Teflon towards low-polarity compounds, and Conder[73] showed that with the optimum amount (8%) of stationary phase on this carrier the contribution from adsorption to V_N is significant for all classes of sorbate.

Diatomaceous carriers have been found[74] to have a smaller contribution from adsorption to V_N than glass micro-spheres coated with n-octadecane.

Because of the adsorption effects at the *sl* interface fixed values of w_l must be used to ensure reproducible retention data from different laboratories. However the poor reproducibility of retention data for diatomaceous carriers arises from the curvature of the adsorption isotherm[54] as well as from adsorption. A typical manifestation of this effect is the "tailing" of peaks, and also the observed dependence of V_N on the size of the sample[75–78]. Obviously, this dependence may completely invalidate V_N as a source of information for qualitative analysis, and therefore the achievement of reproducible retention data in non-linear GLC has become a very important problem.

The effect of non-linearity in the adsorption isotherm for the *sl* interface is most marked in the separation of polar sorbates on non-polar or weakly polar stationary phases. In this case the molecules of the stationary phase are competing with those of the sorbate for adsorption on the carrier surface. Since diatomaceous carriers are polar, the molecules of the polar sorbate (in spite of their lower molecular weight) can penetrate close to the carrier surface and be adsorbed, the inhomogeneity of the carrier surface resulting in a non-linear adsorption isotherm[79–82]. When a polar stationary phase is used the sorbate molecules cannot penetrate the layer of adsorbed stationary phase, and the adsorption isotherm of the sorbate molecules on the energetically uniform adsorbed layer of stationary phase is approximately linear. With other (non-diatomaceous) types of carrier the general behaviour is very similar. Thus the adsorption isotherm of alcohols on Teflon coated with squalane is found to be curved[75].

The strong effect of sample size on V_N in polar sorbate–non-polar stationary phase systems can be ascribed to the curvature of the isotherm describing the adsorption at the *sl* interface (since the effect disappears when polar stationary phases are used). This prompted a search for methods of modifying the carrier surface to make it homogeneous towards interfacial adsorption. The first attempts were made in the early days of GLC [1,83] by adding a polar modifier (a fatty acid) to a weakly polar stationary phase used to separate a mixture of fatty acids. However the modifier did not prove to be universally effective. More recent attempts at modifying the carrier surface include the use of an inert polymer[84], silver[85], and copper[86], but even these were not fully successful in screening the active surface of the carrier.

The first successful results were obtained by chemically modifying the surface of the carrier (silanation[87,88] and polymerisation on the carrier[10,12,89]). Convincing results were obtained also by physical modification of the carrier with polar substances[31,90–92]. It was shown that not all polar liquids are suitable for physical modification: for example, poly(vinyl alcohol) is less successful than diglycerol as a modifier[11], and polyglycols (of different molecular weight) are now the most commonly used physical modifiers. When the carrier surface is coated with a thin layer of physical modifier the polar sorbate molecules are unable to reach the carrier surface, and adsorption is confined to the interface between the adsorbed layer of modifier and the capillary liquid.

"Self-modification" of the carrier surface under the influence of the polar sorbate can be important in the separation of polar sorbates on non-polar sorbents. In this case the sorbate peak has a highly extended trailing edge, and the carrier surface remains exposed to the modifying effect of the polar component (which influences its sorption properties) until that component has been completely eluted from the column. Therefore if the next sample is added to the column before complete elution of the previous polar sample grossly erroneous retention data may be obtained: thus in the case of ethyl methyl ketone on a squalane column the discrepancy can be as high as 50% in the retention volume and 1 kcal mole^{-1} in the relative molar heat of dissolution. Hence the retention data of these systems should be measured only by injecting pure compounds into the column, and the possibility of mutual effects of the sorbates on the individual retention volumes should be borne in mind when mixtures of polar substances are analysed.

Chemical modification by grafted polymers offers a useful increase in the maximum working temperature of sorbents. Thus sorbents modified with grafted Carbowax 20 M have been used (in conjunction with a flame-ionisation detector) at temperatures up to ~260 °C, i.e. well above the maximum working temperature of Carbowax 20 M.

The effect of adsorption at the *sl* interface on the retention indices can be observed also in capillary columns[93]. Thus it is found that the effect of the surface of a stainless steel capillary on the adsorption of the substances to be separated depends on the method of production of the capillary and on the treatment applied to its surface before deposition of the stationary phase: for example, thorough washing of the capillary surface with various solvents can increase its adsorption properties very markedly[94], though the optimum amount of solvent has to be used for the greatest effect. For this reason workers have turned their attention to glass capillaries[95], but the adsorption activity of glass was found to depend on the presence of sodium, boron, and hydroxyl groups[96,97]. The presence of OH groups causes irreversible adsorption of several polar compounds as well as introducing curvature into the adsorption isotherm[10,96,98–101]. Silanation[102,103], etching with hydrogen fluoride, and physical or chemical modification have been used to lower the adsorption activity of the surface of glass capillaries. One of the best methods is the glass surface deactivation procedure described in Refs. 10 and 12 and applied to capillary columns[104,105] in conjunction with etching with hydrogen fluoride[106]. After

being etched the capillary is coated with Carbowax 20 M, its ends are sealed, and the column is heated in a nitrogen atmosphere for 24 h at 280 °C. The physisorbed Carbowax 20 M is then washed out of the column with dichloromethane and methanol. However there is at least one report[102] of unsatisfactory reproducibility of the retention data after this treatment.

The extent of adsorption on the *sl* interface of capillary columns depends also on the purity of the stationary phase. For example it was shown[104] that "tailing" of the peaks of polar components occurs with SF-96 silicone oil but not with a high-purity grade of silicone oil (OV-101).

Thus the results discussed in this Section lead to the following recommendations for improving the reproducibility of retention data: a) only glass columns modified by Carbowax 20 M (or silanised) should be used in capillary chromatography; b) in packed columns, high-grade carriers of the Chromaton N Super type should be used, and non-silanised carriers should be chemically modified with Carbowax 20 M (amines and alkalis for the separation of amines, phosphoric acid for the analysis of acids); c) stationary phases of the highest possible purity should be used. These precautions should minimise the effects of adsorption at the *sl* interface (especially those associated with the curvature of the adsorption isotherm) on the effective value of V_N.

IV. ADSORPTION AT THE LIQUID-GAS INTERFACE

Adsorption of the compounds to be separated at the free surface of the stationary phase is possible[107]. A combination of static and chromatographic experiments[108,109] has shown that the value of V_N for the benzene–thiodipropionitrile and cyclohexane–thiodipropionitrile systems is significantly affected by adsorption at the *gl* interface.

Since the surface tension of non-polar stationary phases is relatively low we cannot expect large adsorption effects at the *gl* interface with non-polar or weakly polar stationary phases. Thus effects of adsorption at the *gl* interface on V_N were not detected in studies[110] of the retention of isooctane, cyclohexane, benzene, toluene, acetone, ethyl methyl ketone, and methanol on squalane and tricresyl phosphate: this result is consistent with other similar work[60,111,112]. However some workers consider[113–116] that V_N is affected by adsorption at the *gl* interface for polar sorbates in non-polar stationary phases, though their conclusions seem to be based on an incorrect treatment of the experimental results. Thus the change in $\ln\gamma$ brought about by an increase in the mole fraction of sorbate is treated[115] as a manifestation of interfacial adsorption, in spite of the anti-Langmuir shape of the adsorption isotherm (which suggests a concentration effect). Similarly erroneous conclusions are drawn from measurements[116] of sorption in dinonyl phthalate at high solution concentrations.

Polar stationary phases have a high surface tension, and adsorption at the *gl* interface is very marked on sorbents coated with stationary phases of this type, especially in the separation of hydrocarbons. For example, the adsorption contribution to V_N in the separation of hydrocarbons with thiodipropionitrile varies from 10 to 70%.[60] Similar effects were observed[117] for poly(ethylene glycol succinate).

A detailed study[118] of interfacial adsorption on a Carbowax 20 M column was based on the equation

$$V_g = V_g^{\infty} + k_1/w_l + k_2(1/w_l - 1/10);$$

where k_1 and k_2 are constants describing the contribution of adsorption at the *gl* and *sl* interfaces respectively. The coefficient 1/10 is introduced to allow for the authors' assumption[118] that when $w_l \geq 10\%$ adsorption at the *sl* interface is negligible.

The results of that study[118] lead to the following conclusions: a) the parameter k_1 increases along a homologous series, i.e. the contribution of adsorpton to V_N increases with the length of the alkyl radical, and it is negligibly small in the case of cyclic molecules; b) the k_2 values for isomeric ketones differ by ~10–15%, and this can affect the selectivity of stationary phases towards ketones (as compared to the solubility of ketones in the pure stationary phase).

The dependence of adsorption at the surface of the stationary phase upon the number of methylene groups in the alkyl radical of the sorbate can be expressed at[119]

$$K_{gl}^{p}/K_{gl}^{x} \approx (K_{gl})^{\Delta C},$$

where ΔC is the difference between the numbers of carbon atoms in the molecules of two compounds with the same retention volume, one of which is a n-paraffin (superscript *p*); the subscript *gl* denotes the gas-liquid interface.

Since the effect of adsorption at the surface of the stationary phase on V_N is usually smaller than the effect of adsorption at the *sl* interface it is useful to distinguish the systems in which the contribution to V_N of interfacial adsorption on the stationary phase surface is less than 1% by using the criterion[120]

$$K_{gl}/K_l < V_l/100S_{gl}.$$

As a rule the contribution to V_N of adsorption at the surface of the stationary phase can be ignored in systems with $\gamma < 5$, i.e. in the chromatography of substances of comparable polarity.

Liquid surfaces are energetically far more uniform than solid surfaces: for this reason the curvature of the adsorption isotherm is detectable only after completion of the first monolayer in the case of adsorption at the *gl* interface. Indeed, effects arising from non-linearity of the adsorption isotherm are observed[48] only at very low vapour pressures (~10^{-3} mmHg).

In GLC the stationary phase can be in two different energy states on the carrier, as was pointed out above. Hence it is correct to consider two types of adsorption at the stationary phase–gas interface: capillary liquid–gas adsorption and adsorbed liquid–gas adsorption. The properties of the two liquid surfaces are different, and as w_l is increased the area of the adsorbed liquid layer decreases while the area of the capillary liquid correspondingly increases. These differences can give rise to discrepancies between the retention data for polar stationary phases obtained with capillary and with packed columns.

V. EFFECT OF CHANGES IN EXPERIMENTAL CONDITIONS ON THE RETENTION VOLUME

Allowing for all possible sorption mechanisms we can write the following equation for real GLC situations (i.e. assuming normal analytical values of w_l):

$$V_N = \int_0^{V_{cl}} \left(\frac{\partial c_{cl}}{\partial c_g}\right) \mathrm{d}V_{cl} + \int_0^{V_{al}} \left(\frac{\partial c_{al}}{\partial c_g}\right) \mathrm{d}V_{al} + \\ + \int_0^{S_{sl}} \left(\frac{\partial q_{sl}}{\partial c_g'}\right) \mathrm{d}S_{sl} + \int_0^{S_{alg}} \left(\frac{\partial q_{alg}}{\partial c_g'}\right) \mathrm{d}S_{alg} + \int_0^{S_{clg}} \left(\frac{\partial q_{clg}}{\partial c_g'}\right) \mathrm{d}S_{clg},$$

where c_g is the volume concentration of sorbate in the gas phase, c_g' is the weight concentration of sorbate in the gas

phase (g ml^{-1}), c_l is the volume concentration of sorbate in the liquid, and q is the amount of adsorbed material (g cm^{-2}).

To a first approximation the terms of this equation can be evaluated separately as follows.

1) The distribution coefficient K_{cl} is the parameter which most directly determines the value of V_N: the smaller the activity coefficient, the greater is the contribution of solubility in the capillary liquid to V_N. If the system contains an average amount of stationary phase, and $\gamma \leq 1$, we can ignore adsorption effects on the retention volume (to a precision of 1%). This behaviour is observed in non-popar and weakly polar systems.

2) The distribution coefficient K_{al} has a substantial effect on V_N for low values of w_l. The contribution of this term to the relative retention quantities is small for $w_l > 10\%$.

3) The distribution coefficient K_{sl} can have a powerful influence on the retention, especially in systems consisting of a non-polar or weakly polar stationary phase and a polar sorbate. The numerical value of this distribution coefficient is significantly influenced by the size of the sample.

4) The distribution coefficients K_{alg} and K_{clg} can affect V_N when the stationary phase is polar and the sorbate is weakly polar or non-polar. These effects can be ignored (to a precision of 1%) for $\gamma < 5$ and normal values of w_l.

Since in a real chromatographic system the relative contributions of these sorption mechanisms depend on the experimental conditions it is interesting to consider the way in which the basic solubility characteristic (V_g) varies as w_l increases. As the stationary phase is first added to the carrier a film of adsorbed liquid is formed on the solid surface, but further additions of stationary phase cause a shrinkage of the *gl* interface due to the filling of capillaries and pores. The increased amount of capillary liquid on the carrier lowers the adsorption contributions to V_N: the combined result of all these effects is to lower V_g to ~10–15% as stationary phase is added to the carrier. Still further additions of stationary phase to the sorbent has practically no effect on the surface area of the *gl* interface, and the amount of adsorbed liquid also remains constant. Only the amount of capillary liquid on the carrier increases. Since the components of the mixture are more soluble in the capillary liquid than in the adsorbed layer, a small (~3–8%) increase in V_g is observed[25,121] as w_l increases beyond 15%, but V_g becomes independent of w_l when $w_l > 30\%$. As a result, reproducible inter-laboratory comparisons are obtained only with sorbents for which $w_l \cong 12$ to 15% (i.e. sorbents for which the dependence of V_g on w_l is a minimum).

There are various recommendations[18,122] on methods for obtaining invariant qualitative retention data by extrapolating plots of V_N/w_l against $1/w_l$ to $1/w_l = 0$ [see Eqn.(3)], and the K_l values obtained by this method are affected only by the solubility in the capillary liquid. However the method is laborious and the measurement of w_l has a low precision, and therefore the results are of doubtful value. Furthermore the non-linear dependence of V_g on w_l at fairly high values of w_l limits the validity of extrapolations from experimental data. However if we wish to identify the components of a complex mixture we are unlikely to achieve satisfactory separation over a wide range of w_l values. Therefore it is preferable to adopt a fixed value of w_l (~12–15%) in order to achieve reproducible measurements of retention data.

1. Size of Sample

The effect of sample size on V_N is usually caused by the non-linearity of the adsorption isotherm. The concentration of sorbate at the maximum of the chromatographic band c_g (in the gas phase) falls as the band travels along the column [Eqn.(49)]. The parameters of this equation are the effective diffusion coefficient D, the column length L, the velocity of the carrier gas u, and the sorption coefficient per unit length of column K' [123]:

$$c_g = \frac{q_s}{3.54K'\sqrt{DL/u}}. \qquad (4)$$

The steepest fall of c_g occurs near the inlet of the chromatographic column, where deviations from Henry's law can be expected; at large enough values of L the retention is affected more markedly by the curvature of the isotherm which describes the adsorption at the interface. Allowing for both dissolution and adsorption gives a complex picture of the dependence of V_g on L: as the column length is increased V_g initially decreases, before going through a shallow minimum. This minimum occurs at a column length of ~1 m, and therefore it is desirable to use columns with $L \geq 1$ m when the aim is identification of the components[48].

For a constant column length the variation of V_N with q_s also goes through an extremum, with a much sharper minimum in the region of mutual compensation of the dissolution and the adsorption isotherm, which creates an apparent independence of V_N on q_s.[48] This region can be very narrow (as in the alcohol–squalane system) or relatively broad (five orders of magnitude of q_s for the benzene–squalane system). For practical reasons it is preferable to measure retention data in the region of the minimum of the V_N–q_s relationship.

However in a real GLC apparatus it may be impossible (for a number of reasons) to measure retention data in the region of the minimum. This is the case, for example, in the analysis of trace impurities (especially, in the atmosphere) when the size of the sample is insufficient to bring the measurement to the region of the minimum and the retention volume is affected by the curvature of the adsorption isotherm. In these circumstances we can resort to one of the following procedures: a) measure V_N at a fixed value of q_s or at a fixed peak height h, or b) extrapolate V_N to infinite dilution of the solution. The latter variant implies adsorption and dissolution in the Henry's law region: it is very attractive, but in the majority of non-linear systems it has to be operated at the limit of sensitivity of the detector, with signals not much above noise level, and therefore it may be impossible in practice to work with sufficiently low sorbate vapour pressures. However for theoretical work the second variant is undoubtedly very important.

The first variant is by far the more important in practical work. In order to use it we must know the dependence of V_N on q_s or on h: the V_N values for fixed values of h or q_s are found by interpolation from experimental data. Retention data obtained at a fixed value of q_s lack physicochemical meaning, because (at different column temperatures) they correspond to different vapour pressures of sorbate and different degrees of column loading (or solution concentration), i.e. these data are neither isobaric nor isosteric[58]. Values referred to a fixed value of h are more useful, because they correspond to isobaric experimental conditions[45].

Various ways of obtaining invariant retention data in non-linear GLC have been proposed. One method[74] involves extrapolation of the concentration-dependent part of the dependence of V_N on q_s to infinite dilution. Thus it was shown experimentally[74] that the V_g values for n-propanol and diethylamine in heptadecane and dioctyl ether are identical for 10 and 15% concentrations of the stationary phase on the carrier when referred to infinitely dilute solutions. Other workers[124] allowed for adsorption effects by correcting the retention data extrapolated to infinite dilution for the amount of stationary phase in the column, as recommended in Ref.45.

Though the data were processed on a computer, there is some uncertainty in the extrapolation of the non-linear relationships, leading to an error of at least 1–1.5%. The method is laborious, and it gives a low precision in the measurement of w_l.

The measurement of retention data under isosteric conditions is described in Ref.45: the value of h at which V_N is measured is chosen by using the expression

$$h_j/h_0 = V_{Nj}/V_{N0} = V_{lj}/V_{l0}. \quad (5)$$

The measurements are made by using a set of columns [from zero to j, see subscripts in Eqn.(5)] containing different amounts of stationary phase. Since fairly high concentrations of solution are permitted, a significant proportion of the sorbate may be in the gas phase. We allow for this effect by introducing the concentration of sorbate in the gas phase (y) and the Martin compressibility factor (J). Isosteric solubility data are obtained by extrapolating the plot of $V_N/V_l(1-Jy)$ against $1/V_l$ to $1/V_l = 0$. The value of V_N at the given value of h is obtained from the trailing, diffuse edge of the peak, but this procedure causes substantial errors arising from the diffusion processes in the column. On the whole the method can be very useful in physicochemical research but it is difficult to exploit in practical analytical GLC.

Reproducible retention data in the adsorption region of the dependence of V_N on q_S (i.e. for sample sizes more typical of analytical GLC) can be obtained by using the equation[125,126]

$$V_N = A_3/\lg h + B, \quad (6)$$

where A_3 and B are constant. The region over which this equation is valid is limited to 2–5 orders of magnitude of h, but within this region we can evaluate V_N at any value of h by interpolation of plots of V_N against $1/\lg h$. Eqn.(6) was derived on the assumption that the interfacial adsorption in GLC (which makes the greatest contribution to adsorption at the sl boundary) is described by the Temkin isotherm equation: its validity has been demonstrated with a large number of systems, including a polar sorbate in a non-polar (or weakly polar) stationary phase.

Eqn.(6) can be used to obtain isobaric or isosteric retention data under given column operating conditions. For example, isobaric data could be obtained for $1/\lg h = 0.3$ (flame-ionisation detector; full-scale deflection 10^{-11} A; all values of h recalculated for this sensitivity and expressed in mm; specified column length, amount of stationary phase on the carrier, and velocity of carrier gas). In this way the experimental conditions can be standardised sufficiently to give reproducible retention data in different laboratories for non-linear GLC.

Isosteric retention quantities are often useful for calculating thermodynamic values: these can be calculated by inserting into Eqn.(5) the V_N values for given values of h obtained by interpolation from Eqn.(6).

2. Time-changes of the Sorption Properties of Columns

At high column temperatures the low-molecular fractions of the stationary phase can evaporate from the first parts of the column[21,127–130], causing a change in the selectivity of the column with time. Data on the separation of alcohols on a poly(ethylene glycol) column have shown[21] that the slope of the $\ln V_g - 1/T$ plot is not affected by evaporation of the stationary phase from the first part of the column, though the straight lines are shifted along the ordinate axis: this suggests a constant molar heat of sorption and a varying molar entropy of sorption, which is typical of an adsorbed liquid layer[48]. Thus the adsorbed layer has a greater temperature stability than the capillary layer, and initially only the capillary liquid evaporates from the first part of the column while the adsorbed layer remains on the carrier. The evaporation of some of the stationary phase from the first part of the column causes a local increase in concentration of the solution and a significant influence of interfacial adsorption on the retention data, which increases the dependence of V_N on q_S. This phenomenon sets a limit to the range of column temperatures consistent with reproducible retention results: the highest temperature at which a stationary phase is used should be 30–60 K below the usually recommended value. The use of large samples can also contribute to the loss of stationary phase from the first part of the column[130].

The time-changes in the properties of the column due to evaporation of the stationary phase are relatively slight. Far more serious obstacles to the acquisition of reproducible retention data arise from changes in the chemical composition of the stationary phase. Thus prolonged heating of squalane at 80 °C is found[131] to increase the concentration of lower hydrocarons from 6.1 to 14.7%: this effect is accompanied by changes in the relative retention volume of n-pentane, n-hexane, and benzene by 1.0, 2.5, and 1.5% respectively.

The most serious problems in the acheivement of reproducible retention data arise from the formation of polar compounds, which modify the surface of the carrier. These reactions usually occur at high temperatures in the presence of traces of oxygen (introduced by the carrier gas). Thus the passage of oxygen through a squalane column at 100 °C has been shown[132] to lower the retention index of polar compounds by more than 40 units, and similar effects have been observed in columns containing octadecanol. This behaviour is consistent with the formation of polar compounds as a result of the oxidation of squalane. The retention of polar (or readily polarisable) compounds is very sensitive to the concentration of impurities belonging to other classes in the squalane[133]: for example, in the presence of 0.1% of squalene the Kovats index for aromatic hydrocarbons is altered by 0.15 units.

Many commercial stationary phases consist of a mixture of polymers of different molecular weight (for example, polyglycols). The influence of molecular weight distribution on the selectivity of the stationary phase has been studied[134,135] in the poly(ethylene glycol) system (PEG). A comparison of three different PEG of average molecular weight 400 but prepared from individual PEGs taken in different proportions revealed an arithmetic mean deviation of the Kovats indices on these sorbents varying from 1.4 to 4 units. Alcohols are especially sensitive to changes in composition of the PEG, because of the change in the number of free hydroxyl groups in the stationary phase. However after prolonged operation at the highest permissible working temperatures, which cause partial evaporation of the lower fractions from the column, the spread of retention indices of PEG columns operated with different sorbents was only 0.4–0.8 units (i.e. of the same order as the experimental error).

The selectivity of the stationary phase is affected not only by the number of polar (active) functional end-groups per unit volume, but also by the molecular weight. The latter effect is observed also in stationary phases of the paraffin type, which do not contain functional groups[136–138]. It is stressed[136] that the polarity of the paraffin stationary phase increases with its molecular weight. These observations underline the importance of careful purification of the stationary phase when reproducible retention data are required, and the disadvantages of using stationary phases consisting of mixtures of polymers.

The water content of the sorbent can also influence the retention of polar compounds on non-polar stationary phases[81], and also of all classes of sorbate on polar stationary phases[134]. When non-polar stationary phases are used the *sl* interface is modified by the presence of water in the sense of decreasing the retention of polar compounds. Moisture in PEG produces a sharp fall in V_g for all sorbates, but the original properties of the sorbent can be recovered by drying.

The column history (i.e. its length of service, and the nature of the mixtures which have been analysed on the column) can have a significant effect on the retention properties, especially in columns with non-polar or weakly polar stationary phases. It has been pointed out[139] that in stainless steel capillary columns the retention index for hydrocarbons changes after prolonged operation, and adsorption effects increase at the same time. Thus after 1200 h operation of the column using Apiezon L the Kovats indices for cyclic and aromatic hydrocarbons increased by 2–3 units, an effect ascribed[139] to the catalytic activity of stainless steel towards the oxidation of Apiezon oil. No such effects were observed on glass capillaries.

After 3 years' operation between 50 and 70 °C with hydrocarbon mixtures the Kovats index for aromatic hydrocarbons of a stainless steel capillary column containing squalane changed by less than 0.1 unit[140], but when the same column was operated between 80 and 95 °C for several weeks the Kovats index for aromatic hydrocarbons rose by 0.2 units. The highest permissible operating temperature of stainless steel columns containing squalane can be inferred from these results. Operation of the same column for 6 years at temperatures between 86 and 130 °C produced a 10 unit change in the Kovats indices for aromatic hydrocarbons, and a 2 unit change in the indices for alkenes.

If polar stationary phases are used the retention data are unaffected by adsorption at the *sl* interface, but the role of adsorption at the *gl* interface becomes much more marked (depending on the concentration of impurities in the stationary phase, since these impurities become concentrated at interfaces). The impurity content can vary during the operation of the column: thus after three months' operation of a column containing acetyl tributyrate the relative retention of paraffins varied by 0.5%, whereas that of aromatic hydrocarbons (which are less sensitive to this type of adsorption) varied by only 0.1%.[140] On a highly polar stationary phase (1,2,3-*tris*-(2-cyanoethoxy)propane) at 94 °C the retention indices of aromatic hydrocarbons vary by 0.3 units per day as a result of differences in the adsorption of n-paraffins (introduced as standards) on the stationary phase[140].

Some interesting observations on the ageing of sorbents in packed columns have been reported[81]. After treatment of a squalane sorbent for 35 h at 110 °C in a stream of nitrogen the V_g value for n-propanol falls off sharply, and similar effects are observed after prolonged heating in vacuum or refluxing of the sorbent under hexane[141,142].

Thus the basic reason for the lack of reproducibility of retention data in analytical GLC is interfacial adsorption, coupled with the non-linearity of the isotherm describing this adsorption. We must stress that interfacial adsorption effects are most marked in systems consisting of molecules of different polarity, which form non-ideal solutions (with $\gamma > 5$). Under these conditions it is most important to choose and standardise the experimental conditions carefully in order to optimise the reproducibility of the retention data. In other types of system these requirements are less stringent unless the highest precision is required (errors of less than 0.1% in the relative retention and 0.05 units in the retention indices).

VI. METHODS OF PRESENTING RETENTION DATA FOR IDENTIFICATION

In this Section we shall discuss the "apparatus" errors in the measurement of retention parameters and we shall propose rational methods of calculating retention quantities for later use in inter-laboratory identifications and comparisons.

1. Specific Retention Volumes

Theoretically the parameter V_g is independent of the amount of stationary phase in the column, but it is influenced by variations in the velocity of the carrier gas and the temperature of the column. Both temperature fluctuations and temperature gradients can affect V_g. In commercial apparatus the temperature of the column thermostat is controlled to give fluctuations of less than 0.1 K and local temperature differences of less than 0.5 K along the column. In many of the currently available models the flow rate of the carrier gas is automatically controlled, but nevertheless some modifications to the gas control part of the apparatus are usually needed for the highest precision in the measurement of V_g.

The first high-precision chromatograph for the measurement of retention is described in Ref.143. Subsequently several papers on high-precision chromatography were published, with emphasis on achieving a constant flow rate of the carrier gas and a constant column temperature, and on accurate measurement of the main parameters of the chromatographic experiment. The most successful development was an apparatus with manual (semi-automatic) control[131], in which the input pressure was measured with a standard deviation of 0.24 mmHg, the output pressure with a standard deviation of 0.1 mmHg, and the column temperature to ±0.05 K. An *a-priori* calculation of the possible standard deviation s^0 in the measurement of V_g gave a value of 0.19%.

According to error theory, the overall error of the experiment is determined mainly by the two or three experimental parameters which introduce the largest errors. In the measurement of V_g the precision is limited by the error in w_l: in packed columns the standard deviation of this parameter is $s^0 = 0.16–0.32\%$, and in capillary column $s^0 = 0.24–0.42\%$.[131] An additional error in the measurement of V_g in capillary columns arises from the difficulty of measuring small gas-flow rates accurately.

We can measure w_l by weighing the sorbent before and after filling the column, and extracting the stationary phase from the sorbent after removing it from the column[131], but it is important to allow for the loss of stationary phase during activation of the column. The "burning off" and extraction of the stationary phase from the sorbent could be incomplete if some of the stationary phase becomes chemically bound to the surface of the carrier by the high-temperature activation[10]. The error of the measurement of w_l in the column determines the overall error of the measurement of V_g (0.15%), even if the chromatographic apparatus is ideal in all respects. These problems explain the large scatter of V_g values reported from different laboratories[144]. Thus we cannot recommend the use of V_g as a reliable criterion for identifying the components of a mixture from retention data.

2. Absolute Retention Volume

This parameter does not require measurement of w_l, and therefore its measurement error is lower than that of V_g. For qualitative analysis the parameter has a serious drawback: its dependence on w_l. Hence it cannot be recommended for

identification in GLC. However it is useful to analyse the sources of error in the determination of V_N, because they explain the shortcomings of various methods of measuring relative retention characteristics widely used in qualitative analysis.

The errors in the measurement of V_N with a soap-bubble gas flow-meter are discussed in detail in Ref.145. Before analysing these errors we should stress the requirement for high efficiency of the chromatographic column used to measure the retention data, since this parameter does not appear in the classical equations for calculating the errors of the measurement of V_N. The efficiency of the column affects the precision of the measurement of retention quantities through two parameters: a) it is essential to work with a sharp, narrow, steep-fronted peak in order to obtain an accurate measurement of the time of emergence of the peak from the column, and b) in the measurement of retention data for mixtures it is important to achieve separation of the components as early as possible in order to avoid mutual interactions. In order to locate the peak maximum with a precision of 0.1% the efficiency of the column should be at least 500 theoretical plates[145]. However it has been suggested[146] that a column efficiency an order higher is needed to achieve this level of precision, but the arguments used are not convincing.

When retention data are determined simultaneously for several components displacement effects and interactions between incompletely resolved bands are possible. The displacement effect consists in the replacement of the less strongly sorbed by the more strongly sorbed components, which decreases the retention time of the less strongly sorbed components. It has been shown[145] that in the case of two poorly resolved bands the appearance time of the first peak is shorter, and that of the second peak is longer, than the corresponding times for the pure components, but this phenomenon does not appear to involve the mutual solubility of the components[147]. In general the separation criterion should not be less than 3 to ensure that the mutual effect of the components on their measured retention is less than 0.1%.[145]

a) Measurement of the retention time of a non-sorbed gas (t_0). The method of measuring this quantity depends mainly on the type of detector used. With a katharometer it is convenient to measure t_0 by the appearance time of helium or other inert gas. However inorganic gases are not detected by a flame-ionisation detector, and therefore in this case it is convenient to use methane: at a column temperature of 100 °C the appearance times of air and methane are indistinguishable, but at lower temperatures the sorption of methane can cause a systematic error in the measurement of t_0.[148]

A more correct method of measuring t_0 with a flame-ionisation detector is to determine the retention time of helium against a background provided by the diffuse trailing edge of any other peak (vacancy chromatography method) at a high setting of the detector sensitivity, or by injecting a sample of helium into the column with nitrogen containing a trace of methane as the carrier gas (the function of the methane being to provide a steady base-line detector current[149]). A base-line detector current can also be produced by raising the column temperature until the vapour of the stationary phase or of its decomposition products appears at the column outlet. In every case the helium sample is detected as a negative peak.

Many of the recommended methods of calculating t_0 [150-153] rely on linear approximations of the retention data for n-paraffins. However a comparison[117] of calculated and experimental values of t_0 clearly shows the greater precision of the values obtained experimentally.

b) Measurement of the retention time of the component under study. The appearance time of the peak maximum of a component can be measured as the distance (on the chromatogram) between the sample injection and the appearance of the peak, or it can be measured directly with a stop-watch. If the former method is used the measurement error can be considerable[154]: a 2 s error in the sample injection marker, a 30 s error due to variations in chart speed, an additional error of 2% due to the effect of mains frequency fluctuations on the chart speed, and a 10 s error in locating the peak maximum. It is usually easier to measure the retention time with a stop-watch, when the error is less than 0.02% for retention times of >10 min. In this method the overall error is at least four times smaller than in the determination of retention times from measurements of length on the chromatogram[155]. However the latter method is convenient because it does not require the presence of the experimenter at the appearance time of the peak: it is often used, therefore, in approximate measurements.

Electronic chronometers offer a high precision for the measurement of the appearance time of individual peaks, but this precision cannot be exploited to the full because of the limitations of the experimenter's reaction times (0.1–0.3 s). By using a computer to detect the injection of the sample and to measure the appearance time of the peak we can reduce the error of the measurement of retention time 5–7-fold in the case of a non-polar stationary phase, but if the sorbent is coated with a polar stationary phase the precision is not significantly improved by using a computer[94].

The absolute error of the measurement of retention time is proportional to the retention time, and for very long retention times the relative error of the measurement is constant[156].

In addition to the errors associated with the measurement of retention time, which can be minimised, we need to consider errors in the determination of retention time arising from instability of the experimental parameters. These errors are mainly responsible for the overall experimental error of measured retention times[157-167].

Stable conditions for the measurement of retention times are most easily obtained by using a computer-controlled chromatograph, especially in the separation of complex mixtures of many components[22,160-164]. Conventional electronic proportional temperature controllers can stabilise the temperature of the column thermostat to within 0.05 K, and this uncertainty can be lowered to 0.02 K by using computer control[165,166]. The fluctuations in the flow rate of the carrier gas can be less than 0.1 ml min^{-1} with computer control. Some workers recommend the use of liquid-filled thermostats[167], which offer a temperature stability ranging from 0.0025 to 0.01 K, but these thermostats also have a number of shortcomings (corrosion of the apparatus, high thermal inertia, and large temperature gradients along the column). Air thermostats can give temperature differences as low as 0.02 K in the vertical direction and 0.2 K in the radial direction[168].

The use of computer control of the operating parameters of the column can greatly reduce the lack of reproducibility of the experimental conditions but it cannot eliminate it completely. Therefore allowance for the residual fluctuations of the experimental parameters, and appropriate corrections to the measured quantities, are as important as control[163,169,170]. All the experimental parameters were measured at intervals varying from 0.05 s to several seconds and the retention volume was obtained as the sum of micro-elementary volumes corresponding to the measured column temperatures and carrier gas flow rates[171]. The detectors were thermo-anemometers, manometers, and resistance thermometers: for a column temperature stability of 0.01 K and a pressure measurement precision of 0.05 mmHg the standard deviation of

the measurement of retention volume of n-heptane in octadecane at 60 °C was 0.43% with manual processing of the data and 0.02% with computer processing[171].

Thus by using commercial apparatus with appropriate modifications to the gas handling system the standard deviation of the measurement of V_N is 0.1–0.2%: an order of magnitude improvement in precision is possible by using computer control and data processing methods.

3. Relative Retention Volume

This parameter was first proposed for the identification of components in 1952 [172]: its value is independent of the amount of stationary phase (if interfacial adsorption is negligible), but it is affected by changes in the flow rate of the carrier gas and by changes in column temperature.

The precision of the measurement of relative retention volume (r) can be raised by correctly choosing the reference standard. With high-grade apparatus the method of introducing the standard does not affect the error of the measurement of r: it can be introduced with the components of the mixture to be analysed, or after each analysis, or even after several analyses[156]. A 20–50% improvement in precision in the measurement of r by introducing the standard as part of the unknown mixture (rather than separately) has been reported[139]. However adding the standard as part of the mixture is legitimate only when the peak of the standard is completely resolved from those of the unknown components, and therefore the retention times of the components are unaffected by the presence of the standard. The best compromise is to add the standard to the column once every 2–4 h, depending on the stability of the control of experimental conditions.

The standard substance should appear at the outlet of the column in 5–15 min, its adsorption at the interfaces should be negligibly small, and it should be readily available. For these reasons aromatic hydrocarbons are often used as standards, since their adsorption at the *sl* and *gl* interfaces makes a negligible contribution to V_N, and the compounds are easily obtained. For example, at low temperatures (up to 100 °C) benzene can be used as a standard, naphthalene at temperatures up to 200 °C, and anthracene or phenanthrene at still higher temperatures.

In general r can be measured with any arbitrarily chosen standard, but if the results are to be published and used in other laboratories for qualitative analysis they should be recalculated on the basis of one of the above standards. This involves determining the r value of the arbitrary standard with respect to one of the aromatic hydrocarbons. In the R_{x9} system of r values with a single standard[101,173,174] n-nonane is used as the standard compound: the reproducibility of the measurement of retention indices in this system is given as 10. An important disadvantage of the use of a n-paraffin as the standard is the large contribution to V_N from adsorption at the surface of the stationary phase when polar liquids are used.

In the early experiments[175] the error in the measurement of r was 0.5%, but the use of computers has lowered this error to 0.02% [168,176–180]. With manual processing of the data the error of the measurement of r in glass capillary columns was 0.16–0.19% for OV-17 silicone oil, 0.26–0.28% for Carbowax 20M, and 0.38–0.55% for SF-96 silicone oil[181]; the increase in error caused by the last two stationary phases is probably due to poor wetting of the capillary surface by the liquid and hence to adsorption at the glass–gas interface[182]. In stainless steel capillary columns the error in the measurement of r is slightly higher[183].

4. Systems of Retention Indices

A detailed mathematical analysis of the errors in the calculation of retention indices has been published[156,184–186]. The first report of high reproducibility in the measurement of retention indices was made in 1970 [187], and it was shown that the error in the measurement of retention indices can be decreased by an order of magnitude by using a computer. The conditions for precise measurement of the retention indices are formulated in Refs. 131, 188, and 189, and an error of 0.03 units was claimed[94]. Sojak and Rijks[140] describe the conditions which allow the retention indices of hydrocarbons on squalane to be measured with an error of 0.02 units. Attempts to calculate retention from the centre of gravity rather than from the apex of the peak[190,191] failed to reduce the error below 0.05 units.

The reliability of the determination of retention indices on capillary columns is discussed in detail in Ref. 140. Changes in the input pressure of the carrier gas from 2.5 to 4 atm produced changes of 0.08–0.13 units in the retention indices of hydrocarbons when hydrogen was used as the carrier gas, whereas with nitrogen as the carrier gas the retention indices varied by 0.27–0.33 units when the pressure at the column inlet was varied from 1 to 4 atm. Within the limits of experimental error (0.05 units is the retention index) there was no effect from changes in helium pressure. The response to changes in carrier gas pressure increases in the sequence paraffins < alkenes < cycloparaffins < aromatic hydrocarbons[140].

In Kovats' conventional system of retention indices the standard components are n-paraffins, for which the retention data on polar stationary phases are strongly affected by interfacial adsorption (leading to poor reproducibility). It was pointed out[119] that the error in the calculation of the retention indices increases with the polarity of the stationary phase. According to Bonastre and coworkers[118] a change from 10 to 30% in the w_l value of Carbowax 20M on a sorbent increases the retention indices from 14 to 22 units because of the decreased retention of n-paraffins. In order to overcome this difficulty the use of a homologous series of n-alcohols as standards is proposed[192] when polar stationary phases are used. This suggestion is not incompatible with the concept of a system of retention indices, based on the assumption of direct proportionality between $\lg V_N$ and C (where C is the number of carbon atoms in the molecule) for a homologous series[193,194].

The desirability of choosing polar standard substances when polar stationary phases are used has been stressed by many workers[122,133,195–203], with a tendency to use as standard the homologous series whose members are being studied. However there are objections to the use of a homologous series as standard on polar sorbents, because interfacial adsorption increases sharply with the length of the alkyl radical and this lowers the reliability of the results. Another important shortcoming of the retention index system is the assumed linear dependence of $\lg V_N$ on C, which does not apply in a number of systems[193,204–206]. Deviations from linearity arise from the parity rule[206], and from the interaction of methyl groups[207], which led to the principle of non-calculability of the indices (according to which the linear dependence of $\lg V_N$ on C is only approximate, with a confidence interval of two units). When the molecules of the stationary phase contain aromatic rings the relationship is no longer linear[204].

The consistency of retention indices obtained in different laboratories has been analysed in several papers. The error in the measurement of the retention index from data reported by different laboratories is stated[140] to be 0.2 unit, but we should note that recalculation of the quoted results[140] gives

an error varying from 0.6 to 1.5 unit. The discrepancies between retention indices obtained in different laboratories may be due to effects from the material of the capillary column or to changes in composition or in concentration of the stationary phase during operation of the column. Thus it has been shown[208] that after high-temperature activation of a non-polar capillary column the retention index of aromatic hydrocarbons varies by 8 units. Standardisation of the capillary surface is said[94] to lower inter-laboratory discrepancies (to 0.2 unit of index). The work of Schomburg (quoted in Ref.155) has shown that if the capillary columns are prepared in one laboratory and distributed to other laboratories the discrepancy between the results is less than 0.05 unit, whereas if the columns are prepared in the different laboratories the reproducibility falls to 1 unit.

A careful comparison of the retention data for n-paraffins on squalane obtained in different laboratories under a satisfactorily controlled experimental conditions is given in Ref.209: the error varies from 0.09 to 0.28 unit whereas the reproducibility within each laboratory is 0.025 unit. For an internal reproducibility of 0.2 unit[19,95] an inter-laboratory comparison gave a discrepancy of 1 unit[95,205-213]. Hence the consistency of the retention quantities between laboratories is 4–5 times worse, on average, than the measurement error within one laboratory, though we should note that all these results apply to systems in which the retention of the components is almost unaffected by adsorption effects. When the influence of interfacial adsorption is not negligible the above recommendations for achieving reproducible retention data must be strictly observed.

In conclusion we shall briefly dwell on some systems of retention indices which have been developed to remedy the shortcomings of the Kovats system. In view of the non-linearity of the dependence of $\lg V_N$ or C Matukuma[214] proposed a new form of index in which three successive homologues of the n-paraffin series are used as standards:

$$I_w = 100C + \frac{\lg(1 + i/a - i/b)}{\lg(b/a)} 100,$$

where $i = t_{Nx} - t_{Nc}$, $a = t_{Nc} - t_{N(c-1)}$, $b = t_{N(c+1)} - t_{Nc}$, t_{Nx} is the appearance time of the unknown component, and t_{Nc}, $t_{N(c+1)}$, $t_{N(c-1)}$ are the appearance times of the n-paraffins with the same number of carbon atoms as the unknown, one carbon atom fewer, and one carbon atom more respectively. Though this system of indices yields more accurate results it suffers from a loss of generality in comparison with the Kovats system.

The arithmetical indices proposed by Vigdergauz[215] are the simplest form of indices:

$$I_a = \frac{t_{Rx} - t_{Rc}}{t_{R(c+1)} - t_{Rc}},$$

where t_R are the appearance times of the components uncorrected for the dead volume of the column (the unknown components and the n-paraffins with the same number of carbon atoms). Expressions relating the arithmetic indices to the Kovats indices have been obtained[216-218], and some applications of the arithmetic indices have been described[219,220]. Though the calculation of the arithmetic indices is extremely simple the indices are not particularly useful because they contain no physicochemical information and they lack the generality of the Kovats indices for identification.

The differences between different systems of retention indices are not fundamental in principle, and the choice of a particular type of index is usually dictated by tradition or by convenience. Evidently, the Kovats index was historically the first and it will continue to be widely used in analytical practice.

5. Comparison of Different Methods of Presenting Retention Data

The basic characteristics of the four most widely used retention parameters are compared in the Table. The specific retention volume V_g has some important advantages over the other parameters because it contains physicochemical information, but it cannot be recommended as an identification parameter because the precision of its measurement is low.

The relative retention volume r and the Kovats index I are similar in many ways, and the choice between them is often a matter of convenience or tradition. The parameter I lends itself particularly well to calculations by the additivity principle: any n-paraffin with an appearance time comparable to that of the unknown component can be used as standard for the calculation of this parameter. However with polar stationary phases we must use homologous series of polar compounds as standards, and even this procedure does not exclude interfacial adsorption effects on the retention parameters of the standards. Another shortcoming of the Kovats indices is the need to assume a linear dependence of $\lg V_N$ on C, which is often not appropriate. Furthermore the error in the measurement of I is almost twice as great as the error in the measurement of r.

Characteristics of the retention parameters.

Parameter	Reproducibility, %		Advantages	Disadvantages
	within laboratory	between laboratories		
Specific retention volume V_g	0.2	4.5	A thermodynamic parameter, describing the gas–liquid equilibrium; can be used to calculate all the thermodynamic characteristics of the phase equilibrium; independent of the amount of stationary phase in the column	Laborious measurement of the amount of stationary phase in the column, and associated errors
Net retention volume V_N	0.1 (0.02)	–	–	**
Relative retention volume r	0.1 (0.02)	0.8	Simple to calculate, consistent with the order of appearance of the peaks, few parameters to be measured. No assumptions needed	The need to recalculate the results to a single standard from secondary standards
Kovats index I	0.2 (0.05)	2.3	Rational presentation of the results as a sum of increments associated with the atomic groups in the sorbate molecule; any member of the homologous series can be used as standard	The need to postulate linearity of the logarithm of the retention volume as a function of number of carbon atoms in the molecule for members of a homologous series; the need to use at least two standards

*The errors obtained in computer-controlled experiments are shown in brackets.

**Not recommended for identification, not reproducible between laboratories.

Though the equivalence of I and r as identification parameters has been convincingly demonstrated[184] the r values are more convenient to use because they are simpler. They are also more accurate because no assumptions are made in their derivation. Since the choice between I and r does not raise

any fundamental questions, it is desirable to standardise on one of these quantities: the choice of r (with aromatic hydrocarbons as standards) appears to be the best overall approach to a standard identification procedure in GLC.

Because of the complexity of sorption processes in chromatographic columns the following experimental parameters should be stated in publications to ensure reproducibility of the retention data in other laboratories: 1) the column temperature (to the nearest 0.1 K), 2) a full description of the stationary phase (purity, origin, amount of liquid phase on the carrier, details of the activation process), 3) a full description of the carrier, 4) length, diameter, and material of the column, and (in the case of capillary columns) pretreatment conditions, 5) size of injected sample and dependence of the appearance time on sample size, 6) method of measuring the dead time of the system, 7) nature, input pressure, and flow rate of the carrier gas, 8) sensitivity of the detector and chart recorder, 9) type and model of the chromatograph, 10) errors in the determination of retention data.

It is also desirable to state the operating life of the column, and to point out any changes in retention behaviour observed after lengthy operation of the column, as well as the role of adsorption effects. Lastly, the results being reported should be compared with published data if possible.

6. Choice of Parameters for Identification in GLC

Reliable identification of a component requires the coincidence of two independent retention parameters for the unkown peak and for the peak of the standard. We shall discuss two variants of the method of identification from retention data, though non-retention methods (spectral, chemical, etc.) are also widely used.

a) Chromatographic spectra. Coincidence of the retention parameters for the unknown and the standard component on two or three different stationary phases is a good criterion of identify of the substances being compared. Stationary phases of very different polarity and chemical nature are often used for comparison. The following can be recommended for identifications: squalane (up to 100 °C), the C_{87} hydrocarbon[221] (up to 250 °C), oxydipropionitrile (up to 80 °C), *hexakis*(2-cyanoethoxy)hexane (up to 180 °C), polyphenyl ether from 6 rings (up to 250 °C).

The separation of not very complex mixtures on two or three columns with different stationary phases yields "chromatographic spectra" which can be used to identify the components[222-228]. Analogous to the chromatographic spectrum is the parameter ΔI, calculated as the difference between the Kovats indices for the unknown component on two stationary phases. Both these methods are useful for the identification of the components in mixtures of 5–10 substances present at different concentrations. The main difficulty in identification from chromatographic spectra is the "recognition" of the peaks of a particular component when the mixture is separated on different columns, since the peaks appear in different order at the column outlet and they can only be recognised by their relative height. Another drawback of the chromatographic spectra is the difficulty of obtaining an acceptably complete resolution of all the peaks for a complex mixture on a number of stationary phases. Often only one stationary phase is available for identifying the components of a complex mixture. In this case we need another independent parameter determined on the same stationary phase—the temperature dependence of the retention quantities—in addition to the indices r or ΔI for reliable identification.

b) Temperature dependence of the relative retention volume and of the Kovats index. These temperature dependences are determined directly by the enthalpic selectivity of the stationary phase (the relative molar heat of dissolution ΔH_S°, whose value can be calculated relatively simply by using the additivity principle). The quantity ΔH_S° can be used directly for identification[229,230], because it is much less sensitive to experimental conditions (such as interfacial adsorption) than the parameter r. It can be evaluated very simply from experimental data by using the expression

$$\Delta H_s^0 = \frac{4.58\,(\lg r_1 - \lg r_2)}{1/T_1 - 1/T_2},$$

where the subscripts 1 and 2 refer to different column temperatures.

The temperature dependence of the retention can be described also by indirect parameters (e.g. the constants of an equation of the Antoine type[231,232]) or by the temperature dependence of the Kovats index δI. The latter type of dependence is widely used to identify substances of different classes[24,233-243,209-212], but we should note that δI can vary with temperature as a result of non-linearity of the relationship between I and the column temperature, and this effect must be allowed for when δI is used for identification. Since neither the constants of the Antoine equation nor δI contain as much physicochemical information as ΔH_S° we recommend the two quantities r and ΔH_S° as the basic independent parameters to be used for identification.

REFERENCES

1. A.T.James and A.J.P.Martin, Biochem.J., **50**, 679 (1952).
2. E.R.Adlard, M.A.Khan, and B.T.Whitham, in "Gas Chromatography 1960", (R.P.W.Scott, Editor), Butterworth, London, 1960, p.251.
3. W.O.McReynolds, "Gas Chromatographic Retention Data", Preston Technical Abstracts, 1966.
4. E.R.Adlard, M.B.Evans, A.G.Butlin, A.B.Littlewood, and W.T.Swarton, in "Gas Chromatography 1964", (A.Goldup, Editor), Elsevier, Amsterdam, 1965, p.348.
5. D.Ambrose, A.J.M.Keulemans, and J.H.Purnell, Analyt.Chem., **30**, 1582 (1958).
6. H.W.Johnson and F.H.Stross, Analyt.Chem., **30**, 1586 (1958).
7. S.G.Perry, Chromatogr.Rev., **9**, 1 (1967).
8. V.G.Berezkin, Symposium "Uspekhi Khromatografii" (Advances in Chromatography), Izd.Nauka, Moscow, 1972, p.213.
9. J.C.Giddings, Analyt.Chem., **34**, 458 (1962).
10. W.A.Aue, C.R.Hastings, and K.O.Gerhardt, J. Chromatogr., **77**, 299 (1973).
11. M.B.Evans, Chromatographia, **4**, 441 (1971).
12. C.R.Hastings and W.A.Aue, J.Chromatogr., **89**, 379 (1974).
13. J.H.Purnell, in "Gas Chromatography 1962" (M.van Swaay, Editor), Butterworth, London, 1962, p.13.
14. A.F.Williams, in "Gas Chromatography 1960" (R.P.W. Scott, Editor), Butterworth, London, 1960, p.210.
15. V.G.Berezkin, C.Eon, and G.Guiochon, Bull.Soc. chim.France, 94 (1975).
16. J.C.Giddings, Analyt.Chem., **35**, 440 (1963).
17. M.R.Burnett, Analyt.Chem., **35**, 1567 (1963).
18. J.R.Conder and J.H.Purnell, Trans.Faraday Soc., **65**, 839 (1969).
19. A.J.B.Cruickshank, M.L.Windsor, and C.L.Young, Proc.Roy.Soc., **A295**, 271 (1966).

20. G.V.Filonenko and A.N.Korol, J.Chromatogr., **119**, 157 (1976).
21. R.A.Keller and G.H.Stewart, J.Chromatogr., **9**, 1 (1962).
22. J.W.McBain, "Colloid Science", Heath, Boston, 1950, ch.4.
23. B.M.Craig, in "Gas Chromatography" (N.Brenner, J.E.Callen, and M.D.Weiss, Editors), Academic Press, New York, 1962, p.37.
24. B.V.Deryagin and V.V.Karassev in "Proceedings of the Second International Congress on Surface Activity", Vol.3, Academic Press, New York, 1957, p.531.
25. A.N.Korol, J.Chromatogr., **67**, 213 (1972).
26. L.B.Rogers and J.C.Spitzer, Analyt.Chem., **33**, 1959 (1961).
27. W.D.Harris and G.Jura, J.Amer.Chem.Soc., **66**, 919 (1944).
28. S.J.Hawkers and J.C.Giddings, Analyt.Chem., **36**, 2229 (1969).
29. A.N.Korol', "Nepodvizhnaya Faza v Gazo-zhidkostnoi Khromatografii" (The Stationary Phase in Gas–Liquid Chromatography), Izd.Naukova Dumka, Kiev, 1969.
30. R.Condon, Analyt.Chem., **31**, 1717 (1959).
31. M.E.Goley, in "Gas Chromatography" (D.H.Desty, Editor), Butterworth, London, 1958, p.38.
32. J.H.Clint, J.F.Goodman, and J.R.Tate, Nature, **233**, 51 (1969).
33. D.H.Everett and G.H.Findenberg, Nature, **223**, 52 (1969).
34. S.G.Ash and G.H.Findenberg, Spec.Discuss.Faraday Soc., 1, 105 (1970).
35. J.Serpinet and J.Robin, Compt.rend., **272**, 1765 (1971).
36. J.Serpinet, J.Chromatogr., **68**, 9 (1972).
37. J.Serpinet, J.Chromatogr., 77, 289 (1973).
38. G.Unitz and J.Serpinet, J.Chim.phys., **73**, 912 (1976).
39. J.Serpinet, Chromatographia, **8**, 18 (1975).
40. C.Daneyrolle, J.Serpinet, M.Troccaz, and C.Eyrand, Compt.rend., **C276**, 129 (1973).
41. J.Serpinet, Analyt.Chem., **48**, 2264 (1976).
42. J.R.Conder, in "Progress in Gas Chromatography" (J.H.Purnell, Editor), Wiley, New York, p.209.
43. A.J.Cruickshank and D.H.Everett, J.Chromatogr., 11, 289 (1963).
44. G.F.Freeguard and R.Stock, in "Gas Chromatography 1962" (M.van Swaay, Editor), Butterworth, London, 1962, p.102.
45. J.R.Conder, J.Chromatogr., **39**, 273 (1969).
46. P.E.Porter, C.H.Deal, and F.H.Stross, J.Amer. Chem.Soc., **78**, 2999 (1956).
47. N.R.Krichevskii, "Fazovye Ravnovesiya v Rastvorakh Pri Povyshennykh Davleniyakh" (Phase Equilibria in Solutions at High Pressures), Goskhimizdat, Moscow, 1952.
48. G.V.Filonenko, T.I.Dovbush, and A.N.Korol, Chromatographia, **7**, 293 (1974).
49. R.S.Henly, A.Rose, and R.F.Sweeny, Analyt.Chem., 36, 744 (1964).
50. A.N.Korol', Ukrain.Khim.Zhur., **32**, 329 (1966).
51. M.B.Evans, J.Gas Chromatogr., **4**, 1 (1966).
52. T.R.Mon, R.R.Forrey, and R.Teranishi, J.Gas Chromatogr., **4**, 176 (1966).
53. R.I.Sidorov and Yu.A.Batyrev, Zhur.Fiz.Khim., **27**, 1428 (1972)[Russ.J.Inorg.Chem., No.5 (1972)].
54. R.A.Keller and G.H.Stewart, Analyt.Chem., **34**, 1834 (1962).
55. V.G.Berezkin, V.P.Pakhomov, L.L.Starobinets, and L.G.Berezkina, Neftekhimiya, **5**, 438 (1965).
56. V.G.Berezkin, V.P.Pakhomov, and L.G.Berezkina, Symposium "Gazovaya Khromatografiya" (Gas Chromatography), Izd.Dzerzh.Filiala OKBA MKhP, Dzerzhinsk, 1966, p.267.
57. V.G.Berezkin, N.S.Nikitina, and V.M.Fatseva, Zhur.Anal.Khim., **25**, 2023 (1970).
58. J.R.Conder, D.C.Locke, and J.H.Purnell, J.Phys. Chem., **73**, 700 (1969).
59. C.Eon, A.K.Chatterjee, and B.L.Karger, Chromatographia, **5**, 28 (1972).
60. B.G.Berezkin, V.P.Pakhomov, V.S.Tatarinskii, and V.M.Fateeva, Dokl.Akad.Nauk SSSR, **180**, 1135 (1968).
61. M.B.Evans and J.F.Smith, J.Chromatogr., **30**, 325 (1967).
62. V.G.Berezkin, V.S.Gavrichev, and G.P.Zorina, Izv. Akad.Nauk SSSR, Ser.Khim., 1975 (1972).
63. V.G.Belen'kii, A.G.Vitenberg, and I.A.D'yakonov, Izv.Akad.Nauk SSSR, Ser.Khim., 193 (1964).
64. T.Fucuda, Japan Analyst, **8**, 627 (1959).
65. R.G.Scholtz and W.W.Brandt, in "Gas Chromatography" (N.Brenner, J.E.Callen, and M.D.Weiss, Editors), Academic Press, New York, 1962, p.7.
66. F.Wolf and A.Losse, J.Chromatogr., **39**. 475 (1969).
67. E.Grushka and T.A.Goodwin, Chromatographia, **10**, 549 (1977).
68. J.J.Kirkland, Analyt.Chem., **35**, 2003 (1963).
69. C.Landault and C.Guichon, J.Chromatogr., **9**, 133 (1962).
70. D.M.Ottenstein, J.Gas Chromatogr., 1, 11 (1963); 11, 136 (1973).
71. W.Jequier and J.Robin, Chromatographia, **1**, 297 (1968).
72. D.P.Graham, J.Phys.Chem., **69**, 4387 (1965).
73. J.R.Conder, Analyt.Chem., **43**, 367 (1971).
74. D.E.Martire and P.Riedl, J.Phys.Chem., **72**, 3478 (1968).
75. L.J.Lorenz and L.B.Rogers, Analyt.Chem., **43**, 1593 (1971).
76. J.Lenoir and A.Rojev, Separ.Sci., **5**, 545 (1970).
77. C.H.Bosanquet and G.O.Morgan in "Gas Chromatography" (R.P.W.Scott, Editor), Butterworth, London, 1959, p.107.
78. R.P.W.Scott, Analyt.Chem., **35**, 481 (1963); **36**, 1455 (1964).
79. P.Urone and J.P.Parcher, Analyt.Chem., **38**, 270 (1966).
80. P.Urone, J.F.Parcher and E.N.Baylor, Separ.Sci., 1, 595 (1966).
81. J.Conder, J.Chromatogr., **39**, 273 (1967).
82. P.Urone, Y.Takahashi, and G.H.Kennedy, J.Phys. Chem., **74**, 2326 (1970).
83. A.T.James and A.J.P.Martin, Biochem.J., **52**, 238 (1952).
84. T.Onaka and T.Okamoto, Chem.Pharm.Bull.Japan, **10**, 757 (1962).
85. E.C.Ormerod and R.P.W.Scott, J.Chromatogr., 2, 65 (1959).
86. V.G.Belen'kii, A.G.Vitenberg, L.D.Turkova, and N.N.Chernyshkov, Izv.Akad.Nauk SSSR, Ser.Khim., 269 (1967).
87. E.C.Horning, E.A.Moscatelli, and C.C.Sweeley, Chem.Ind.(London) 751 (1959).
88. G.A.Howard and A.J.P.Martin, Biochem.J., **46**, 532 (1950).

89. W.A.Aue and D.R.Younker, J.Chromatogr., **88**, 7 (1974).
90. W.Averill, in "Gas Chromatography" (N.Brenner, J.E.Callen, and M.D.Weiss, Editors), Academic Press, New York, 1962, p.1.
91. T.Johns, in "Gas Chromatography" (V.J.Coats, N.J.Noebels, and J.S.Fagerston, Editors). Academic Press, New York, 1958, p.31.
92. B.A.Knights, J.Gas Chromatogr., **2**, 338 (1964).
93. I.A.Raiks, I.A.Leiten, K.A.Kramers, and V.G.Berezkin, Zhur.Anal.Khim., **29**, 858 (1974).
94. J.A.Rijks and C.A.Cramers, Chromatographia, **7**, 99 (1974).
95. G.Schomburg, Chromatographia, **4**, 286 (1971).
96. J.J.Franken and M.M.Trijbels, J.Chromatogr., **91**, 425 (1974).
97. M.L.Hair and W.Hertl, J.Phys.Chem., **77**, 1965 (1973).
98. L.Blomberg and G.Widmark, J.Chromatogr., **106**, 59 (1975).
99. K.Grob, Chromatographia, 7, 94 (1974).
100. K.Grob, Helv.Chim.Acta, **51**, 718 (1968).
101. J.F.Smith, Chem.Ind.(London) 1024 (1960).
102. Th.Welsch, W.Engewald, and Ch.Klaucke, Chromatographia, **10**, 22 (1977).
103. C.Watanabe and H.Tamita, J.Chromatogr., **13**, 123 (1975).
104. L.B.Blomberg, J.Chromatogr., **115**, 365 (1975).
105. D.A.Cronin, J.Chromatogr., **97**, 263 (1974).
106. K.Tesařik and N.Novotny, in "Gas Chromatographie 1968" (H.G.Struppe, Editor), Acad.Verlag, Berlin, 1968, p.575.
107. R.L.Martin, Analyt.Chem., **33**, 347 (1961).
108. D.E.Martire, R.L.Pecsok, and J.H.Purnell, Trans. Faraday Soc., **61**, 2496 (1965).
109. D.E.Martire, R.L.Pecsok, and J.H.urnell, Nature, **203**, 1279 (1964).
110. P.Urone and J.F.Parcher, in "Advances in Chromatography" (J.C.Giddings and R.A.Keller, Editors), Marcel Dekker, New York, 1968, p.298.
111. J.F.Huber and R.G.Gerritse, J.Chromatogr., **80**, 25 (1973).
112. D.E.Martire, Analyt.Chem., **38**, 244 (1966).
113. D.F.Cadogan, J.R.Conder, D.C.Locke, and J.H.Purnell, J.Phys.Chem., **73**, 708 (1969).
114. J.C.Loewenguth and D.A.Tourres, Z.anal.Chem., **236**, 170 (1968).
115. R.L.Pecsok and B.H.Gump, J.Phys.Chem., **71**, 2202 (1967).
116. Z.Suprynowicz, A.Waksmundzki, and W.Rudzinski, J.Chromatogr., **67**, 2 (1972).
117. M.Heintz, A.Druilhe, J.Gregoir, and D.Lefort, Meth.Phys.Anal., **5**, 370 (1969).
118. J.Bonastre, P.Grenier, and P.Cazenave, Bull.Soc. chim.France, 1270 (1968).
119. L.V.Semenchenko and L.T.Lantsova, Zhur.Anal. Khim., **29**, 1663 (1974).
120. D.E.Martire and L.Z.Pollara, in "Advances in Chromatography" (J.C.Giddings and R.A.Keller, Editors), Marcel Dekker, New York, 1966, p.335.
121. R.Fontaine, C.Pommier, C.Eon, and G.Guichon, J.Chromatogr., **104**, 1 (1975).
122. V.G.Berezkin, J.Chromatogr., **98**, 477 (1974).
123. A.A.Zhukhovitskii and N.M.Turkel'taub, "Grazovaya Khromatografiya" (Gas Chromatography), Gostoptekhizdat, Moscow, 1962.
124. H.L.Liao and D.E.Martire, Analyt.Chem., **44**, 498 (1972).
125. L.S.Lysyuk, G.V.Filonenko, and A.N.Korol', Teor. Eksper.Khim., **12**, 796 (1976).
126. L.S.Lysyuk and A.N.Korol, Chromatographia, **10**, 712 (1977).
127. R.A.Keller, R.Bate, B.Costa, and P.Forman, J. Chromatogr., **8**, 157 (1962).
128. M.O.Burova, M.Kh.Lunskii, and A.A.Zhukhovitskii, Zavod.Lab., **39**, 1194 (1973).
129. G.P.Hildebrand and C.N.Reiley, Analyt.Chem., **36**, 47 (1964).
130. M.Kh.Lunskii and A.F.Shlyakov, Zavod.Lab., **42**, 1174 (1976).
131. A.Wicarova, J.Novak, and J.Janak, J.Chromatogr., **51**, 3 (1970).
132. M.B.Evans and J.F.Smith, J.Chromatogr., **28**, 277 (1967).
133. A.Grobler, J.Chromatogr.Sci., **10**, 128 (1972).
134. M.B.Evans and J.F.Smith, J.Chromatogr., **36**, 489 (1968).
135. M.B.Evans and J.F.Smith, J.Chromatogr., **6**, 293 (1961).
136. G.A.Huber and E.sz.Kovats, Analyt.Chem., **45**, 1155 (1973).
137. D.F.Fritz and E.sz.Kovats, Analyt.Chem., **45**, 1175 (1973).
138. D.E.Martire, Analyt.Chem., 46, 626 (1974).
139. X.Guardino, J.Albages, G.Firpo, R.Rodriguez-Vinals, and M.Gassiot, J.Chromatogr., **118**, 13 (1976).
140. L.Sojak and A.Rijks, J.Chromatogr., **119**, 505 (1976).
141. A.A.Zhukhovitzki, M.L.Sazonov, M.Kh.Lunski, and V.Yusfin, J.Chromatogr., **58**, 87 (1971).
142. A.A.Zhukhovitskii, M.L.Sazonov, M.Kh.Lunskii, and A.F.Vyatkin, Zhur.Anal.Khim., **27**, 748 (1972).
143. E.Sz.Kovats, E.Kugler, and P.Toth, Helv.Chim. Acta, **42**, 2519 (1959).
144. E.C.Pease and S.Thornburn, J.Chromatogr., **30**, 344 (1967).
145. F.Dondi, A.Betti, and C.Bigni, J.Chromatogr., **60**, 1 (1971).
146. S.A.Reznikov and R.I.Sidorov, Zhur.Fiz.Khim., **51**, 1796 (1977)[Russ.J.Phys.Chem., No.10 (1977)].
147. P.E.Barker and D.L.Lloyd, J.Inst.Petroleum, **49**, 471, 73 (1963).
148. C.A.Gramers, J.Luyten, and J.A.Rijks, Chromatographia, **3**, 441 (1970).
149. B.Versino, Chromatographia, 3, 231 (1970).
150. H.J.Gold, Analyt.Chem., **34**, 174 (1962).
151. H.L.Hansen and K.Andersen, J.Chromatogr., **34**, 246 (1968).
152. H.Groenedijk and W.C.van Kamenade, Chromatographia, **1**, 472 (1968).
153. M.Haferkampf, in "Chromatographie in der Gasphase" (R.Kaiser, Editor), Pt.2, Bibliographisces Institut AG, Mannheim, 1966, p.93.
154. R.Kaiser, Chromatographie, **3**, 127 (1970).
155. R.Kaiser, Chromatographie, **3**, 383 (1970).
156. J.Uhdeova, J.Chromatogr., **51**, 23 (1970).
157. W.Ebing, Chromatographia, **2**, 442 (1969).
158. M.Goedert and G.Guiochon, Analyt.Chem., **45**, 1188 (1973).
159. M.Goedert and G.Guiochon, Analyt.Chem., **42**, 962 (1970).
160. D.A.Graven, E.S.Everett, and M.Rubel, J. Chromatogr., **9**, 541 (1971).
161. J.P.Hettinger, J.P.Hublard, J.M.Gill, and L.A.Miller, J.Chromatogr., Sci., **9**, 710 (1971).

162. B.A.Landawne, R.W.Morosani, R.A.Herrman, R.M.King, and H.G.Schmus, Analyt.Chem., **44**, 1961 (1972).
163. R.S.Swingle and L.B.Rogers, Analyt.Chem., **43**, 810 (1971).
164. J.A.Jonsson, J.Chromatogr., **139**, 156 (1977).
165. M.F.Burke and R.G.Thurman, J.Chromatogr.Sci., **8**, 39 (1970).
166. R.G.Thurmann, K.A.Mueller, and M.F.Burke, J.Chromatogr.Sci., **9**, 77 (1971).
167. A.Sabatier, M.Goedert, and G.Guichon, Chromatographia, **7**, 560 (1974).
168. J.E.Oberholtzer and L.B.Rogers, Analyt.Chem., **41**, 1234 (1969).
169. J.A.Jonsson and R.Jonsson, J.Chromatogr., **111**, 265 (1975).
170. J.A.Jonsson, R.Jonsson, and K.Malm, J.Chromatogr., **115**, 57 (1975).
171. E.Grushka, H.N.Myers, P.D.Schletter, and J.C.Giddings, Analyt.Chem., **41**, 889 (1969).
172. A.T.James and A.J.P.Martin, Analyst (London), **77**, 915 (1952).
173. M.B.Evans, J.Chromatogr., **12**, 2 (1963).
174. M.B.Evans and J.F.Smith, J.Chromatogr., **9**, 147 (1962).
175. O.Grubner, in "Advances in Chromatography" (J.C.Giddins and R.A.Keller, Editors), Vol.6, Marcel Dekker, New York, 1968, p.173.
176. R.A.Gulp, C.H.Lochmuller, A.K.Moreland, R.S.Swingle, and L.B.Rogers, J.Chromatogr.Sci., **9**, 6 (1971).
177. L.J.Lorenz, R.A.Gulp, and L.B.Rogers, Analyt. Chem., **42**, 979 (1970).
178. D.Macnauhtan and L.B.Rogers, Analyt.Chem., **43**, 822 (1971).
179. A.K.Moreland and L.B.Rogers, Separ.Sci., **6**, 1 (1971).
180. J.E.Oberholtzer and L.B.Rogers, Analyt.Chem., **41**, 1590 (1969).
181. M.J.Hartigam and L.S.Ettre, J.Chromatogr., **119**, 187 (1976).
182. G.Schomburg, H.Husmann, and F.Weeke, J. Chromatogr., **99**, 63 (1974).
183. G.Guiochon, J.Chromatogr.Sci., **9**, 512 (1971).
184. V.S.Gavrichev and V.G.Berezkin, Zavod.Lab., **40**, 14 (1974).
185. J.Takacs and D.Kralik, J.Chromatogr., **50**, 379 (1970).
186. J.Takacs, D.Kralik, and F.Poy, Magyar Kém. folyóirat, **78**, 43 (1972).
187. G.Schomburg, D.Hennenberg, and E.Ziegler, "Cleveland Conference on Analytical Chemistry and Spectroscopy", March, 1970.
188. J.E.Oberholtzer and L.B.Rogers, Analyt.Chem., **41**, 1325 (1969).
189. A.W.C.van Kamenade and K.Groenendijk, Chromatographia, **2**, 148 (1969).
190. M.H.J. van Rijswick, Chromatographia, **7**, 491 (1974).
191. J.J.M.Wijtvliet, Thesis, Eindhova, 1972.
192. P.A.T.Svoboda, in "Gas Chromatography 1966" (A.B.Littlewood, Editor), Elsevier, Amsterdam, 1967, p.395.
193. D.A.Leathard and B.C.Shurlock, "Identification Techniques in Gas Chromatography", Wiley, New York, 1970, p.8.
194. J.Novák, J.Ruzickova, S.Wicar, and J.Janak, Analyt.Chem., **45**, 1365 (1973).
195. R.G.Ackman, J.Chromatogr.Sci., **10**, 535 (1972).
196. R.G.Ackman, J.Amer.Oil Chemists' Soc., **40**, 558 (1963).
197. G.Castello, G.D.Amato, and E.Bragini, J. Chromatogr., **41**, 313 (1969).
198. F.H.Dymond and V.D.Kilburn, in "Gas Chromatography 1966", (A.B.Littlewood, Editor), Elsevier, Amsterdam, 1967, p.753.
199. R.Louis. Erdöl u.Kohle, **25**, 582 (1972).
200. T.K.Miwa, K.L.Mikolajczak, F.R.Earle, and J.A.Wolf, Analyt.Chem., **32**, 1739 (1960).
201. W.J.A.Vandenheuvel and E.C.Horning, Biochim. Biophys.Acta, **64**, 416 (1962).
202. F.Woodford and C.M.van Gent, J.Lipid Res., **1**, 188 (1960).
203. M.Wurst and J.Churacek, Coll.Czech.Chem. Comm., **36**, 3497 (1971).
204. A.N.Korol', Teor.Eksper.Khim., **4**, 234 (1968).
205. L.Rohrschneider, Chromatographia, **2**, 437 (1969).
206. M.S.Vigdergauz and V.I.Semkin, Zhur.Fiz.Khim., **45**, 948 (1972)[Russ.J.Phys.Chem., No.5 (1972)].
207. A.W.Ladon, Chromatographia, **4**, 171 (1971).
208. L.Soják and L.Barnoky, Ropa a Uhlie, **16**, 654 (1974).
209. C.A.Cramers, J.A.Rijks, V.Pacakova, and J.R.de Andrade, J.Chromatogr., **51**, 13 (1970).
210. G.Schomburg, F.Weeke, B.Weimann, and E.Ziegler, in "Gas Chromatography 1970" (Dublin), Institute of Petroleum, London, 1970, Preprint Paper No.15.
211. Data Subcomittee Gas Chromatography Discussion Group, J.Gas Chromatogr., **4**, 1 (1960),
212. R.H.Hively and R.E.Hinton, J.Gas Chromatogr., **6**, 203 (1968).
213. A.Matukuma, Nippon Kagaku Zasshi, **84**, 770, 774 (1963).
214. A.Matukuma, in "Gas Chromatography 1968" (C.L.A.Harbourn and R.L.Stock, Editors), Institute of Petroleum, London, 1969, p.55.
215. M.S.Vigdergauz, in "Gas Chromatographie 1968" (H.G.Struppe, Editor), Akad.Verlag, Berlin, 1968, p.625.
216. N.C.Saha and G.D.Mitra, Technology (India), **8**, 3 (1971).
217. N.A.Saha and G.D.Mitra, Technology (India) **8**, 65 (1971).
218. M.S.Vigdergauz and A.A.Martinov, Chromatographia, **4**, 463 (1971).
219. C.L.A.Harbourn, J.Chromatogr.Sci., **7**, 583 (1969).
220. M.S.Vigdergauz and V.V.Pomazanov, Symposium "Uspekhi Khromatografii" (Advances in Chromatography), Kazan', 1969, p.61.
221. F.Riedo, D.Fritz, G.Tarjan, and E.sz.Kovats, J.Chromatogr., **126**, 63 (1976).
222. S.M.Csicsery and H.Pines, J.Chromatogr., **9**, 34 (1962).
223. J.Franc, M.Frantisek, and V.Pines, Abhandl.Dtsch. Akadem.Wiss., Berlin, Kl.Chem.Geol.u.Biol., 543 (1966).
224. J.Franc and S.Michajkova, J.Chromatogr., **12**, 22 (1963).
225. R.A.Hively, J.Chem.Eng.Data, **5**, 237 (1960).
226. M.H.Clouwen and R.Heide, in "Gas Chromatography" (N.Brenner, J.E.Callen, and M.D.Weiss, Editors), Academic Press, New York, 1962, p.485.
227. G.J.Pierotti, C.H.Deal, E.L.Stross, and P.E.Porter, J.Amer.Chem.Soc., **78**, 2989 (1956).
228. T.Toth, Magyar Kém.Folyóirat, **77**, 492 (1971).
229. A.N.Korol, Chromatographia, **3**, 372 (1970).

230. A.N.Korol', "Gazokhromatografichnii Yakisnii Analiz" (Gas-chromatographic Analysis), Izd.Naukova Dumka, Kiev, 1971.
231. V.G.Arakelyan, L.S.Sarycheva, and V.P.Evdakov, Zhur.Anal.Khim., **23**, 109 (1968).
232. V.G.Arakelyan and K.I.Sakodynski, Chromatogr., Rev., **15**, 93 (1971).
233. C.A.Cramers, Thesis, Eidhoven, 1967.
234. J.K.Holem, J.Chromatogr., **50**, 114 (1970).
235. A.T.James, J.Chromatogr., **2**, 552 (1959).
236. L.S.Ettre and K.Billeb, J.Chromatogr., **30**, 1 (1967).
237. G.D.Mitra and N.C.Saha, Technology (India), **7**, 312 (1970).
238. E.B.Molnar, R.Moritz, and J.Takacs, J.Chromatogr., **66**, 205 (1972).
239. J.H.Purnell, in "Vapour Phase Chromatography" (D.H.Desty and C.A.Harbourn, Editors), Butterworth, London, 1957, p.52.
240. N.C.Saha and G.D.Mitra, Technology (India), **5** 212 (1968); **7**, 84 (1970).
241. D.A.Tourres, J.Chromatogr., **30**, 357 (1967).
242. M.S.Vigdergauz, Symposium "Teoriya i Primenenie Nepodvizhnoi Fazy v Gazo-zhidkostnoi Khromatografii" (Theory and Applications of the Stationary Phase in Gas–Liquid Chromatography), Izd.Znanie, Kiev, 1971, p.7.
243. H.Widmer, J.Gas Chromatogr., **5**, 506 (1967).

Institute of Physical Chemistry
of the UkrSSR Acadmey of
Sciences, Kiev.

Translated from *Uspekhi Khimii*, **49**, 931 - 943 (1980) U.D.C. 547.963.32.001.8

Gas-chromatographic Analysis of Nucleic Acids

V.V.Tets

Problems of the gas-chromatographic analysis of the components of nucleic acids are examined and data for the conditions governing such studies are presented. Since the investigation of the composition of nucleic acids involves, apart from gas chromatography, their isolation from natural sources and the preparation of volatile derivatives, particular attention is devoted to the problem of the preparation of samples for analysis. The fundamental trends in the practical applications of the method are discussed.
The bibliography includes 120 references.

CONTENTS

I. Introduction 488
II. Preparation of samples for the gas-chromatographic analysis of nucleic acids 488
III. Analytical conditions 491
IV. Examples of the applications of the gas-chromatographic analysis of nucleic acids 492

I. INTRODUCTION

The unflagging interest in nucleic acids (NA) is due to their relation to such most important problems of vital activity as heredity and the development and regulation of various functions. One of the most important aspects of the study of NA involves the investigation of their composition, i.e. the separation, identification, and quantitative determination of purine and pyrimidine NA derivatives. For this purpose, studies have been made of a wide variety of fractionation methods, including ion-exchange chromatography[1-4], paper chromatography[5-8], paper electrophoresis[9-12], and thin-layer chromatography[13-15]. With their aid, most of the studies on the composition of NA have been carried out. The characteristics of the above methods have been widely discussed in a series of detailed reviews[16-21].

The majority of the methods employed require milligrams of material for investigation if a radioactive tracer is not employed. Since biological samples are frequently very small (micrograms of material), there was a need for methods which would yield satisfactory quantitative results under these conditions also. The attention of investigators was therefore attracted to liquid and gas–liquid chromatography. Gas–liquid chromatography (GLC), which ensures rapid separation of the test systems, selectivity, and sensitivity of the analysis, is becoming increasingly popular in the study of various biological substances. A GLC technique for numerous biological components has now been developed: aliphatic acids, cyclic compounds, alcohols, aldehydes, ketones, essential oils, steroids, lipopolysaccharides, amino-acids, and others[22-24].

The first attempt to use the GLC analysis in the study of NA was undertaken in 1962.[25] Since the NA components are inert and involatile in the temperature range used in gas chromatography, the authors used their acetyl, methyl, and isopropylidene derivatives. In 1964 MacGee[26] investigated *N*-methyl derivatives of purine and pyrimidine bases. However, the data presented were unsuitable for quantitative analysis, because numerous derivatives were obtained for each NA component after esterification (thus, four such derivatives obtained for adenine alone). Despite the fact that MacGee[27] was able to obtain certain quantitative data in 1966, this method for the analysis of NA has not been widely used. Progress in the application of GLC in the analysis NA became possible when silylating agents began to be used to prepare their volatile derivatives.

The majority of the studies on NA by gas chromatography have now been carried out using their trimethylsilyl (TMS) esters, their acetylation and methylation being used only in a few investigations[28-33]. Silylated NA derivatives were first obtained by Hancock and Coleman[34] who used for this purpose hexamethyldisilazane (I) and chlorotrimethylsilane (II) in pyridine. They authors obtained numerous derivatives of the constituents and asymmetric peaks were recorded on the chromatogram. In the same year Hancock[35] reported a successful separation of various adenosine derivatives and showed that, after silylation, they can be used for quantitative analysis.

In 1966–1968 Hashizume and Sasaki[36-38] published studies devoted to the separation and quantitative determination of TMS derivatives of the bases, nucleosides, and nucleotides obtained using compounds (I) and (II) as silylating agents. The possibility of using this method for the analysis of bases forming part of the composition of TNA and RNA was also demonstrated in these investigations. Gehrke and Ruyle[39] proposed a quantitative method for the GLC analysis of TMS derivatives of NA obtained in the reaction with *N*,*O*-bis(trimethylsilyl)acetamide(III) and *N*,*O*-bis(trimethylsilyl)trifluoroacetamide(IV), which had been used earlier to modify aminoacids[40]. Subsequently *N*-trimethylsilylimidazole, *N*-diethyl-*N*-trimethylsilylamine, *N*-methyl-*N*-trimethylsilylacetamide and their various combinations were used to silylate NA derivatives[41-44]. All the reagents enumerated above are used nowadays to prepare TMS derivatives of NA. Silylation of the NA components made it possible to obtain quantitative data by the gas chromatography of microamounts of the test material, which permits a wide scale application of the method.

The present review deals with problems of the preparation of NA samples for GLC analysis, the experimental technique, and aspects of its practical applications.

II. PREPARATION OF SAMPLES FOR THE GAS-CHROMATOGRAPHIC ANALYSIS OF NUCLEIC ACIDS

1. Hydrolysis of Nucleic Acids

For the GLC analysis of NA, it is necessary in the first place to hydrolyse the polymer to various monomers: purines, pyrimidines, nucleosides, or nucleotides (depending on the

method of depolymerisation). The characteristics of the silylation method show that the best procedure involves decomposition to the bases or nucleosides carried out with the aid of various acids and enzymes[45-47]. The method of hydrolysis of NA by $HClO_4$ has come to be widely used. This method, followed by purification of the product by ion-exchange chromatography, has been employed in the preparation of samples for GLC.[36,37] However, the method of hydrolysis of NA by trifluoroacetic acid or a mixture of trifluoroacetic and formic acids must be regarded as more useful, since the two acids can be separated from the sample by simple evaporation and there is therefore no need for an additional purification of the sample. The depolymerisation of the NA in this way greatly simplifies the procedure involving the preparation of the sample and increases the overall reliability and sensitivity of the method. Purines and pyrimidines, prepared in this way, have been studied successfully by GLC.[48,49]

2. Silylation of Nucleic Acids

Detailed information about the properties of the silylating agents and about the nature of their interaction with the NA component has been published in a number of reviews[50-52]. According to Muni and Altschuler's data[53], the formation of the TMS esters of NA derivatives involves the substitution of an active proton by a trimethylsilyl group. This phenomenon decreases the possibility of the formation of hydrogen bonds and increases the stability of the mixture. The silylated derivatives of purines and pyrimidines are less strongly bound and are more volatile compared with their unmodified analogues.

The conversion of NA into volatile components can be regarded as ideal when it proceeds in accordance with the "one base (nucleoside, nucleotide)–one derivative" principle. However, such a ratio cannot always be maintained for each component of the test mixture. In certain cases purines and pyrimidines containing a functional amino-group each form two derivatives[52,54]. The cause of this is a whole series of factors: the nature of the silylating agent, the solvent, the reaction temperature, and certain others[55]. At the same time the presence of two peaks corresponding to a single base (nucleoside, nucleotide) on the chromatogram does not interfere with the quantitative analysis and is fully reproducible[39,56,57]. Cytosine and the corresponding nucleoside and nucleotide most frequently give rise to two such compounds[48,56]. According to the results of the mass-spectrometric analysis of TMS-cytosine, the two peaks of its derivatives correspond to di-TMS-cytosine and tri-TMS-cytosine[58].

The available information about the proposed structures of various TMS-nucleosides and TMS-nucleotides as well as the isomers has been published in a number of communications[44,59-63]. According to the data obtained, cytidine forms tetra-TMS-cytidine and penta-TMS-cytidine. The reactions of minor derivatives of cytosine (5-methylcytosine) and adenine (6-methylaniline) with compound (III) or (IV) also each gave rise to two TMS-derivatives[56,64,65]. It is noteworthy that, when other silylating agents or other modification conditions are used, it is possible to obtain only one derivative of the base[49,66,67].

Much attention is devoted nowadays to the selection of both the best silylating agent and of the optimum esterification method. The data for the silylation conditions and the agents employed are compiled in Table 1. Among the substances enumerated which are used to prepare the TMS esters of NA, compounds (III) and (IV) are the most popular in view of their high modifying activity in relation to NA compared with other silylating agents[44,54,68,69].

It has been suggested that the optimum conditions for the interaction of bases and nucleotides with compound (III) involve heating of the reaction mixture for 45 min at 150 °C in the presence of 100 moles of the above agent in excess[39]. It has also been suggested that, in the treatment of nucleosides with compound (III), the latter be present in excess (225 moles) and that the mixture be heated for 2 h at 120 °C.[44] In the optimisation of the conditions in the modification of bases and nucleosides using compound (IV) best results were obtained on heating the mixture for 15 min at 150 °C in the presence of 225 moles of the silylating agent in excess[57,70]. The same amount of compound (IV) was chosen as optimal also in the silylation of nucleotides. An increase of the volume of the silylating agent led in this case to the appearance in the mixture of the corresponding TMS-bases. Deoxycytosine gave rise to a TMS-cytosine peak on the chromatogram also under all other silylation conditions using both compound (III) and compound (IV).[44]

The optimum conditions in the esterification of nucleotides and dinucleotides using compound (IV) as the silylating agent have been studied by Patel and Gehrke[71], who concluded that, for a more successful modification and chromatography, mono- and di-nucleotides from biological samples must be converted into the corresponding nucleosides or bases. According to the data of Miller et al.[54] optimum silylation using compound (IV) is attained in the case of bases by heating at 150 °C in the presence of 100 moles of compound (IV) in excess for 15 min, while in the case of nucleosides the heat treatment should last 30 min. It is noteworthy that NA are silylated also at room temperature but less efficiently[42,44,49]. The silylation of NA has been studied quantitatively by Řehák and Pacáková[72], who established, using spectrophotometric and radioisotope methods to follow the process, that if the latter takes place at 150 °C over a period of 45 min in the presence of 50 moles of compound (IV) in excess, then at least 95% of the initial amount of the bases investigated are converted into TMS-derivatives.

Dichloroethane, hexane, benzene, acetonitrile, pyridine, dimethylformamide, toluene, and certain other substances have been used as solvents for the preparation of volatile NA derivatives. Pyridine and acetonitrile are most widely used nowadays. Comparative data for the solvents employed are listed in Table 1. According to the available information about the influence of various solvents on the silylation process, acetonitrile must be regarded as the best[44,65]. Data on the efficiency of the silylation of nucleosides using various solvents are presented in Table 2.

Apart from all the factors enumerated, the preparation of TMS ethers of purines and pyrimidines and the results of their subsequent GLC analysis can be influenced by various salts in water, which sometimes remain in the NA sample after its isolation or hydrolysis. The studies carried out to elucidate this problem have shown that the NA components respond in different ways in the presence of particular salts. When compounds such as Na_2SO_4 and $CaSO_4$ were added to the reaction mixture, the results of the GLC analysis remained unchanged, while the presence of added $CaCl_2$ caused some decrease of the guanine peak[57]. The Na^+, K^+, Ca^{2+}, Mg^{2+}, and Cu^{2+} cations added to the reaction mixture in the silylation of guanine and hypoxanthine had a negative influence on the esterification process, apparently owing to the decrease of the volatility of TMS-derivatives[43]. The presence of NH_4^+ cations did not affect this process.

In their study of the influence of salts such as NaCl, KCl, NH_4Cl, $(NH_4)_2SO_4$, $MgCl_2$ $CaSO_4$, $CaCl_2$, and Na_2SO_4 and the silylation and chromatography of nucleosides, Patel and

Table 1. Experimental conditions in the silylation and gas-chromatographic analysis of purines and pyrimidines*.

Components investigated	Silylating agent	Solvent	Silylating conditions		Carrier	Liquid phase, %	Type of detector	Carrier gas	Refs.
			t, °C	τ, min					
Nucleotides	(I):(II) = 2:1	Pyridine	155	60	Diasolid, 30-50 mesh	DC-430 (5)	TCD	Nitrogen	36
Bases	(I):(II) = 2:1	Pyridine	155	60	Zeolite 540, 80-100 mesh	DC-430 (5)	TCD	Helium	38
Bases, nucleosides	(I):(II) = 2:1	Pyridine	155	60	Diasolid, 30-50 mesh	Apiezon L (5); SE-30 (2); SE-52 (5); QF-1 (1); DC-430 (5); LAC-2R446 (1)	TCD	Helium	66
Bases, nucleotides	(I):(II) = 2:1	Pyridine	155	60	Ditto	DS-430 (5)	TCD	Helium	74
Nucleosides	(III)	Pyridine	120	120	Gas Chrom Q, 100-120 mesh	OV-17 (4)	FID	Argon	75
Bases, nucleosides	(III)	Pyridine	150	45	Gas Chrom Q, 100-120 mesh	SE-30 (3)	FID	Nitrogen	64
Bases, nucleosides	(IV) + 1.0% (II)	Pyridine	60	960	Chromosorb W, 80-100 mesh	OV-1 (3)	FID	Helium	67
Bases	(IV)	Pyridine	150	45	Chromosorb W, 60-80 mesh	OV-17 (3)	FID	Nitrogen	72
Bases	(IV)	Acetonitrile-dichloroethane (1:1)	150	15	Chromosorb W, 80-100 mesh	OV-101 (10)	FID	Nitrogen	76
Bases	(II), (III), (IV) etc.	Pyridine	room		Diatoport S	OV-17 (3)	FID	Helium	43
Nucleosides	(IV)	Acetonitrile	150	15	Supelcoport, 100-120 mesh	SE-30 (4) SE-30 (3); OV-17 (3); OV-11 (4)	FID	Nitrogen	70
Bases	(IV)	Acetonitrile	150	15	Ditto	SE-30 (10); OV-3 (5); OV-7 (5)	FID	Nitrogen	65
Bases, nucleosides	(III), (IV)	Pyridine	150	45,20, 30	Chromosorb W, 100-120 mesh	OV-17 (3) OV-101 (3)	FID	Argon	54, 77
5-Fluorouracil, florafur, 6-azauridine, allopurinol	(IV)	Pyridine	150	20	Chromosorb W, 100-120 mesh	OV-101 (3) OV-17 (3)	FID	Argon	51
Nucleosides	(III), (IV), trimethylsilylimidazole	Acetonitrile	**	**	Supelcoport, 100-120 mesh	OV-11 (4)	FID	Argon	44
Nucleosides	(IV) + 1.0% (II)	Pyridine	75	180	Chromosorb W, 80-100 mesh	SE-30 (5)	FID	Helium	68
Nucleosides	IV + 1.0% (II)	Pyridine	75	180	Gas Chrom Q, 100-120 mesh	SE-30 (3)	FID	Helium	78
Bases	(IV)	Acetonitrile	150	15	Supelcoport, 100-120 mesh	SE-30 (10)	FID	Nitrogen	73
Nucleosides	(III)	Hexane	150	40	Chromosorb W	OV-1 (1)	FID	Helium	79
Nucleosides	(IV)	Acetonitrile:dichloroethane = 1:1	150	15	Chromosorb W, 80-100 mesh	OV-7 (3)	FID	Helium	80
Bases	(III), (IV)	Pyridine	room	–	Gas Chrom Q, 100-120 mesh	SE-30 (3); OV-225 (2); OV-17 (3); OV-210 (2)	FID	Nitrogen	49
Nucleosides	(II) + (IV)	Pyridine	80	60	Gas Chrom P, 100-120 mesh	SE-30 (1); OV-17 (1)	FID	Nitrogen	59

*Notation: (I) = hexamethyldisilazane, (II) = chlorotrimethylsilane, (III) = *N*,*O*-bistrimethylsilylacetamide, and (IV) = *N*,*O*-bis(trimethyl)trifluoroacetamide; TCD = thermal conductivity detector and FID = flame ionisation detector.

**Different values for different silylating agents.

Gehrke established that thymidine is most sensitive to them on modification with compound (IV). If a mixture of the above salts was involved in the reaction, an appreciable decrease of the relative weight sensitivity coefficients of all the nucleosides was observed. According to the authors[71], these solvents can decrease the degree of silylation of nucleosides by reducing their solubility and the molar excess of compound (IV) as a result of the formation of derivatives of TMS anions such as TMS-SO_4 and TMS-PO_4 and the decomposition of the TMS-nucleosides in the sample. A similar response to the presence of these salts apparently occurs also in the silylation of the bases.

Various workers obtained data according to which the maintenance of anhydrous conditions is obligatory for the successful GLC analysis of NA derivatives. After the silylation of guanine and hypoxanthine by compound (III), the peaks of these substances were not observed on the chromatograms when 100 μl of water had been added to a sample containing 5 mg of each substance[43]. According to the data of Gehrke and Lakings[57], the presence of 5 μl of water in a 200 μl sample of the bases reduced the second peak corresponding to cytosine on the chromatograph up to its complete disappearance. On further increase of the concentration of water, the first peak also diminished as well as the peak corresponding to guanine. In the reaction of nucleosides with compounds (III), (IV), and trimethylsilylimidazole a negative influence of water on the silylation process was observed. The necessity to maintain anhydrous conditions in the GLC analysis of NA has also been reported by other workers[53].

The retention of the TMS derivatives of NA from the instant of their preparation until the gas-chromatographic

investigation is of practical importance. Thus the TMS derivatives of bases stored at room temperature for five days yielded a clearly reproducible result in their GLC analysis[57]. TMS derivatives of nucleosides stored under the same conditions remained stable for 48 h. After more prolonged storage of the samples, numerous peaks, corresponding to the TMS-bases of the initial nucleosides and other products of the decomposition of the TMS-derivatives of nucleosides, appeared on their chromatogram[70]. At the same time there are data[53] according to which the majority of the silylated purines and pyrimidines are chromatographically stable for a year and more when stored in a tightly closed vessel in the presence of an excess of the silylating agent at 3–5 °C.

Thus reliable methods have now been developed for the quantitative preparation of volatile derivatives of bases and nucleosides suitable for GLC analysis.

Table 2. The effect of various solvents (relative weight sensitivity coefficient) on the silylation of nucleosides by compound (IV).[70]

Compound	Aceto-nitrile	Pyri-dine	Dimethyl-formamide	Methylene chloride	Chloroform	Benzene	Toluene	Hexane
Pyrimidines								
Thymidine	0.50	0.48	*	0.48	0.44	0.36	0.38	0.43
Uridine	0.78	0.75	0.67	0.76	0.74	0.32	0.33	0.56
Cytidine	0.37	0.35	0.01	0.34	0.31	0.16	0.17	0.28
Purines								
Inosine	0.78	0.78	0.76	0.38	0.33	0.05	0.16	0.48
Adenosine	1.01	0.97	0.99	0.58	0.51	0.54	0.56	0.85
Xanthosine	0.78	0.73	0.78	0.38	0.34	0.13	0.19	0.40
Guanosine	0.70	0.70	0.70	0.30	0.28	0.12	0.19	0.40

*The peak was not obtained.

III. ANALYTICAL CONDITIONS

1. Liquid Phases

Non-polar and moderately polar liquid phases have been used successfully for the separation of TMS derivatives of NA. With their aid, it is possible to separate TMS derivatives of the bases, nucleosides, and the phosphates (Table 1). Among non-polar liquids, phases such as SE-30, OV-1, OV-101, DC-430, and certain others are employed. Among moderately polar phases, those containing phenyl groups have been used: OV-3, OV-17, XE-60, OV-7, and others. The characteristics of these phases are quoted in a handbook[81]. The non-polar liquid phase SE-30, which is a methylsiloxane polymer, has been most frequently used for the separation of NA derivatives.

The concentration of the liquid vary within fairly wide limits—from 0.2 to 10%.[39,65,72] Universally prescibed concentrations are lacking for each phase. In choosing the concentration of the liquid phase, one must bear in mind that the presence of a large amount of the latter entails an increase of the separation time, while the phase present in a small amount cannot fully compensate for the inertness of the carrier, which impairs the quality of the separation and decreases the sensitivity of the method. The selection of the liquid phases and their concentrations is related to the nature of the mixtures separated and the purposes of the investigation. Thus in the separation of ribonucleosides, best results were obtained using phases such as 4% of OV-11 and 3% of OV-17.[70] The best separation of the minor bases was achieved on 0.5% of OV-3.[65] The separation of 5-methylcytosine from cytosine in preparation of bases obtained from calf thymus DNA and bacteriophages was observed on the following liquid phases: 3% of SE-30 and 2% of OV-225.[49] According to Muni and Altschuler[53], a satisfactory separation of the TMS derivatives of purines and pyrimidines was attained using 3–5% of the SE-30 and OV-17 phases.

Substances lacking catalytic activity, exhibiting a minimal adsorption capacity, and having highly homogeneous surfaces, dimensions, and shapes are used as carriers for the liquid phase. Such substances are in the first place diatomaceous carriers of the type of Chromosorb W, Supelcoport, Anachrome, Gas Chrom Q, etc. (Table 1). Silylated carriers are frequently used[54,56].

2. Conditions of the GLC Analysis of NA

A relatively wide set of GLC analytical conditions can be used in the study of NA. After the liquid phase, the carrier, and the column length have been chosen, the temperature and the flow rate of the gas are usually regulated in such a way that the required separation can be achieved during a satisfactory time. The GLC analysis of NA can be carried out under both isothermal conditions and with temperature programming. The choice of the conditions in the investigation depends in many respects on its aim. Multicomponent systems are mainly separated using temperature programming[38,64,65,67,75]. The separation of the TMS derivatives of the bases, nucleosides, and nucleotides is as a rule carried out in the temperature range from 80° to 325 °C.[38,65,67,75,78]

The chromatographic columns are in most instances 1–2 m long and have an internal diameter of 2–4 mm. Both glass and metallic columns are used for the chromatography of the TMS derivatives of NA. However, it is believed[82] that the entire GLC analysis should be carried out in glass apparatus, since the TMS derivatives decompose on contact with heated metallic components. An analogous behaviour has been observed also in the gas chromatography of aminoacids[23].

A flame ionisation detector and more rarely thermal conductivity, argon ionisation, and electron capture detectors are used in most studies. The carrier gas is chosen depending on the type of detector employed: nitrogen, argon, and helium (Table 1). Since the TMS derivatives of purines and pyrimidines are highly sensitive to moisture, thorough drying of the gas supplied is necessary.

3. Quantitative Analysis

The quantitative determination of the bases, nucleosides, and nucleotides in the GLC analysis is carried out by an internal standardisation method. The internal standards employed are phenanthrene, pyrene, purene, acenaphthene, n-octacosane, n-tetratriacontane, n-nonadecane, and others[42,43,76,83,84]. Among these, phenanthene and pyrene are most widely used. The internal standard is added to the initial mixture and undergoes all the stages in the preparation of the TMS derivatives. The amount of test substance is calculated using the "relative molar sensitivity coefficient" or the "relative weight sensitivity coefficient"[65,66].

The reproducibility of the data obtained in the GLC analysis of NA has been estimated with the aid of the relative standard deviation calculated from the results of several measurements. Thus the standard deviation for the TMS

derivatives of the minor components, determined in biological liquids, is on average 3.8% according to the results of four measurements[65]. The results of the determination of the relative molar sensitivity coefficients as well as the standard deviations for various nucleosides are presented in Table 3.

The introduction of comparatively large concentrations of the test substance is undesirable if quantitatively reproducible data are to be obtained. Thus, when a flame ionisation detector was used, the introduction of more than 25 μg of the TMS derivative led to the appearance of an additional peak on the elution curve, which may be associated with the moderate cooling of the flame as a result of the combustion of the organosilicon substance[85]. The minimum amount of the TMS derivatives of purines and pyrimidines which can be determined by GLC using a flame ionisation detector is $(3-5)\times10^{-9}$ g, which corresponds to 3×10^{-11} moles of each of the bases introduced[39].

Qualitative investigation of the composition of the DNA bases of salmon sperm and calf thymus and the RNA bases of yeast and tobacco mosaic virus by GLC at a macrolevel (1 mg), semimicrolevel (100 μg), and microlevel (5 μg) yielded data identical with those obtained earlier for the same systems when the latter were studied with the aid of other fractionation methods[48,75].

Table 3. The reproducibility of the results of etherification and the GLC of the TMS derivatives of the methylated bases.

Compound	Retention time, min	Relative molar sensitivity coefficient	Standard deviations*
6-Methyladenine	13.2	0.58	0.024
6-Dimethyladenine	13.0	0.64	0.029
6-Isoadenine	18.4	0.86	0.025
2-Methyladenine	16.4	0.57	0.008
2-Methylguanine	17.2	0.58	0.017
2,2-Dimethylguanine	18.0	0.83	0.020
7-Methylguanine	19.6	0.39	0.320
5-Methylcytosine	9.6—12.0	0.73**	0.024
Thymine	6.8	0.63	0.025

*The standard deviation was determined from the results of four independent experiments.

**Two peaks were obtained, each being independently integrated, and were then added to determine the overall area and to calculate the relative molar sensitivity coefficient.

4. Qualitative Analysis

The gas-chromatographic analysis of the composition of NA is extremely sensitive; it ensures a high degree of resolution and detection of the components present at very low concentrations. The identification of the unknown TMS components of the mixture by GLC in a pure form is in most cases carried out by comparing their retention times with those of known standards. Another procedure involves the comparison of the behaviour of the TMS derivatives on different phases. In order to obtain data permitting the identification of the unknown components and in the first place those for which comparison standards are not already available, it is necessary to employ an additional technique. The possibility of employing spectrometric methods such as ultraviolet and infrared scanning, NMR, mass spectrometry, and certain others for the identification of the TMS derivatives of NA has therefore been investigated[64,66,86-88]. The combination of modern GLC with the above methods[64,72] greatly extends the scope of the analysis of NA.

The absorption by purines and pyrimidines in the ultraviolet and infrared is highly specific and is widely used for their identification and quantitative determination[89-94]. The study of the spectroscopic properties of the TMS derivatives of NA obtained by GLC showed that, although the ultraviolet absorption differs to a considerable extent from that observed for the intact purines and pyrimidines, it is nevertheless specific[53,64]. The ratios of the absorption at 260 and 280 nm and at 250 and 280 nm have been used as characteristics of the TMS derivatives of NA and of their unmodified precursors. The absorption of TMS derivatives of NA in the infrared is also fairly characteristic[64,66].

The specificity of the properties of the TMS-bases has been demonstrated also in their study by NMR.[64,66] However, one should note that the application of this method is limited, because a comparatively large amount of the starting material is required for the investigation.

One of the most promising procedures for the study of mixtures of TMS derivatives of NA components is the combined GLC–mass-spectrometric method. The possibility of using it for this purpose was first demonstrated by McCloskey et al.[88] The mass spectra of the bases, nucleosides, and nucleotides, obtained on silylation with compounds (III) and (IV) as well as trimethylsilylimidazole, proved to be simple to interpret. Derivatives obtained from NA components by methylation, acetylation, trifluoroacetylation, trimethylsilylation, and the synthesis of 2′,3′-*O*-isopropylidene and 2′,3′-*O*-phenylborate ethers and esters have been investigated by this method[33,58,60,88,95]. The above combined method has been used successfully to investigate bacterial RNA and rare NA components[79,87,96,97]. Together with gas chromatography, a new mass-spectrometric method—mass-fragmentography has been employed in the analysis of TMS derivatives of NA. The application of other methods for the qualitative analysis of NA together with GLC greatly increases the accuracy of the latter.

It follows from the data presented that the purine and pyrimidine components of NA can be separated successfully by GLC. Various conditions for the GLC of nucleic acids, whereby they can be studied both quantitatively and qualitatively, have been developed. Bearing in mind the flexibility of the method, in view of the possibility of employing various liquid phases and conditions for the GLC itself, one may claim that virtually any NA component can be separated and identified with its aid.

IV. EXAMPLES OF THE APPLICATIONS OF THE GAS-CHROMATOGRAPHIC ANALYSIS OF NUCLEIC ACIDS

Gas–liquid chromatography has already found extensive applications and is arousing increasing interest, as shown, in particular, by the increase of the number of studies, carried out with its aid, which have been published in the last few years. The composition of the RNA of microorganisms, which are of theoretical and practical importance in agriculture, medicine, and industrial microbiology, has been studied by the above method[38,39,48,75,79,87,96,98,99]. Preparations of DNA from animal and bacterial cells have been investigated, particular attention being devoted to its minor components[38,48,49,74]. The biological importance of these compounds is now being vigorously investigated.

GLC has been employed in pharmacology for monitoring the chemical composition and purity of preparations and for the investigation of their distribution in the organism. The

applications of the method in this field are associated with the use of derivatives of the bases and nucleosides as therapeutic agents in the treatment of various diseases (hypertension, sugar diabetes, malignant neoplasts, etc.). In the study of therapeutic chemical preparations—standard and in biological liquids—with the aid of GLC their various volatile derivatives have been used[28-31,54,77,100-102]. The substances 6-mercaptopurine-nucleoside, 5-fluoro-2-deoxyuridine, ftorafur, investigated in these studies include 5-fluorouracil, 6-azauridine, allopurinol, β-phenylethylbiguanidine, and certain others.

The GLC analysis of NA has acquired major importance for clinical laboratory diagnosis. A method for the detection of minor NA components in biological liquids has now been developed in greater detail. It is known that the quantity of these compounds in such liquids increases in certain diseases as a result of the degradation of transport RNA.[103,104]. An increase of the content of these bases has also been observed in diseases such as accute leukaemia, psoriasis, melanoma, etc.[105,110]. The possibility of obtaining TMS derivatives of the purines and pyrimidines encountered in urine and of their analysis by GLC has been demonstrated[67,78]. Comparative GLC study of the minor derivatives of NA present in the urine of healthy and ill humans revealed diagnostically significant differences between them. Such studies have been carried out in instances of leukaemia, various malignant neoplasts, and other diseases[65,76,80,83,111,112].

The information presented in this review justifies the claim that GLC ensures a highly effective separation and identification of minimal amounts of the test substance combined with a high degree of reproducibility. The extensive possibilities of the employment of GLC in the manufacture of preparations containing NA components and in clinical laboratory diagnosis are due to the fact that, apart from the advantages already mentioned, the method can be fully automated.

---o0o---

During the preparation of the manuscript for the press, certain studies of fundamental importance on the GLC of NA were published. Conditions were proposed for the GLC investigation of DNA bases under isothermal conditions[113,114] and the first successful attempt was made to separate the TMS derivatives of NA components using capillary columns[115]. The possibility of investigating certain pyrimidines by GLC without their preliminary conversion into volatile derivatives was demonstrated[116]. It is noteworthy that the method of pyrolytic GLC study of NA, which had been used earlier[117-119] but had not found extensive applications, is nowdays used successfully for the comparative analysis of biological samples containing NA.[120]

REFERENCES

1. M.Mukarami, "Methods for the Investigation of Nucleic Acids" (Translated into Russian), Izd.Mir, Moscow, 1970, p.113.
2. A.Sibatani and N.Mizuno, Biochim.Biophys.Acta, **76**, 188 (1963).
3. R.B.Hurlbert, H.Schartz, A.F.Brumm, and V.R.Potter, J.Biol.Chem., **209**, 23 (1954).
4. M.Adler, B.Weissman, and A.B.Gutman, J.Biol. Chem., **209**, 23 (1954).
5. B.F.Vanyushin, Symposium, "Sovremennye Metody v Biokhimii" (Modern Methods in Biochemistry), Medgiz, Moscow, 1964, p.236.
6. R.Markham, Methods in Enzymology, **3**, 743 (1957).
7. P.L.Bergquist and R.E.Matthews, Biochem J., **85**, 305 (1962).
8. K.K.Tsuboi and T.D.Price, Arch.Biochem.Biophys., **81**, 223 (1959).
9. A.H.Gordon and P.Reichard, Biochem.J., **48**, 569 (1951).
10. T.D.Price, H.A.Hinds, and R.S.Brown, J.Biol. Chem., **29**, 430 (1963).
11. F.Sanger, G.G.Brownlee, and B.G.Barrel, J.Mol. Biol., **13**, 373 (1962).
12. A.M.Tometsko and N.Delihas, Anal.Biochem., **18**, 72 (1967).
13. K.Randerath and E.Randerath, Methods in Enzymology, **12A**, 323 (1967).
14. T.W.Munns, K.C.Podratz, and P.A.Katzman, J.Chromatog., **76**, 401 (1973).
15. D.P.Holdgate and T.W.Goodwin, Biochim.Biophys. Acta, **91**, 328 (1964).
16. E.I.Budovskii, Symposium, "Fiziko-Khimicheskie Metody Izucheniya, Analiza i Fraktsionirovanya Biopolimerov" (Physicochemical Methods for the Investigation Analysis, and Fractionation of Biopolymers), Izd.Nauka, Moscow–Leningrad, 1966, p.320.
17. K.Kirby, "Nucleic Acids" (Translated into Russian), Izd.Mir, Moscow, 1966, p.10.
18. G.A.Georgiev, Symposium, "Khimiya i Biokhimiya Nukleinovykh Kislot" (The Chemistry and Biochemistry of Nucleic Acids) (Edited by I.B.Zbarskii and S.S.Debov), Izd.Meditsina, Leningrad, 1968, p.74.
19. T.N.Davidson, "The Biochemistry of the Nucleic Acids" (Translated into Russian), Izd.Mir, Moscow, 1976.
20. L.I.Gus'kova and V.V.Demushkin, Uspekhi Khim, **43**, 1241 (1974)[Russ.Chem.Rev., No.7 (1974)].
21. W.E.Cohen, "The Nucleic Acids" (Edited by E.Chargaff and J.N.Davidson), Acad.Press, New York, 1955, Vol.1, p.211.
22. K.M.Sinyak and Z.T.Vasyurenko, Izv.Akad.Nauk SSSR, Ser.Biol., 715 (1974).
23. S.V.Vitt, M.B.Saporovskaya, T.V.Avakumov, and V.M.Belikov, Uspekhi Khim., **45**, 548 (1976)[Russ. Chem.Rev., No.3 (1976)].
24. T.P.Efimova and I.M.Tereshin, Uspekhi Sovr. Biol., **83**, 2 (1977).
25. H.T.Miles and H.M.Fales, Anal.Chem., **34**, 860 (1962).
26. J.MacGee, Fed.Proc., **23**, 2 (1964).
27. J.MacGee, Anal.Biochem., **14**, 305 (1966).
28. K.Beyermann and A.Wiesser, Z.Anal.Chem., **245**, 376 (1969).
29. J.H.Hengstmann, F.C.Falkner, J.T.Watson, and J.Oates, Anal.Chem., **46**, 34 (1974).
30. P.Erdtmansky and T.J.Goehl, Anal.Chem., **47**, 750 (1975).
31. M.Mottale and C.J.Sewart, J.Chematog., **106**, 263 (1975).
32. T.Kawabata, H.Ohshima, T.Ishibashi, M.Matsui, and T.Kitsuwa, J.Chromatog., **140**, 47 (1977).
33. D.L.Von Minden and J.A.McCloskey, J.Amer. Chem.Soc., **95**, 7480 (1973).
34. R.L.Hancock and D.L.Coleman, Anal.Biochem., **10**, 365 (1965).
35. R.L.Hancock, J.Gas Chromatog., **4**, 363 (1966).
36. T.Hashizume and Y.Sasaki, Anal.Biochem., **15**, 199 (1966).
37. T.Hashizume and Y.Sasaki, Anal.Biochem., **21**, 316 (1967).

38. T.Hashizume and Y.Sasaki, Anal.Biochem., **24**, 232 (1968).
39. C.W.Gehrke and C.D.Ruyle, J.Chromatog., **38**, 473 (1968).
40. D.L.Stalling, C.W.Gehrke, and R.W.Zumwalt, Biochem.Biophys.Res.Comm., **31**, 616 (1968).
41. E.Chambaz and E.C.Horning, Anal.Biochem., **30**, 7 (1969).
42. V.Pacáková, W.Miller, and J.I.Cernohorsky, Anal. Biochem., **42**, 549 (1971).
43. H.Iwase, T.Kimura, T.Sugiyama, and A.Murai, J.Chromatog., **106**, 213 (1975).
44. C.W.Gehrke and A.B.Patel, J.Chromatog., **130**, 102 (1977).
45. N.I.Gold and S.H.Sturgis, J.Biol.Chem., **196**, 143 (1952).
46. A.Bendich, Methods in Enzymology, **3**, 751 (1957).
47. A.Shatkin, "Metody Virusologii i Molekulyarnoi Biologii" (Methods in Virology and Molecular Biology), Izd.Mir, Moscow, 1972, p.405.
48. D.B.Lakings and C.W.Gehrke, Clin.Chem., **18**, 810 (1972).
49. A.Razin and J.Sedat, Anal.Biochem., 77, 370 (1977).
50. M.V.Kashutina, S.P.Ioffe, and V.A.Tartakovskii, Uspekhi Khim., **44**, 1620 (1975)[Russ.Chem.Rev., No.9 (1975)].
51. R.J.Helbes, Tijdshr.Chem.Instr., 118 (1968).
52. V.Miller and V.Pacáková, Chem.Listy, 67, 1121 (1973).
53. I.A.Muni and C.H.Altschuler, Amer.Lab., **6**, 5 (1975).
54. V.Miller, V.Pacáková, and E.Smolkova, J.Chromatog., **119**, 355 (1976).
55. A.M.Lawson, K.N.Stillwell, M.M.Tacker, K.Tsuboyama, and J.A.McCloskey, J.Amer.Chem. Soc., **93**, 1014 (1971).
56. C.W.Gehrke, D.L.Stalling, and C.D.Ruyle, Biochem. Biophys.Res.Comm., **28**, 869 (1967).
57. C.W.Gehrke and D.B.Lakings, J.Chromatog., **61**, 45 (1971).
58. J.J.Dolhum and J.L.Wiefers, Org.Mass Spectrom., **3**, 669 (1970).
59. S.E.Hattok and J.A.McCloskey, Anal.Chem., **46**, 1378 (1974).
60. S.Tsuboyama and J.A.McCloskey, J.Org.Chem., **37**, 166 (1972).
61. D.L.Von Minden, R.N.Stillwell, W.A.Koenig, K.J.Liman, and J.A.McCloskey, Anal.Biochem., **50**, 110 (1972).
62. J.B.Westmore, D.C.K.Lin, K.K.Ogilvie, H.Wayborn, and J.Berestinsky, Org.Mass Spectrom., **6**, 1243 (1972).
63. M.A.Quilliam, K.K.Ogilvie, and J.B.Westmore, Biomed.Mass Spectrom., 1, 78 (1974).
64. I.A.Muni, C.H.Altschuler, and J.C.Neicheril, Anal. Biochem., **50**, 354 (1972).
65. D.B.Lakings, C.W.Gehrke, and T.P.Waalkes, J.Chromatog., **116**, 69 (1976).
66. Y.Sasaki and T.Hashizume, Anal.Biochem., **16**, 1 (1966).
67. W.C.Butts, Anal.Biochem., **46**, 187 (1972).
68. W.C.Butts, J.Chromatog.Sci., **8**, 474 (1970).
69. S.N.Alam and R.H.Hall, Anal.Biochem., **40**, 424 (1971).
70. C.W.Gehrke and A.B.Patel, J.Chromatog., **123**, 335 (1976).
71. A.B.Patel and C.W.Gehrke, J.Chromatog., **130**, 115 (1977).
72. V.Rehâk and V.Pacáková, Anal.Biochem., **61**, 294 (1974).
73. D.B.Lakings and C.W.Gehrke, J.Chromatog., **62**, 347 (1971).
74. T.Hashisume, S.Higa, Y.Sasaki, H.Yamazaki, H.Iwamura, and H.Matsuda, Agr.Biol.Chem., **30**, 319 (1966).
75. M.Jacobson, J.F.O'Brien, and C.Hedgooth, Anal. Biochem., **25**, 363 (1968).
76. S.Y.Chang, D.B.Lakings, R.W.Zumwalt, C.W.Gehrke, and T.P.Waalkes, J.Lab.Clin.Med., **83**, 816 (1974).
77. V.Miller, V.Pacáková, and E.Smolková, J.Chromatog., **123**, 216 (1976).
78. J.E.Mrochek, W.C.Butts, W.T.Rainey, Jr., and C.A.Burtis, Clin.Chem., 17, 72 (1971).
79. J.P.Seiler, Anal.Biochem., **75**, 45 (1976).
80. T.P.Waalkes, C.W.Gehrke, R.W.Zumwalt, S.Y.Chang, D.B.Lakings, D.C.Tormey, D.L.Ahmann, and C.G.Moertel, Cancer, **36**, 390 (1975).
81. N.Kotsev, "Spravochnik po Gazovoi Khromatografii" (Handbook of Gas Chromatography), Izd.Mir, Moscow, 1976.
82. C.W.Gehrke and K.Leimer, J.Chromatog., 57, 219 (1971).
83. G.Casale and G.B.Cerber, Clin.Chem.Acta, **69**, 545 (1976).
84. B.H.Most, J.C.Williams, and K.J.Parker, J.Chromatog., **38**, 136 (1968).
85. V.Pacáková and J.Nekvasil, J.Chromatog., **91**, 459 (1974).
86. R.L.Hancock, J.Gas Chromatog., **6**, 431 (1968).
87. H.Kasai, K.Murao, S.Nichimura, J.G.Liehr, P.F.Crain, and J.A.McCloskey, Eur.J.Biochem., **69**, 435 (1976).
88. J.A.McCloskey, A.M.Lawson, K.Tsuboyama, P.M.Krueger, and R.N.Stillwell, J.Amer.Chem.Soc., **90**, 4182 (1968).
89. A.S.Spirin and A.N.Belozerskii, Biokhimiya, **21**, 768 (1956).
90. T.V.Venkstern and A.A.Baev, "Spektry Pogloshcheniya Minornykh Komponentov i Nekotorykh Oligonukleotidov Ribonukleinovykh Koslot" (The Absorption Spectra of the Minor Components and Certain Oligonucleotides of Ribonucleic Acids), Izd.Nauka, Moscow, 1967.
91. G.H.Beaven, E.R.Holiday, and E.A.Johnson, "The Nucleic Acid" (Edited by E.Chargaff, J.N.Davidson), Acad.Press, New York, 1955, Vol.1, p.493.
92. S.K.Vasilenko, S.G.Kamzolova, and A.G.Knorre, Biokhimiya, 27, 142 (1962).
93. Yu.A.Romakov, "Khimiya i Biokhimiya Nukleinovykh Kislot" (The Chemistry and Biochemistry of Nucleic Acids) (Edited by I.B.Zbarskii and S.S.Debov), Izd.Meditsina, Leningrad, 1968, p.10.
94. G.L.Cantoni, H.V.Gelboin, S.M.Luborsky, H.H.Riehards, and M.F.Sibger, Biochim.Biophys. Acta, **61**, 354 (1962).
95. U.I.Krahmer, J.G.Liehr, K.J.Luman, E.A.Orr, R.N.Stillwell, and J.A.McCloskey, Anal.Biochem., **82**, 217 (1977).
96. D.F.Babcock and R.O.Morris, Biochemistry, **9**, 3701 (1970).
97. J.Z.Deutsch, A.Razin, and J.Sedat, Anal.Biochem., **72**, 586 (1972).
98. C.W.Gehrke, Journal of the Association of Official Agricultural Chemists, **55**, 449 (1972).

99. C.D.Upper, J.P.Helgesoh, J.D.Kemp, and C.J.Schmist, Plant.Physiol., **45**, 543 (1970).
100. C.Pantarotte, A.Martini, G.Belvedere, A.Bossi, M.G.Donelli, and A.Friegerio, J.Chromatogr., **99**, 519 (1974).
101. F.Chrzanowski, P.J.Niebergall, R.Mayock, J.Taubin, and E.Sugita, J.Pharm.Sci., **65**, 732 (1976).
102. J.A.F.Wickromashinge and S.R.Shaw, J.Chromatog., **71**, 265 (1972).
103. E.S.McFarlane and G.J.Shaw, Canad.J.Microb., **14**, 185 (1968).
104. E.Borek, Cancer Res., **31**, 596 (1971).
105. B.Weissman, P.A.Bromberg, and A.B.Gutman, J.Biol.Chem., **224**, 423 (1957).
106. B.M.Bollard, R.H.Cuplan, N.Marks, and H.McIlwain, J.Mental.Sci., **106**, 1220 (1960).
107. K.Fink, W.S.Adams, and F.W.Davis, Cancer Res., **23**, 1824 (1963).
108. K.Fink and W.S.Adams, Arch.Biochem.Biophys., **126**, 27 (1968).
109. R.W.Park, J.F.Holland, and A.Jenkins, Cancer Res., 22, 469 (1962).
110. K.Fink and W.S.Adams, Arch.Biochem.Biophys., **126**, 33 (1968).
111. T.R.Waalkes, G.W.Gehrke, W.A.Bleyer, R.W.Zumwalt, C.L.M.Oeweny, K.C.Kuo, D.B.Lakins, and S.A.Jacobs, Cancer Chemother. Rep., **59**, 721 (1975).
112. K.R.Leimer, R.N.Loeppky, and C.W.Gehrke, J.Chromatog., **143**, 104 (1977).
113. V.V.Tets, Vop.Med.Khim., **5**, 585 (1979).
114. V.V.Tets, "Materialy Nauchno-Prakticheskoi Konferentsii Molodykh Spetsialistov Uchrezhdenii Zdravookhraneniya Leningrada" (Proceedings of the Scientific and Practical Conference of Young Specialists in the Establishments of the Leningrad Health Service), Leningrad, 1979, p.71.
115. J.Stadler, Anal.Biochem., **86**, 477 (1978).
116. O.Driessen, D.Devos, and P.J.A.Timmermans, J.Chromatog., Biomed.Appl., **162**, 451 (1979).
117. L.P.Turner, Anal.Biochem., **28**, 288 (1969).
118. L.P.Turner and W.R.Barr, J.Chromatog.Sci., **9**, 176 (1971).
119. E.S.Jennings, Jr. and K.P.Dimick, Anal.Chem., **34**, 1543 (1962).
120. B.S.Emswiler and A.W.Kotula, Appl.Environm. Microbiol., **35**, 97 (1978).

Pavlov First Leningrad Medical Institute,
Holder of the Red Badge of Labour

RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

June 1980

Translated from *Uspekhi Khimii*, 49, 945-965 (1980)

U.D.C. 536.46-543.225

The Use of Mass Spectrometry to Study the Structure of Flames and Combustion Processes

O.P.Korobeinichev

The general characteristic methods of the mass-spectrometric study of flames and combustion processes, and the latest achievements in experimental technique in the molecular-beam diagnostics of flames have been examined. The problems associated with the use of probe methods—the effects of freezing the chemical reactions, translational-vibrational relaxation, and perturbations introduced by the probe in the combustion process—have been analysed. The possibilities provided by the technique have been demonstrated for various examples in the study of the combustion of gaseous, liquid, and solid fuels, including that in various technical arrangements—internal combustion engines and liquid rocket motors. Questions related to the use of mass-spectrometric probes for the study of the mechanism and kinetics of chemical reactions in flames and for the determination of the rate constants of the elementary stages have been discussed. The bibliography contains 53 references.

CONTENTS

I.	Introduction	497
II.	Analysis of problems associated with the use of the mass-spectrometric method of probing flames for the study of the structure of flames and combustion processes	498
III.	Studies of the microstructure of flames and the mechanism and kinetics of chemical reactions in gaseous flames	502
IV.	Non-stationary processes	504
V.	Combustion of condensed and heterogeneous systems	505
VI.	Liquid rocket motors	506

I. INTRODUCTION

Mass spectrometry provides one of the most popular and effective methods of studying flames and combustion processes[1,2]. One reason for this is the universal character of the method, by means of which it is possible: 1) to identify the components present in flames, 2) to determine their quantitative composition (concentrations), and 3) to measure the distribution of these components in the combustion zones (to study the structure of flames) and on this basis to calculate the component fluxes and reaction rates.

Flames involve high-velocity fluxes of reactive gases with high temperature gradients and concentrations of the original components and final and intermediate reaction products. The gaseous components in flames can be classified as stable or highly active—atoms, radicals, ions, and excited species. Their typical maximum concentrations in flames are given below.

Species	N, mole fraction
Stable (CH_4, O_2, H_2O)	0.1—1
Atoms and free radicals (H, O, OH)	10^{-1}—10^{-2}
Ions (CHO^+, H_3O^+)	10^{-7}—10^{-12}
Excited (HF^*)	10^{-6}

The first important problem in the mass spectrometry of flames is the removal of the particles from the combustion zone and their introduction into the ion source of the mass spectrometer. The maximum temperatures in flames lie in the range 1000–3000 °C, and the characteristic times of chemical reactions under these conditions are 10^{-4}–10^{-7} s. To ensure preservation of the particles, the times taken to remove them from the combustion zone must be much shorter than their lifetimes. In the process of probe sampling, it is necessary to lower the temperature rapidly. With "quenching" in this way, it is easiest to preserve stable particles, and most difficult to preserve active species.

Comparison of the mass-spectrometric probe method with non-contact spectroscopic methods reveals two advantages of the former for probing flames: 1) the possibility of recording all species (this is particularly important for such complex systems as flames); and 2) the greater spatial resolving power. For example, in the latest method of laser Raman spectroscopy, the limiting sensitivity of the measurement amounts to 10^{11} particles[3], which for a pressure of 25 mmHg, $T = 2000$ K, and an accuracy of recording of 1% corresponds to a zone with characteristic dimensions of 2 mm. The spatial resolving power of infrared spectroscopy under the same conditions is not better than 0.1 mm.[4] Moreover, in the last case the probing is not local, but is carried out along a straight line, so that the method is applicable only to uniform one-dimensional systems with rigorously parallel fronts—lines of equal concentration (with deviations from the parallel arrangement $\ll 0.1$ mm).

Because of the complexity of the spectrum, the spectroscopic method cannot detect many of the particles existing in flames. At the same time, the spectroscopic method has the important advantage over mass spectrometry that it is a non-contact method, and does not perturb the process being studied. Thus the two methods supplement one another, and to achieve best results in the study of flames and combustion processes it is necessary to use both methods.

Mass spectrometry has for several decades been used successfully to study flames and combustion processes. The monograph by Fristrom and Westenberg[1] described the results of studies in this field obtained up to 1965. In recent years, as a result of the rapid development of experimental technique, new achievements and promising possibilities have appeared in the mass-spectrometric study of flames and combustion processes, but these developments have not yet been adequately reflected in the literature.

II. ANALYSIS OF PROBLEMS ASSOCIATED WITH THE USE OF THE MASS-SPECTROMETRIC METHOD OF PROBING FLAMES FOR THE STUDY OF THE STRUCTURE OF FLAMES AND COMBUSTION PROCESSES

1. Technique for Removing the Specimen

Probe sampling is an extremely simple process. Two types of apparatus are used as probes. The first are the so-called "isokinetic" micro-probes—cones with a small aperture angle (10–20°), which remove a specimen of gas with the velocity of the advancing flux; the aperture in the apex of the probe being ~10–100 μm. The advantages of samplers of this type are the small aerodynamic and thermal perturbations of the flame; their disadvantages are the poor conditions for quenching the chemical reactions and preserving active species. Samplers of this type are used to study systems which react slowly. Probes of the second type are sonic probes, at the inlet to which the velocity of the gas is equal to the velocity of sound; they consist of cones having an aperture angle of 30–40° or more. As a result of the expansion of the flow at the inlet into the cone, a supersonic stream is formed. The decrease in temperature and the quenching of the chemical reactions take place at a distance of several times the diameter of the opening in the probe. After the sample has been removed, it is necessary to introduce it without distortions into the ion source of the mass spectrometer. The input systems are of two types. In the first, the gas being analysed is introduced into the ion source in the form of a molecular beam, and in the second it is introduced in the form of a supersonic stream, from which the molecular beam may subsequently be formed.

2. Application of the Molecular-beam System for Specimen Removal

Molecular beams represent the most effective system for transporting the particles removed from the flame to the ion source of the mass spectrometer, since the absence of collisions of the particles of the beam with one another and with the walls of the sampling and input system ensures the best conditions for preserving the particles. There are two types of source of molecular beams: effusion and gas-dynamic (supersonic). The molecular beam is formed as a result of the flow of the gas into a vacuum through a small opening of diameter d. Depending on the value of the Knudsen number $\mathrm{Kn} = \lambda/d$ (where λ is the mean free path of the gas molecules in the source), it is possible to have two flow conditions: effusive for $\mathrm{Kn} \gg 1$, and supersonic for $\mathrm{Kn} \ll 1$.[5]

The most important advantage of the gas-dynamic source compared with the effusion source is that it can be used to obtain beams which are two orders of magnitude more intense than those obtained using the effusion source.

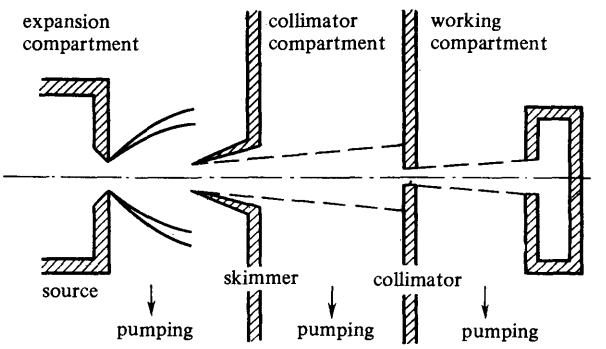


Figure 1. Basic elements of the beam created by a gas-dynamic source.

The principal elements of the beam created by a gas-dynamic source are represented in Fig. 1. The flux expands, flowing through the opening, and forms usually a hypersonic free stream in the expansion compartment, which is evacuated to 10^{-2}–10^{-4} mmHg.[5,6] The purpose of the conical separator (skimmer) is to pass the main body of the free stream without perturbations and with a highly ordered motion into the collimator compartment, in which a high vacuum (typically ~10^{-6}–10^{-7} mmHg) to exclude scattering, is created. The collimator

is designed to separate the working beam, which passes into the working compartment of the mass spectrometer.

The general idealised characteristics of the system have been determined[7], with the following assumptions: 1) the expansion is isentropic as far as the skimmer; 2) the flux passes unperturbed through the skimmer; and 3) collisions between the molecules do not take place after the skimmer. For Mach numbers greater than 3, these assumptions lead to the following basic equations defining the characteristics of the beam[5].

The flow rate through the skimmer N_S (molecule s^{-1}) is

$$N_s = \frac{1}{4}\pi d_s^2 n_s a_0 M_s \{1 + [(\gamma - 1)/2] M_s^2\}^{-1/2},$$

where a_0 is the velocity of sound in the gas at rest, γ the ratio of the specific heats, d_S the diameter of the opening in the skimmer, and M_S and n_S the Mach number and density of the molecules at the inlet to the skimmer, related isentropically to the parameters in the source. These quantities can be calculated, and are functions of the distance between the sonic opening and the skimmer. The rate of flow of gas through the collimator N_C is

$$N_c = \frac{1}{2} n_s a_0 \left(\frac{\pi}{4} d_c^2\right)\left(\frac{\pi}{4} d_s^2\right) \frac{M_s (3 + \gamma M_s^2)}{\pi L_s^2 \{1 + [(\gamma - 1)/2] M_s^2\}},$$

where d_C is the diameter of the collimator, and L_S the distance from the collimator to the skimmer.

The picture of the flow given above relates to the ideal case where the scattering of the molecules of the beam is negligible. These conditions can be established only in an assembly in which a high degree of evacuation of the background and scattered gases is ensured by the use of: a) highly efficient pumps and the required geometry of vacuum compartments having a high transmitting capacity at all stages of the evacuation; b) sufficiently large openings in the skimmer and aperture angles of the cone of the skimmer; and c) sufficiently sharp edges of the opening in the skimmer and a high degree of cleanliness in the mechanical treatment of its surface. Otherwise, the formation of shock waves, the penetration of the background gas into the beam, can occur, leading to scattering of the molecules of the beam, etc.

According to calculated data, the intensity of the molecular beam should increase continuously with decrease in the distance between the openings of the jet and the skimmer. In practice, however, decrease in this distance is accompanied by an increase in the pressure between the jet and the skimmer, as a consequence of the decrease in the transmitting capacity of the gap between the jet and the skimmer (particularly in the case where a cone having a small aperture angle is used as jet–sampler). This in turn leads to decreased intensity of the beam due to scattering.

3. Effects of Freezing the Chemical Reactions

To obtain a representative sample, it is necessary that effective freezing of the chemical reactions and the internal state of the particles takes place during their removal. In a typical case, the expansion takes place in several microseconds and involves several thousand bimolecular collisions. Relaxation of the translational temperature is achieved; at the end of the expansion, the rotational temperatures are considerably higher than the translational temperatures; the vibrational relaxation is much less complete than the rotational relaxation. In molecules frozen as a result of the expansion, unimolecular reactions may take place along the path of their track in the detector compartment. The disappearance of active species, atoms, radicals, and ions may take place during the expansion of the gas, as a result of bimolecular reactions. Calculations have been carried out[8], which make it possible to estimate the probability of the disappearance of particular species during the expansion of the flux in the removal of a sample, if the rate constants of the reactions taking place are known. These calculations give encouraging results, which make it possible to neglect the above effect in many cases of interest.

It should be borne in mind that the above applies fully only to the molecular-beam method of removing the specimen using samplers in the form of a cone having an aperture angle of 30° and with a sufficiently large opening at the apex. In this case the main body of the stream from which the molecular beam is subsequently formed is unperturbed. This is due to the small dimensions (compared with the diameter of the stream) of the width of the boundary layer, which is formed on the inner walls of the probe during the expansion of the specimen and in which chemical reactions may take place with a high probability (including heterogeneous catalytic reactions on the walls of the probe). When capillary micro-probes having cones with small aperture angles (10°) are used, freezing of the chemical reactions does not take place effectively.

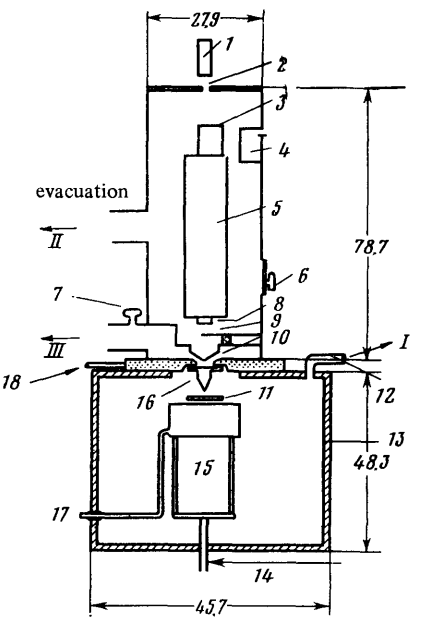


Figure 2. Apparatus of Biordi and coworkers[10]: *1*) laser, *2*) window, *3*) detector, *4*) cold trap, *5*) detector of the mass spectrometer, *6,7*) ionisation lamps, *8*) ion source, *9*) beam modulator, *10*) skimmer, *11*) flame, *12*) copper flange, *13*) combustion chamber, *14*) device for moving the burner in the combustion chamber, *15*) planar burner, *16*) probe, *17*) inlet for the gaseous components of the fuel, *18*) cooling water; *I*) to booster pump. *II,III*) to diffusion pump.

4. Apparatus with Molecular-beam Removal of Specimens from the Flames and Mass-spectrometric Detection

In recent years, with the development of experimental technique in various laboratories throughout the world (the National Bureau of Standards[9], the Bureau of Mines[10,11], the

Institute of Gas Technology[12], etc.[13] in the USA, the Rocket Propulsion Establishment[14] in England, in Belgium[15], etc.), assemblies have been produced with molecular-beam removal of the sample and subsequent mass-spectrometric analysis of the flames, making it possible to record atoms and radicals in the flames.

In the USSR there are assemblies for studying the kinetics of the reactions of atoms and radicals under isothermal conditions in the stream (the "diffusion cloud in the flux" method[16]). An important contribution to the molecular-beam mass spectrometry of flames (particularly atmospheric flames) was made by Greene and Milne[17], whose review systematised work carried out in this field up to 1968.

Fig. 2 represents a typical assembly (that of Biordi and coworkers[10,11]) used to study the structure of gaseous flames and the mechanism of their inhibition. It includes a combustion chamber with a stationary planar burner, capable of moving relative to the probe, which consists of a quartz cone. The assembly also includes a system for forming and detecting the molecular beam (skimmer, modulator, etc.). A quadrupole mass spectrometer was used as detector.

Similar assemblies have been used to study the distribution of the concentrations of atoms, molecules, and radicals in flames. Quadrupole and time-of-flight mass spectrometers are mainly used as detectors. The choice of quadrupole mass spectrometers is related to their very high sensitivity (reaching 10^{-15} mmHg). Time-of-flight mass spectrometers, which have a lower sensitivity than quadrupole instruments, have a much higher speed of operation, which makes it possible to use them to study fast processes. To separate the signal of the beam against the background of the molecules scattered by the walls of the compartment, mechanical modulation of the beam (by chopping it) and subsequent synchronous detection are used; the frequency of the modulation varies from several tens to several hundred Hertz. When modulation of the beam is used, the signal : noise ratio increases by a factor of 10^2–10^4. When this technique is used, the sensitivity of the detecting apparatus also increases considerably. A tendency to use computer control with mass spectrometers can be observed.

An important problem is to increase the heat resistance of the material of the probe. The maximum temperatures in the combustion zone amount to 1000–3000 °C, and are often higher than the melting point of the material used as sampler. The material of the sampler should satisfy the following requirements: 1) it should have a high melting point, and 2) it should be inert, and should not be broken down in the high-temperature active gaseous medium. The materials most frequently used for samplers are quartz, corundum, and refractory metals (platinum, tantalum, and a tantalum–hafnium alloy). Probes consisting of metals having a much higher coefficient of thermal conductivity than quartz and corundum, however, remove heat from the combustion zone much more rapidly than probes of quartz and corundum, and hence introduce greater thermal distortions into the flame. High-temperature ceramics can be recommended as probe materials. Difficulties arise in the construction of microprobes, however, when ceramics are used. The opening at the apex of the probe should be small and have a small wall thickness, and the length of the channel should be less than the diameter of the opening in the probe. The skimmer should have sharp edges, and the walls a small roughness factor, to prevent the production of reflected shock waves.

To select the optimum parameters for the assembly (in particular the distance between the sampler and the skimmer L), a number of authors have studied the dependence of the intensity of the beam I on L/d (for a fixed pressure p in the source; d is the diameter of the opening in the sampler) or the relationship $I = f(p)$ for different L/d. The data obtained by different authors do not show satisfactory agreement. According to some workers[18,19], the $I = f_1(L/d)$ curve has a maximum at $L/d = 30$–100, whereas according to others[12], the intensity increases continuously with decrease in L/d to 2–3. In the apparatus of Greene and Milne[18], the intensity of the molecular beam reached 10^{17} molecule cm^{-2} s^{-1} at a pressure of 1 atm in the source. The authors cited carried out detailed studies with individual gases and their mixtures, and showed that the intensity of the peak I_i of a component in a mixture is proportional to its partial pressure in the source p_i and its molecular mass M_i:

$$I_i = kp_iM_i.$$

5. Perturbations Introduced by the Probe

This question is one of the basic factors determining the quantitative aspect of the mass-spectrometric probing of flames. It is therefore not surprising that a large number of experimental and theoretical studies have been devoted to its examination. The most important perturbations introduced by the probe in the combustion process are aerodynamic and thermal. The probe acts as a material and heat sink, and this leads to the distortion, close to the probe, of the lines of equal concentrations and temperature in the flow. Since the component of the gas velocity along the axis of the probe is, close to it, greater than the gas velocity in the advancing flux, the lines of equal concentrations will be displaced in the direction of the probe (bent towards it) by an amount proportional to the diameter of the opening in the probe. This feature must be taken into account when matching the temperature (generally measured without the probe) and concentration profiles.

It should also be noted that with change in the temperature distribution in a flame without a probe as a result of the flow around the thermocouple, an aerodynamic track is formed; this produces a displacement of the lines of equal concentrations and temperatures by an amount proportional to several times the diameter of the thermocouple junction; an analogous effect is observed when the flux flows around the probe. These displacements must also be taken into account when matching the temperature and concentration profiles. It should be noted, however, that up to the present there has been insufficient quantitative study of these questions. A method for matching temperature and concentration profiles has been proposed[20], but it requires a more rigorous quantitative basis.

The aerodynamic perturbations introduced by a point sink into an advancing plane-parallel flux were calculated by Rosen[21], who found the velocity field close to the sink and calculated the dependence of the distance z (in units of the radius of the sink r) at which the vertical component of the velocity v_y/v_∞ is 5% on the sample removal factor $\alpha = Q/\pi r^2 v_\infty$ (where Q is the bulk velocity of the sink). For example, for $\alpha = 2$ (determined experimentally[22]), $z/r = 2$, that is breakdown takes place at a distance from the probe smaller than the diameter of its opening. A real probe, however, consists not only of a sink but also of an obstacle in the form of the walls of the probe, the thickness of which may be many times the diameter of the opening. Allowance for this feature in the quantitative examination of sampling problems may lead to results different from those obtained by Rosen[21].

In calculations of the isentropic flow of a gas close to and inside a probe[13], it was found that cooling as a result of the expansion of the gas specimen being analysed takes place even before the aperture of the probe (where the gas velocity is equal to the velocity of sound) at a distance of

~(1–1.5)d. Thus the gas temperature decreases by 5% at a distance d from the aperture upstream along the flux, and by 20% in the cross-section of the aperture. Thus the freezing of the chemical reactions in the gas specimen being removed begins even before its entry into the probe; the result of the analysis therefore refers to a point separated from the probe by a distance equal to its diameter.

A more important effect than that examined above is the cooling of the gas in front of the probe by the removal of heat by the latter. This question has been examined theoretically[23]; it was shown that the decrease in temperature may reach 8.5% under typical experimental conditions. The question has also been studied experimentally[24]. The experiments were carried out as follows: a thermocouple was placed at a definite point in the flame front, and the probe was placed at different distances from the thermocouple. When the probe was situated at a considerable distance from the thermocouple (greater than the width of the combustion zone), it had no influence on the thermocouple readings. As the probe approached the thermocouple, the temperature decreased; the maximum effect was ~150 K. The distribution of the temperature of the flame of the planar burner was measured by the thermocouple without the probe and with the probe placed at a distance of 2d from the thermocouple (the aperture angle of the probe was varied). The experimental results (Fig. 3) show that a probe with a cone aperture angle smaller than 40° does not distort the temperature profile in the flame zone (except for temperatures close to the flame temperature), but displaces it as described above. In the case given, this displacement amounted to 0.5 mm, which is one tenth of the width of the combustion zone, and was much greater than the diameter of the opening in the probe (which was equal to 0.1–0.14 mm).

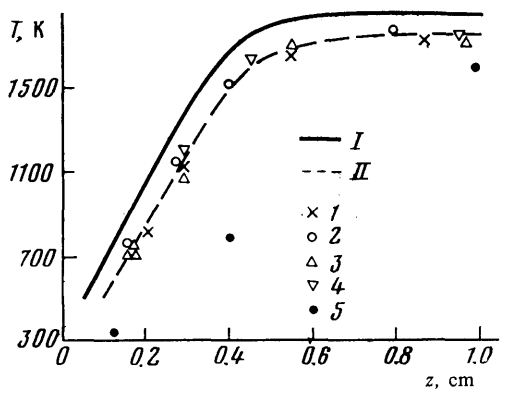


Figure 3. Temperature distribution in the flame of a planar burner (z is the distance from the burner surface) without a probe (I) and with probes (II) having different hole dimensions d and aperture angles α' of the cone. The distance between the thermocouple and the probe was equal to twice the diameter of the opening in the probe; α': 1, 2) 10–15°; 3) 40°; 4) 64°; 5) 78°; d, μm: 1) 137.5; 2) 51; 3) 114; 4) 100; 5) 87.5.

In the experiments described above, the aperture angle of the cone of the probe was varied. When the aperture angle of the cone is greater than 40°, it influences the concentration and temperature distributions[24]. Increase in the aperture angle of the cone apparently increases the heat losses into the probe, and the flame front is no longer one-dimensional. On the other hand, decrease in the aperture angle of the cone of the probe below 40° leads to an increase in the thickness of the boundary layer inside the probe near the inlet hole. This leads to an increase in the probability of the disappearance of the active species (particularly atoms, radicals, and ions) on the walls of the probe. Thus the optimum aperture angle of the cone of the probe is 30–40°.

The distortions of the concentration gradient during sampling with a probe under isothermal conditions have been studied theoretically and experimentally[22]. It was concluded that the effect of distortion of the concentration gradient can be neglected if the ratio of the dimensions of the opening in the probe to the width of the reaction zone is much less than unity. Thus to decrease the distortions it is possible to recommend a reduction in the size of the opening in the probe. Decrease in the size of the opening in the probe, however, leads to an increase in the proportion of the boundary layer and hence to an increase in the distortion of the composition of the gas in the specimen (chiefly the concentrations of the active species, for which the probability of disappearance increases in the boundary layer as a result of homogeneous and heterogeneous-catalytic reactions).

To estimate how the composition and concentration profiles of the specimen are distorted during its removal, a number of authors have carried out independent measurements of various parameters by other non-contact methods. For example, the distributions of the concentrations of hydrogen in an H_2–O_2–N_2 flame have been determined by mass-spectrometric and optical methods (Fig. 4).[9] The concentrations of OH radicals in the flame for 10.3% CH_4–21.6% O_2–68.1% Ar ($p = 0.042$ atm, $T = 1835$ K), measured optically (from the absorption), by mass spectrometry, and by the method of balanced reactions (from the data in Ref. 9) at a point 3 cm above the surface of the burner were 7.8×10^{14}, 15.5×10^{14}, and 16.9×10^{14} particles cm^{-3} respectively.

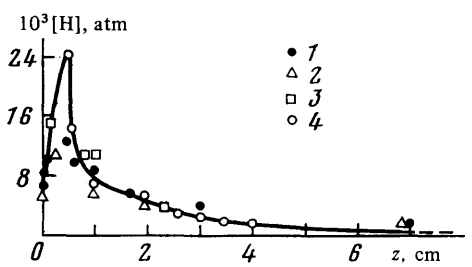


Figure 4. Concentration profiles of hydrogen atoms in an H_2–O_2–N_2 flame, measured by the mass-spectrometric method using ceramic (1) and metallic (2, 3) probes and by an optical method (4).

As shown below, the constants for a number of elementary chemical reactions, found by the treatment of data obtained by mass-spectrometric probe methods, show satisfactory agreement with published data[25] and data obtained independently by other methods. Thus in spite of the perturbations introduced by the probe method, it can be used to determine with sufficient accuracy the chemical structure of the flame front, the concentrations of the reacting components, and the kinetics of chemical reactions in flames.

III. STUDIES OF THE MICROSTRUCTURE OF FLAMES AND THE MECHANISM AND KINETICS OF CHEMICAL REACTIONS IN GASEOUS FLAMES

1. Equations Describing a Planar Laminar Flame

The equations defining the behaviour of a one-dimensional (planar) laminar flame are given below[1].

1. Equation for the conservation of mass:

$$\rho v = \rho_0 v_0 = \text{const},$$

where v is the velocity of the flux, and ρ the density.

2. Equation for the conservation of the fluxes of the individual compounds:

$$\frac{d}{dz}[N_i(v + V_i)] = \sum_{j,k=1}^{N'} k_{jk} N_k N_j;$$

Thus the derivative of the flux of a compound at any point in the flame should be equal to the rate of the appearance or disappearance of this compound as a result of the chemical reaction; k_{jk} is the rate constant for the reaction of the two compounds j and k; the sign of k_{jk} depends on whether the compound i appears or disappears in this reaction; N_i is the concentration of the ith component; V_i the diffusive flux of the ith component; N' the total number of components; and z the coordinate in the direction of which all the characteristics change.

3. The equation of state:

$$p = NRT; \quad N = \sum_{i=1}^{N'} N_i .$$

The velocity of the diffusive flux of the ith component is defined as

$$V_i = \frac{N^2}{N_i \rho} \sum_{j=1}^{N'} M_j D_{ij}^* \frac{d}{dz}\left(\frac{N_j}{N}\right) - \frac{D_i^{*T}}{N_i M_i} \frac{d}{dz} \ln T .$$

Here, D_{ij}^* and D_i^{*T} are the coefficients of binary diffusion and thermal diffusion, and M_i is the molecular mass of the ith component. This is the equation of Fick's law, applied to multi-component systems, with an additional term (the last) which takes account of thermal diffusion.

These equations are the basic equations describing the change in the characteristics in a laminar planar flame. In the analysis of data on the structure of flames, it is sometimes convenient to use an additional variable. This is the fraction of the flux of the mass of the ith component G_i, defined as

$$G_i = \frac{N_i M_i}{\rho v}(v + V_i).$$

It characterises that fraction of the total mass flux through unit area due to the diffusion and convection of the compound i.

The basic equations of a one-dimensional flame can be written in a more compact form using the variable G_i. For a planar flame, the equations for the conservation of the compounds can be written in the form:

$$\frac{\rho_0 v_0}{M_i} \frac{dG_i}{dz} = \sum_{j,k=1}^{N'} k_{jk} N_j N_k = R_i. \qquad (1)$$

If the concentration and temperature distributions are measured experimentally, the differential equations (1) can be used to find the rates of formation or disappearance of the compounds, and then the velocities and rate constants of the elementary reactions in flames for different experimental conditions.

2. Microstructure of Flames and Determination of the Rate Constants of the Elementary Stages

Figs. 5 and 6 give as examples the results of the mass-spectrometric study of the microstructure of the flame CH_4 (9.62%)–O_2 (21.4%)–Ar (68.97%) at a pressure of 32 mmHg.[10] Fig. 7 gives the rates of the reaction of the principal stable compounds in the zone of the flame, obtained by computer treatment of the data in Fig. 5 using the equations given above and specially developed programs[26]. Subsequent treatment of the data on the reaction rates of the stable components in the flame makes it possible to determine the rate constants of the elementary reactions if their mechanisms are known.

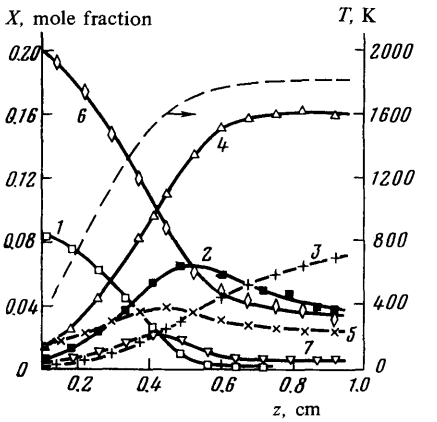


Figure 5. Temperature and concentration profiles for the principal stable components of the flame: *1*) CH_4; *2*) CO; *3*) CO_2; *4*) H_2O; *5*) H_2; *6*) O_2; *7*) CH_2O (× 20).

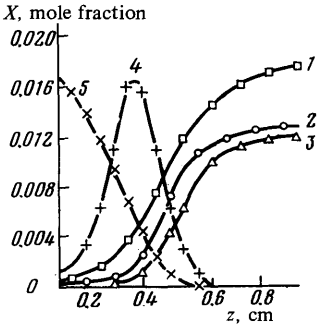


Figure 6. Concentration profiles for the principal intermediate products of the flame: *1*) H (× 0.8); *2*) OH; *3*) O; *4*) CH_3 (× 5); *5*) CH_4 (× 0.2).

Baulch and coworkers[26] give as an example the determination of the rate constant of the forward reaction

$$H + O_2 \underset{k_r}{\overset{k_f}{\rightleftarrows}} OH + O$$

from the data obtained by probing a CH_4–O_2 flame. The rate of the reaction of molecular oxygen in the flame, found from the concentration profile of O_2, is defined by the equation:

$$R_{O_2}=k_f[H]\cdot[O_2]-k_r[OH]\cdot[O].$$

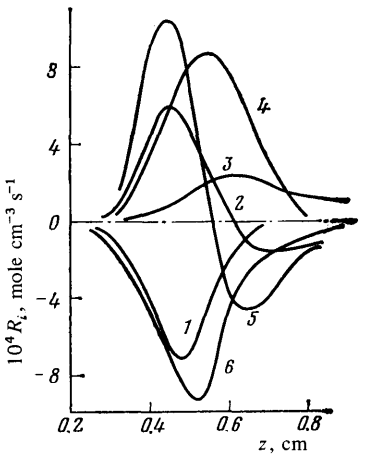


Figure 7. Profiles of the velocities of the reactions of the principal stable components in the flame: *1–6*) see Fig.5.

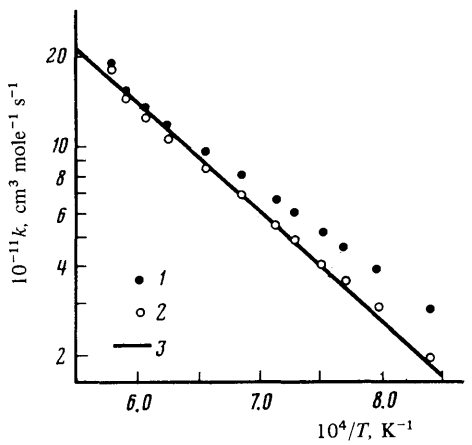


Figure 8. Arrhenius relationship for the rate constant of the reaction $H+O_2\rightarrow OH+O$; *1*) calculation from Eqn.(2) using experimental data; *2*) calculation using a more complex equation, taking account of the consumption of O_2 in its reaction with the radical HCO; *3*) straight line obtained from a critical analysis of published experimental data.

The square brackets denote the concentrations of the corresponding compounds. From the equilibrium constant of the above reaction K_{equil}, the quantity R_{O_2} can be expressed in terms of the mole fractions of oxygen and the radicals X_{OH}, X_{O_2}, X_H, and X_O, the profiles of which are known:

$$R_{O_2}=(p/RT)^2k_f(X_{OH}X_O/K_{equil}-X_HX_{O_2}). \qquad (2)$$

Fig.8 gives in Arrhenius coordinates the results of the calculation of k_f from this equation using experimental data[26], the results of a calculation using a more complicated equation taking account of the consumption of O_2 in the reaction with the radical HCO (using the published values of the rate constant of this reaction), and also the results of a critical analysis of published experimental data obtained independently over a wide range of temperatures using other experimental methods. It can be seen that the agreement is satisfactory.

Table 1. Magnitudes of the errors in the determination of the rate constants of the elementary reactions from mass-spectrometric studies of the microstructure of flames[25].

No.	Reaction	Temp. range, K	Smoothing, %	Matching of the temperature and concentration profiles, %	Temp. dependence of the intensities of the peaks of the fragment ions, %
1	$H+O_2\rightarrow OH+O$	1300—1500	20	35	—
	»	1500—1700	5	20	—
2	$H+CH_4\rightarrow CH_3+H_2$	1325—1500	30	35	20
	»	1500—1700	40	25	10
3	$CO+OH\rightarrow CO_2+H$	1425—1575	20	30	3
	»	1575—1725	10	30	3
4	$CH_3+O\rightarrow H_2CO+H$	1550—1650	20	25	5
	»	1650—1750	30	25	15
5	$H+CF_3Br\rightarrow HBr+CF_3$	1000—1300	15	25	—
	»	1300—1600	20	20	—

Table 2. Comparison of reaction rate constants determined from mass-spectrometric studies of the microstructure of flames[25] and found by other methods (see Table 1 for the numbering of the reactions).

Reaction No.	T, K	Rate constant (Ref.25)	Data obtained by other methods	Refs.
1	1300—1700	$7.5\cdot10^{13}\exp(-13500/RT)$	$2.2\cdot10^{14}\exp(-16900/RT)$; 700—2000K	26
2	1325	$7\cdot10^{11}$	$3.1\cdot10^{13}\exp(-8200/RT)$; 1200—1800K	27
2	1540	$2\cdot10^{12}$		
2	1665	$4.7\cdot10^{12}$	$(3.2\pm0.6)\cdot10^{12}$; 1600 K	15
2	1700	$7.5\cdot10^{12}$		
3	1425—1725	$4.6\cdot10^{11}$	$k=10.83\pm3.9\cdot10^{-4}\ T$	28
4	1550—1750	$8.2\cdot10^{13}$	$2.6\cdot10^{14}\exp(-2000/RT)$; 1000—2000K	29
4	—	—	$7.4\cdot10^{13}$, 297K	30
5	1000—1600	$2.3\cdot10^{14}\exp(-9200/RT)$	$4.36\cdot10^{15}\exp(-17450/RT)$	31

The problems arising in the determination of the rate constants of elementary reactions from data obtained by probing flames have been listed and analysed[25]: 1) the problem of smoothing the curves drawn through the experimental points, arising from the need for double differentiation of the concentration profiles; 2) the matching of the concentration and temperature profiles; 3) the temperature dependence of the intensities of the peaks of the fragment ions; and 4) the problem of calibrating the mass spectrometer with respect to radicals and atoms. Table 1 gives the magnitudes of the errors arising in the determination of the rate constants of elementary reactions from the results of mass-spectrometric studies of the microstructure of a flame (with the exception of the errors associated with the determination of the absolute concentrations of atoms and radicals in the calibration, which amount to 100%). Table 2 gives the rate constants of elementary reactions, determined from the results of mass-spectrometric studies of the microstructure of flames using probe

removal of samples, and also calculated from experimental data obtained using other methods. It can be seen that the agreement is satisfactory; thus the mass-spectrometric method can ensure the determination of the rate constants of elementary reactions with an accuracy which at the present time is not less than the accuracy of the measurement of the rate constants by other methods (particularly in the high-temperature range).

3. Vibrational–translational Non-equilibrium in Flames

It is necessary to deal particularly with the question of translational–vibrational non-equilibrium in the reaction zone of a methane–oxygen flame[25] and its study by molecular-beam mass spectrometry. The existence of vibrational disequilibrium for certain diatomic radicals in the reaction zone of a flame has been proved directly by spectroscopic methods[32]. The mass-spectrometric probing of flames makes an additional contribution to the study of this question. The translational–vibrational disequilibrium of molecules is revealed in a change (compared with the equilibrium case) in the ratio of the intensities of the mass peaks of the "parent" and fragment ions, since the rate of fragmentation of a complex molecule depends on the degree of vibrational excitation.

In the molecular-beam mass-spectrometric probing of flames and the analysis of the data obtained, three questions are closely related: 1) the above-mentioned temperature dependence of the intensities of the peaks of the fragment ions; 2) vibrational–translational relaxation in the flame; and 3) vibrational–translational relaxation in the expansion of the gas during the removal of the specimen from the flame.

These questions have been analysed[25] for CO_2 and CH_4 molecules in a CH_4–O_2–Ar flame. Account was taken of data on the temperature dependence of the peaks of the fragment ions in the mass spectra of CO_2 and CH_4, obtained using effusion and gas-dynamic molecular beams. From the analysis of the experimental data, it was concluded[25] that translational–vibrational disequilibrium exists for the methane molecule both in the flame and in the process of gas expansion during the removal of the specimen from the flame. For CO_2, in both cases, vibrational–translational equilibrium can be established.

To explain this, the following estimates are given[25]. Under the conditions of the flame, the molecules undergo 10^8 collisions per second. The vibrational–translational relaxation times in a CH_4–Ar mixture were measured, and are equal to 3×10^{-5} s under flame conditions, which corresponds to an average of 3000 collisions. With allowance for diffusion, the flow velocity of methane in the flame is 2500 cm s^{-1}, which corresponds to a delay in the establishment of vibrational–translational equilibrium at a distance of 0.07 cm, comparable with the width of the chemical reaction zone and the high spatial resolving power of the probe. For the CO_2 molecules, however, the velocity of the flux under the same conditions is smaller by an order of magnitude than that for the CH_4 molecules (since the diffusion flux of CO_2, unlike that of CH_4, takes place in the opposite direction to the overall flux) and amounts to 300 cm s^{-1}. Thus the spatial lag of the vibrational relaxation for CO_2 is smaller by an order of magnitude and amounts to ~0.007 cm.

4. Mechanism of Inhibition in Flames

The flame probe method also makes it possible to study the mechanism of the action of additives introduced into a flame, for example to inhibit them. The results of studies of the microstructure of a methane–oxygen flame containing the added inhibitor CF_3Br have been used[26] to calculate the rates of consumption of the inhibitor in the chemical reaction zone of the flame.

The possible reactions involving the consumption of the inhibitor, and their contribution to the total rate of consumption of the inhibitor (CF_3Br) in the flame, as percentages of the experimentally observed maximum rate, are given below:

$CF_3Br \rightarrow CF_3 + Br$	8
$CF_3Br + CH_3 \rightarrow CH_3Br + CF_3$	2
$CF_3Br + O \rightarrow BrO + CF_3$	0.1
$CF_3Br + Br \rightarrow Br_2 + CF_3$	0.1
$CF_3Br + H \rightarrow HBr + CF_3$ + 25 kcal $mole^{-1}$	100

The rate of consumption of the inhibitor at a given point in the combustion zone by each of the possible reactions was determined by multiplying the corresponding rate constant, taken from published data, by the experimentally measured[25] concentration of the inhibitor and the radical at this point. The contribution of the reaction to the total maximum rate of consumption of the inhibitor was determined at the point of maximum rate by dividing the rate of consumption, calculated as described above, by the rate of consumption obtained by mathematical treatment of the concentration and temperature profiles in the flame. The data given show that the principal path in the consumption of the inhibitor is its reaction with hydrogen atoms, which are the main chain carriers in the branched chain reaction of methane oxidation. As a result of this reaction, there is a decrease in the concentration of hydrogen atoms; this leads to a decrease in the rate of the oxidation process and hence in the rate of propagation of the flame.

A cycle of studies has been carried out[33] to investigate the structure of the front of hydrocarbon flames (chiefly propane) and the mechanism of their inhibition. A knowledge of the mechanism of chemical reactions in the flame zone and the mechanism of inhibition makes it possible to develop methods for calculating flame propagation velocities and to establish methods for finding effective combustion inhibitors, which are of considerable importance for preventing fires and explosions.

The technique described above has been used to study the structure of the rarefied flames CH_4–O_2,[10,11] $HClO_4$–CH_4,[14] N_2O–H_2,[34] and C_2H_4–O_2[15] and the atmospheric flames CH_4–O_2 and H_2–O_2.[9,12,13] As a result of these studies, it has been possible in a number of cases not only to establish the mechanisms of the chemical reactions in the flames but also to find various previously unknown rate constants of elementary reactions.

IV. NON-STATIONARY PROCESSES

Dynamic mass spectrometry has found extensive application in the study of non-stationary processes in gaseous and condensed systems: in the study of the propagation of flames and shock waves, the kinetics of fast decomposition reactions, processes in internal combustion engines, etc. The propagation of atmospheric cold flames of butane in a tube (at a velocity of 4 cm s^{-1}) has been studied[35]; the products passed directly into the ion source of a time-of-flight mass spectrometer through a hole made in the wall of the tube by means of a laser.

The rarefied flame in mixtures of chlorine azide and hydrogen, being propagated along a tube at a velocity of 6 m s^{-1} has been studied[36]. The mixture was ignited at one end of the tube, and the probe placed at the other end. A Bendix Aviation Corporation time-of-flight mass spectrometer was used to record the change with time in the intensity of the mass peaks as the combustion wave passed the point where the specimen was consumed (the transit time amounted to

several milliseconds). Considerable concentrations of intermediate products—radicals and atoms—were detected.

The formation of nitric oxide in air in a spark discharge, which is important for investigating the mechanism of spark ignition, has been studied in a flow reactor[37]. The molecular-beam removal of specimens from the working compartment of an internal combustion engine during its operation is also of considerable interest[38]. The dependence of the concentration of propane on the angle of rotation of the crankshaft was measured experimentally. The results make it possible to understand the processes of combustion of the fuel in the engine, and this is important for developing measures to improve its operation.

The chemical structure of the turbulent track produced during the flight of a projectile at supersonic velocity has been studied[39]. A sphere of diameter 16 mm was projected in air at a pressure of 60 mmHg and a velocity of 6 km s^{-1} close to a probe having a molecular-beam system for extracting the sample. The formation of NO in the track was detected, and the time dependence of the concentration of nitric oxide in the track was measured: the decrease in [NO] was recorded over a period of several milliseconds after the flight of the sphere.

One of the most striking examples of the application of time-of-flight mass spectrometry to the study of high-temperature chemical processes is the study of the kinetics of reactions in shock waves[40] and in pulse flash photolysis[41-43] (the reaction times amount to tenths or hundredths of a microsecond).

In spite of the efficiency of the method, however, the time-of-flight mass spectrometer does not yet ensure the accuracy of recording required for carrying out kinetic studies of processes lasting for hundredths of a microsecond. Recently, therefore, new systems have appeared for the mass-spectrometric study of fast processes[44], in which the separation of the ions according to mass is carried out in a magnetic field, and each type of ion is recorded by means of its own collector. The dynamic mass spectrometer has also found extensive application in the study of the kinetics of the fast reactions involved in the decomposition of solid fuels (S.F.) as one of the stages of the combustion process. Work carried out in this field up to 1969 has been reviewed in detail[45].

Mass-spectrometric methods for studying the fast processes involved in the decomposition of solid fuels have continued to develop in recent years. Fig. 9 shows an assembly[46] used to study the fast processes involved in the decomposition of specimens of solid fuels at a pressure of 1 atm under isothermal (time ~ 1 s) and non-isothermal conditions (rate of heating 100–1000 K s^{-1}, close to the rate of heating in the combustion wave of the solid fuel). The assembly contains a heating system, a flow reaction vessel, a pumping system, a time-of-flight mass spectrometer (TFMS), and an automatic recording system, which includes a specially developed device, "Strob", which converts the mass-spectrometric information into digital form, and a PL-150 punch machine.

Examples have been given[46,47] of the study of the decomposition of catalyst-containing mixtures, based on ammonium perchlorate, under conditions of rapid heating, close to the rate of heating in the combustion wave. Correlations have been found between the decomposition and combustion processes.

The use of an automatic system for recording mass-spectrometric information has made it possible to reduce by an order of magnitude the time taken to process the results of measurements and to increase by an order of magnitude the accuracy of the measurement.

V. COMBUSTION OF CONDENSED AND HETEROGENEOUS SYSTEMS

The mass-spectrometric method can be used successfully to study the combustion of solid fuels and the flame structures and kinetics of the chemical reactions in solid fuel flames[48-50].

In the probing of solid fuel flames, additional difficulties arise (compared with gaseous flames); one of these is the difficulty of stabilising the combustion surface relative to the probe. The measurement process should therefore be rapid (several seconds) and have a low inertia. These difficulties have been overcome[48-50].

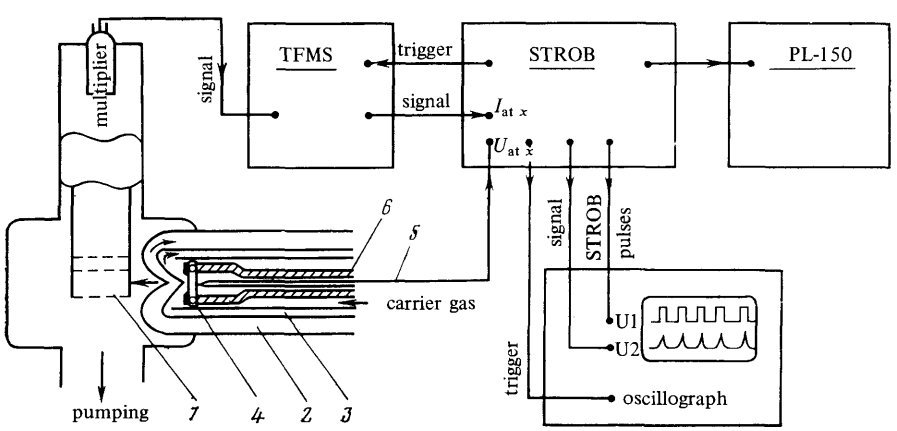


Figure 9. Diagram of the apparatus for studying the fast processes involved in the decomposition of solid fuels: *1*) ion source of the time-of-flight mass spectrometer; *2*) low-pressure compartment; *3*) high-pressure compartment (1 atm); *4*) cell for heating the specimen rapidly; *5*) thermocouple; *6*) current-carrying leads.

As an example, Fig. 10 gives the results of a study of the distribution of the concentration of the reacting components in the flame of a model solid fuel mixture based on ammonium perchlorate (84%) and polymethyl methacrylate (16%) at a pressure of 50 mmHg and an initial temperature of 180 °C.[50] The burning solid fuel specimen was moved in the direction of the stationary probe at a velocity greater than the velocity of combustion. As a result, the probe passed through all the combustion zones, including the reaction layer of the *K*-phase. As the combustion surface approached the probe, in the zone of the flame there was a decrease in the concentrations of the combustion products HCl ($m/e = 36$), $CO_2 + N_2O$ (44), and NO + N_2O (30), and also CO + N_2 (28) and H_2O (18), not shown in Fig. 10, and an increase in the concentrations of the products of the gasification of the oxidant, $HClO_4$, ClO_2 (67), O_2 (32), and NH_3 (16), and the fuel, methyl methacrylate (41).

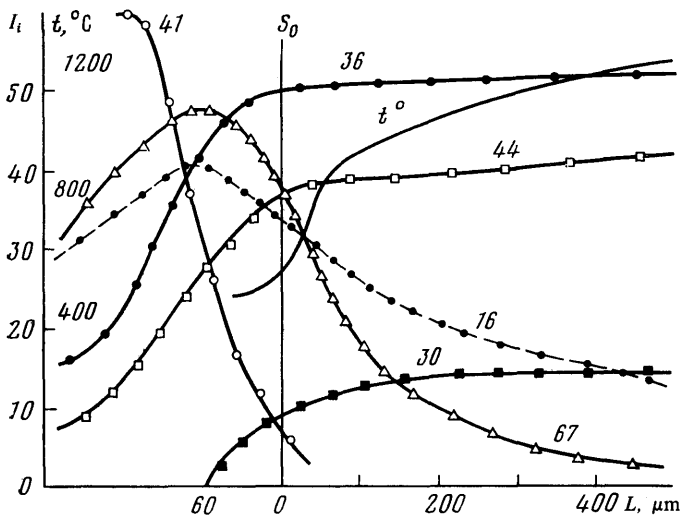


Figure 10. Profiles of the intensities of the peaks of the reacting components I_i in the combustion zone of a solid fuel mixture; S_0 is the combustion surface, $t°$ the temperature, L the distance to the combustion surface, and the figures next to the curve give the values of m/e.

On further movement of the specimen, the probe enters the reaction layer of the condensed phase, making it possible to record (qualitatively at least) the concentrations of gaseous components in the reaction layer of the solid fuel; this cannot yet be done by any other method. As the probe moves into the reaction layer away from the combustion surface, the concentration of oxidant increases, reaches a maximum, and then decreases, whereas the concentration of the products of the gasification of the fuel continue to increase, indicating that the decomposition takes place by a stepwise mechanism. The chemical structure of the combustion wave has also been studied[49,50] for ammonium perchlorate, ballistic powder, and mixtures containing added combustion catalysts.

The results obtained make it possible to deepen and broaden existing ideas regarding the mechanism of the combustion of solid fuels and to obtain data on the kinetics of chemical reactions in solid fuel flames, which can be used to develop mathematical models of their combustion.

There has recently been an increase in interest in the study of the mechanism of the combustion of polymers in connection with the search for polymer combustion inhibitors and methods for decreasing the combustibility of polymers. Mass spectrometry has been used[51] to determine the concentration profiles of the components in the combustion zone of polymethyl methacrylate in air (Fig. 11). The first results have been published[52] on the probing of the diffusion flame of an epoxide resin; the results show the variety of the chemical reactions accompanying the combustion of polymers. Further studies should assist in the investigation of the mechanism of the combustion of polymers.

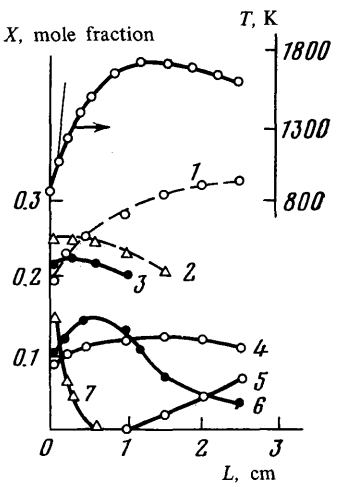


Figure 11. Dependence of the temperature and concentration of the products of the combustion of polymethyl methacrylate in air on the distance L (cm) from the combustion surface of the polymer: *1*) Ar (× 0.5); *2*) H_2 (+0.2); *3*) hydrocarbons (+0.2); *4*) CO_2; *5*) O_2; *6*) CO; *7*) methyl methacrylate.

VI. LIQUID ROCKET MOTORS

The possibilities provided by dynamic mass spectrometry for the study of the processes involved in the mixing of the components and their combustion in liquid rocket motors (LRM) have been demonstrated[53]. An assembly has been developed[53] which makes it possible to study the processes involved in the mixing and combustion of the oxidant (N_2O_4) and the fuel (N_2H_4) in the combustion compartment of a small LRM. Since the final aim of the studies was to analyse the combustion of a system containing the extremely aggressive components F_2–N_2H_4, an attempt was made to create a molecular-beam sampling system. In spite of the fact that a molecular beam was not established in the specimen-removal system, because of the insufficient rate of pumping of the skimmer compartment, it was possible to obtain a number of experimental facts of importance for understanding the processes taking place in the motor.

Fig. 12 shows the experimental assembly, which includes the combustion chamber of the LRM and the sampling system. To study the local concentrations of the components in the combustion compartment of the motor, the jet was replaced by a plate having 29 holes of diameter 0.21 cm, with centres

separated by 1.14 cm. The sampler could be placed at the centre of any of the holes, with a high accuracy. The pressure in the space in which the flow of the combustion products took place was 1 atm.

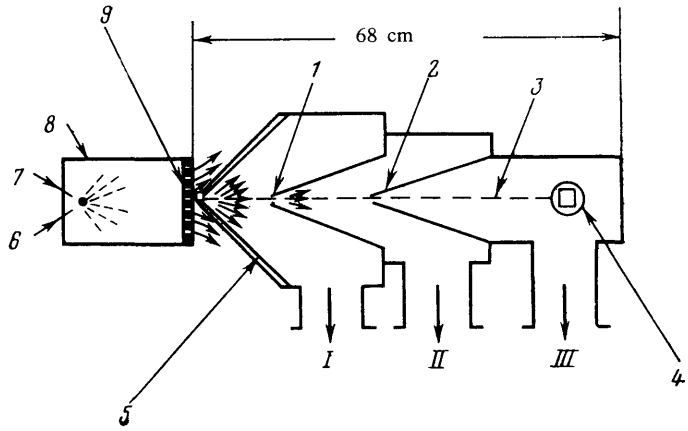


Figure 12. Removal of a specimen from the gases flowing from the combustion chamber of a liquid rocket motor: *1*) skimmer, *2*) collimator, *3*) supersonic molecular beam, *4*) quadrupole mass spectrometer, *5*) water-cooled heat shield, *6*) oxidant, *7*) fuel, *8*) combustion chamber, *9*) water-cooled multi-jet end plate; *I*, *II*, and *III*—evacuation stages.

Preliminary experiments established that the hole in the sampler was closed by fusion when the motor was operated for 6 s, but remained undamaged for a duration of operation of 3–3.5 s, which was found to be sufficient to obtain and record the required experimental results. Treatment of the results of the mass-spectrometric studies established significant non-uniformity of the oxidant/fuel ratio over the cross-section of the combustion chamber of the motor. It was shown that the phenomenon of so-called "stream penetration", previously detected in experiments with cold components, also takes place in the hot working motor. The large quantities of nitric oxide (compared with equilibrium) detected in the mass spectra indicate inadequate efficiency of the combustion in the motor. The results obtained indicate the need to improve the sampling system. The authors cited[53] subsequently intend to increase the rate of pumping the skimmer compartment and to obtain a molecular beam at a pressure at the point of sampling up to 6 atm.

Thus the mass-spectrometric method provides a powerful instrument for studying combustion processes. The possibilities provided by the method have not yet been fully revealed, and are far from exhausted. Mass spectrometry occupies an important position among other methods for studying flames and combustion processes, such as optical, radiospectroscopic, calorimetric, chromatographic, and other methods, each of which has its own advantages and disadvantages. Best results can undoubtedly be achieved by the simultaneous use of the above methods.

REFERENCES

1. R.M.Fristrom and A.A.Westenberg, "Flame Structure" (Translated into Russian), Izd.Metallurgiya, Moscow, 1969.
2. R.M.Fristrom, Int.J.Mass-Spectr.Ion Phys., **16**, 15 (1975).
3. S.A.Akhmanov and N.I.Korotkov, Priroda, 7, 94 (1976).
4. E.M.Davidchuk and V.M.Mal'tsev, Fiz.Goreniya i Vzryva, **5**, 656 (1974).
5. A.M.Brodskii (Editor), "Issledovaniya s Molekulyarnymi Puchkami" (Studies with Molecular Beams), Izd.Mir, Moscow, 1969.
6. J.B.French, AIAA-Journal, **3**, 993 (1965).
7. A.Kantrowitz and J.Grey, Rev.Sci.Instr., **22**, 328 (1951).
8. V.S.Yang, Raketnaya Tekhnika i Kosmonavtika, **11**, 81 (1975).
9. J.W.Hastie, Int.J.Mass Spectr.Ion Phys., **16**, 89 (1975).
10. J.C.Biordi, C.P.Lazzara, and J.F.Papp, Bureau of Mines, Report of Investigation, No.7723 (1974); No.8019 (1975).
11. J.C.Biordi, C.P.Lazzara, and J.F.Papp, in XIV Symp.(Int.) on Combustion, the Comb.Inst., Pittsburgh, 1973, p.367.
12. R.V.Serauskas, G.R.Brown, and R.Pertel, Int.J. Mass Spectr.Ion Phys., **16**, 69 (1975).
13. T.A.Milne and F.T.Greene, in X Symp.(Int.) on Combustion, the Combustion Inst., Pittsburgh, 1965, p.153.
14. G.J.Williams and R.G.Wilkins, Comb.Flame, **21**, 325 (1973).
15. J.Peeters and G.Mahnen, in XIV Symp.(Int.) on Combustion, the Comb.Inst., Pittsburgh, 1973, p.133.
16. V.L.Tal'roze, G.K.Lavrovskaya, A.F.Dodonov, and I.I.Morozov, in Recent Developments in Mass Spectrometry, ed.K.Ogata, T.Hayawaka, University Park Press, Baltimore, 1970, p.1022.
17. T.A.Milne and F.T.Greene, in Advances in High-Temperature Chemistry, Vol.2, ed. by L.Eyring, Acad.Press, New York, 1969, p.107.
18. F.T.Greene, J.Brewer, and T.A.Milne, J.Chem. Phys., **40**, 1488 (1964).
19. A.A.Vostrikov, Yu.S.Kusner, A.K.Rebrov, and B.E.Semyachkin, Zhur.Prikl.Mekhaniki i Tekhn.Fiz., 2, 34 (1975).
20. G.Mahnen, Contribution a l'étude du méchanisme de déflagration. Flammes éthylène–oxygen, Dr.Sc. Thesis, Université Catholique de Louvain, 1973.
21. P.Rosen, Potential Flow of a Fluid into a Sampling Probe, John Hopkins Univ., Appl.Phys.Lab., Rept. C.F.-2248, Silver Spring, 1954.
22. T.Yanagi, Comb.Flame, **28**, 33 (1977).
23. A.N.Hayhurst and D.B.Kittelson, Comb.Flame, **28**, 137 (1977).
24. J.C.Biordi, C.P.Lazzara, and J.F.Papp, Comb. Flame, **23**, 73 (1974).
25. J.C.Biordi, C.P.Lazzara, and J.F.Papp, Comb. Flame, **26**, 57 (1976).
26. D.L.Baulch, D.D.Drysdale, D.G.Horne, and A.C.Lloyd, Evaluated Kinetic Data for High Temperature Reactions, Vol.1, CRC Press, Cleveland, Ohio, 1972, p.9.
27. C.P.Fenimore and G.W.Jones, J.Chem.Phys., **65**, 2200 (1961).
28. D.L.Baulch and D.D.Drysdale, Comb.Flame, **23**, 215 (1974).

29. J.Peeters and C.Vinckier, in XV Symp. (Int.) on Combustion, the Comb.Inst., Pittsburgh, 1975, p.969.
30. N.Washida and K.D.Bayes, Chem.Phys.Letters, **23**, 373 (1973).
31. G.B.Skinner and G.H.Ringrose, J.Chem.Phys., **43**, 3129 (1965).
32. A.G.Gaydon and H.G.Wolfhard, Flames, Chapman and Hall, London, 1970, p.277.
33. G.I.Ksandopulo, Doctoral Thesis, Kirov Kazakh State University, Alma-Ata, 1974.
34. V.P.Balakhnin, J.Vandooren, and P.J.Van Tiggelen, Comb.Flame, **28**, 165 (1977).
35. J.R.Wyatt, J.J.Decorpo, M.V.McDowell, and F.E.Saalfeld, Int.J.Mass Spectr.Ion Phys., **16**, 33 (1973).
36. J.Combourieu, "Tezisy Dokladov Vsesoyuznogo Simpoziuma Kineticheskaya Mass-spektrometriya i ee Analiticheskie Primeneniya, Chernogolovka, 1977" (Summaries of Papers Presented at the All Union Symposium on Kinetic Mass-spectrometry and Its Analytical Applications, Chernogolovka, 1977), p.6.
37. R.M.Fristrom, in F.T.Greene (Editor), "Molecular Beam Sampling Conference Proceedings", Midwest Research Institute, Kansas City, 1972, p.25.
38. E.L.Knuth, in Engine Emissions Pollutant Formation and Measurements, ed.G.Springer, D.Patterson, Plenum, New York, 1973.
39. W.M.Kornegay, in Int.Congr.on Instrumentation in Aerospace Simulation Facilities, Rhode–Saint–Genese, 1971; New York, 1971, p.25.
40. J.E.Dove and D.M.Moulton, Proc.Roy,Soc., A, **283**, 216 (1965).
41. G.B.Kistiakowsky and P.H.Kydd, J.Amer.Chem.Soc., **79**, 4825 (1957).
42. R.T.Meyer, in Time-of-Flight Mass Spectrometry, ed. D.Price, J.E.Williams, Pergamon Press, Oxford, 1969, p.70.
43. K.A.Lincoln, Int.J.Mass Spectr.Ion Phys., **2**, 80 (1969).
44. E.A.Shafranovskii, S.Yu.Semenov, V.D.Grishin, and V.L.Tal'roze, Pribory i Tekh.Eksper., 1, 157 (1974).
45. O.P.Korobeinichev, Uspekhi Khim., **38**, 2113 (1969) [Russ.Chem.Rev., No.12 (1969)].
46. O.P.Korobeinichev, I.N.Skovorodin, S.V.Polozov, Yu.K.Postoenko, I.E.Astrakhantsev, P.G.Safonov, V.A.Kuzin, and V.B.Skomorokhov, Zhur.Fiz.Khim., 51, 1542 (1977) [Russ.J.Phys.Chem., No.6 (1977)].
47. O.P.Korobeinichev, K.K.Kovalenko, and A.I.Lesnikovich, Fiz.Goreniya i Vzryva, **4**, 550 (1977).
48. O.P.Korobeinichev and A.G.Tereshchenko, Dokl.Akad. Nauk SSSR, **231**, 1159 (1976).
49. O.P.Korobeinichev, A.A.Zenin, A.G.Tereshchenko, and V.M.Puchkov, Fiz.Goreniya i Vzryva, **3**, 335 (1977).
50. O.P.Korobeinichev and A.G.Tereshchenko, "Khimicheskaya Fizika Protsessov Goreniya i Vzryva. Gorenie Kondensirovannykh Sistem" (The Chemical Physics of Combustion and Explosion Processes. The Combustion of Condensed Systems), Chernogolovka, 1977, p.73.
51. C.P.Fenimore and F.J.Martin, in The Mechanisms of Pyrolysis, Oxidation and Burning of Organic Materials, Nat.Bur.Stans.Publ., 357 (1972), p.159.
52. V.L.Efremov, B.Ya.Kolesnikov, V.A.Shap'rin, V.K.Manzhos, and G.I.Ksandonulo, "Khimicheskaya Fizika Protsessov Goreniya i Vzryva. Gorenie Geterogennykh i Gazovykh Sistem" (The Chemical Physics of Combustion and Explosion Processes. The Combustion of Heterogeneous and Gaseous Systems), Chernogolovka, 1977, p.14.
53. P.R.Ryason, AIAA Paper No.75-1270 (1955).

Institute of Chemical Kinetics and Combustion,
Siberian Branch,
Academy of Sciences of the USSR,
Novosibirsk

Translated from *Uspekhi Khimii*, 49, 966-997 (1980) U.D.C. 548.31

Theoretical Calculation of the Spatial Distribution of Molecules in Crystals

T.V.Timofeeva, N.Yu.Chernikova, and P.M.Zorkii

The fundamental energetic and geometric framework of the interpretation and prediction of molecular packing is discussed on the basis of results published between 1960 and 1977. The atom-atom potential method is described, and the methods of selecting the parameters of these potentials are examined. An extended tabulation of theoretically determined molecular packing arrangements is presented, listing the form of the chosen potential function, the structure parameters which are treated as adjustable in the minimisation of the energy, and other aspects of the method of calculation. 271 references.

CONTENTS

I. Introduction 509
II. Geometric and energy interpretation of molecular packing 509
III. The atom-atom approximation as a method of calculating the energy of zero-valent interactions 511
IV. Selection of the atom-atom potential parameters from crystallographic data 513
V. Tabulation of theoretical calculations of molecular packing 515

I. INTRODUCTION

The *a-priori* determination of the distribution of molecules in a crystal structure without resorting to experimental data (or with a minimal use of such data) offers many attractive possibilities. Firstly, the very fact that prediction is possible confirms the validity of our views on the fundamental aspects of crystal structure. Secondly, there is now considerable practical interest in the theoretical calculation of structures in cases (e.g. polymers, layered polytypes) where X-ray diffraction cannot give full structural information but it can confirm *a-priori* calculations. Thirdly, these calculations can be useful in computations of approximate, model structures which can then be made more precise by using X-ray diffraction data. Therefore it is not surprising that the early theoretical calculations of the spatial arrangements of molecules in crystals were followed by a large number of publications on the same theme during the past 25–30 years.

The aim of this review is to analyse the results of that work and to assess the prospects of this field of science. We shall examine very recent results, which were not available to previous reviewers[1–4]. Furthermore previous writers[3–5] have tended to ignore work other than their own.

II. GEOMETRIC AND ENERGY INTERPRETATION OF MOLECULAR PACKING

The problem of determining the optimum structure reduces to finding the spatial distribution with a minimum energy. There are at present two ways of formulating the problem. One consists in finding the closest packing of particles, using van der Waals radii. In the absence of directionally specific interactions the tendency to give a close-packed structure is a good guide to finding the arrangement with minimum energy. The second (and stricter) approach is to calculate the arrangement corresponding to a minimum in the intermolecular interaction energy.

In general the calculation of the closest packing of bodies of arbitrary shape presents enormous mathematical difficulties. However in many crystal-chemical problems we can introduce substantial simplifications which allow us to reach a definite solution.

One of these simplifications is to assume that the elementary cell parameters are known. This variant of the problem was solved by Kitaigorodskii[6] for 2,6-dimethylnaphthalene by using a special apparatus (the "structure seeker"), and also for several other crystals[7–9] by computation. The combination of the principle of closest packing with experimentally measured lattice parameters forms the basis of the X-ray method of determining crystal structures developed by Gel'fand, Neigauz, and others[10,11] (the "gully" method).

Another simplification is possible in the case of polymeric molecules. Since the axes of these molecules must be parallel, one degree of freedom is lost. By virtue of this approximation the principle of closest packing allows us not only to predict the arrangement of chains in the cell but also to identify a very limited number of possible elementary cells. Studies of polyethylene by this method were reported by Kitaigorodskii[12,13] and by Segerman[14].

Zorkii and Porai-Koshits[15–17] combine the principle of closest packing with a quantitative calculation of the distribution of objects of arbitrary shape in a plane with the highest reticular density (the streamline trajectory method). This allows them to calculate the most compact type of packing of long-chain molecule (or planar molecules) in a layer whose plane coincides with the plane of the molecule. The crystal structures of $PdCl_2$,[18] $BeCl_2$,[19] Ni dimethylglyoxime[20], and Cu salicylalmethyliminate[21] have been successfully determined by the trajectory method.

The geometric approach continues to be an effective method of interpreting molecular crystal structures. Its value has been enhanced by the publication of an accurate set of van der Waals radii[22,23], obtained by a statistical analysis of a large amount of structural information. However, though it remains a simple and useful tool for qualitative and semi-quantitative estimates, the geometric model is not a serious contender for the quantitative *a-priori* prediction of molecular packing, i.e. the problem to which this review is devoted. The geometric approach is inferior to the energy approach (in that its postulates are less strict and well founded) without in any way making the calculation of the optimum structure (using a computer) more straightforward. Hence it is better to seek a solution of the molecular packing problem directly from calculations of the intermolecular interaction energy. The atom–atom approximation, which is discussed in detail in the next Section, offers a concrete method of calculating this energy.

The energy of a crystal structure consisting of rigid molecules can be expressed as a function of a series of structure parameters:

$$U(a, b, c, \alpha, \beta, \gamma, X_i, Y_i, Z_i, \varphi_i, \theta_i, \psi_i),$$

where a, b, c, α, β, γ are the lattice parameters, X_i, Y_i, Z_i are the coordinates of the centres of gravity of the symmetrical, independent molecules, and ϕ_i, θ_i, ψ_i are the Euler angles which characterise the orientation of these molecules. In special cases the number of independent parameters can be less: thus the energy of rhombic benzene is a function of six parameters only ($U(a,b,c,\phi,\theta,\psi)$). On the other hand the angles which characterise the conformation must be included among the parameters if the molecule cannot be treated as rigid.

By minimising the energy U we can find the structure parameters which offer the optimum molecular packing: in principle this should correspond to the crystal structure experimentally observed. Minimisation is usually applied to the potential energy of the structure. Thus we are in fact examining the structure of the crystal at a temperature close to the absolute zero. However we know experimentally that the vast majority of molecular crystals do not suffer phase transformations over a wide range of temperature (up to room temperature), and their geometric characteristics change very little. Hence the optimum structure for the absolute zero is often also the optimum for room temperature. However a strict formulation of the problem requires calculation of the free energy F of the crystal structure.

Consideration of the simplest model structure, consisting of an assembly of independent oscillators located at lattice sites, shows[24] that the free energy can be expressed as the sum of the following terms:

$$F=U_0+E_0+E_T-TS,$$

where U_0 is the potential energy of the structure at 0 K, and E_0 and E_T are the zero-point vibration and the thermal vibration energy respectively. The free energy of all molecular crystals is usually assumed to consist of these terms.

Molecular crystals are distinguished by a very large difference between the energies of their intramolecular and intermolecular interactions. For this reason Kitaigorodskii suggested[25] expressing the thermodynamic functions of molecular crystals as the sum of two terms: a "molecular" term and a "crystalline" term. The former is related to the structure of the molecules and to their internal vibrations, the latter to the relative position of the molecules and to their external vibrations:

$$U = U^{\text{intra}} + U^{\text{inter}},$$
$$S = S^{\text{mol}} + S^{\text{cryst}},$$
$$E_T = E^{\text{intra}} + E^{\text{ext}}.$$

Using these expressions the free energy of a molecular crystal can be written

$$F = E_0 + (U^{\text{intra}} + E_T^{\text{intra}} - TS^{\text{mol}}) + (U^{\text{inter}} + E_T^{\text{ext}} - TS^{\text{cryst}}) = E_0 + F^{\text{mol}} + F^{\text{cryst}}.$$

Our main interest lies in the evaluation of the term F^{cryst}. In the case of rigid molecules the minimum of the function F^{cryst} coincides with the minimum of the full free energy function.

Two specific ways of calculating F are known at present. The first, described in detail in Ref.26, includes a calculation of the full set of frequencies from the differentials of the potential energy with respect to the structure parameters (expressing the energy U in the atom–atom approximation). The standard free expressions in terms of the frequency distribution function (or density of states function) are then applied. Typical of this approach is a calculation[27] of the equilibrium parameters of the elementary cells of three hydrocarbons at different temperatures.

The second method of calculating the energy F is based on statistical mechanics, and involves a calculation[28] of the configurational integral

$$Q=\frac{1}{N!}\int_{\Omega}\cdots\int_{\Omega}\exp\left\{-\frac{U(q_1,\ldots,q_N)}{kT}\right\}\mathrm{d}q_1\ldots\mathrm{d}q_N,$$

where N is the number of molecules in the system, $U(q_1,\ldots,q_N)$ is the potential energy, and Ω is the volume in configurational phase space occupied by the system. In the calculation the configurations $q_1^{(i)},\ldots,q_N^{(i)}$ are randomly generated in phase space (Monte Carlo method) and the corresponding values of the integrand are averaged. Concrete calculations of this type have been reported for crystals of the intert gases[29,30], N_2,[31] and CO_2.[32] However this approach is too cumbersome for large (or even moderately large) molecules.

Excessive use of computer time can be avoided by using the cell model[33], whose application to the calculation of the thermodynamic functions of molecular crystals is discussed by Holt and coworkers[34]. According to this model the volume occupied by the system is divided into N cells whose centres form the lattice. Each cell contains one molecule whose position and orientation are described by the six-dimensional vector q (which includes three translational and three rotational components). The motion of each molecule is assumed to be independent of the motion of molecules in neighbouring cells. The quantity $U(q)$ is the interaction energy of a given molecule with its neighbours at the centres of their respective cells. If the equilibrium positions of the molecules in the crystal are taken as the centres of the cells, and denoted by $\bar{q}$, then the quantity $U(\bar{q})/2$ is the energy of the crystal structure.

The use of the cell model simplifies the calculation of the configurational integral, which in this case is written

$$Q=\left[\exp\left\{-\frac{U(\bar{q})}{2kT}\right\}\cdot V_t\right]^N.$$

In this expression V_t is the "free volume":

$$V_t=\int_{\Delta}\exp\left\{-\frac{U(q)-U(\bar{q})}{kT}\right\}\mathrm{d}q,$$

where Δ is the cell volume.

This approach, together with the atom–atom potential method[35,36], was used by Pertsin and Kitaigorodskii to calculated the optimum structure and to interpret the polymorphic transitions in benzene[37] and adamantane[38]. We shall discuss this work more fully in a later Section of this review.

The identification of the deepest minima in a multidimensional energy surface constructed from the structure parameters involves calculations as cumbersome as those required by the search for the closest packing. Hence various simplifying assumptions are usually made, and in particular the structure class (the symmetry space group and the type of equivalent positions available to the molecule) is assumed to be known. Thus the reported calculations of molecular structure cannot be claimed to be fully *a-priori*.

The latter difficulty can be largely overcome by the potential function symmetry method developed in Refs.17, 39, and 40. This method allows us to find the structure class most likely to apply to molecules or polymer chains of a given symmetry, and to evaluate the relative probabilities of alternative classes[41,42]. In the calculation of the chain structures of $PdCl_2$ and $BeCl_2$ crystals[18,19] the potential function symmetry method allowed the optimum configuration of the chains to be identified without using an experimental information on the packing of the chains.

III. THE ATOM–ATOM APPROXIMATION AS A METHOD OF CALCULATING THE ENERGY OF ZERO-VALENT INTERACTIONS

Van der Waals (zero-valent) interaction is a quantum effect: in principle it can be described by the standard methods of quantum mechanics. However the difficulties encountered in attempting to solve the Schroedinger equation for systems containing a large number of atoms and molecules are still unsurmountable. Therefore empirical and semi-empirical approaches are almost universally used in concrete calculations of zero-valent interaction energies.

It is usually assumed that the van der Waals interaction consists of several, qualitatively different contributions. Though a strict quantum-mechanical interpretation does not support this assumption, in most cases good agreement between calculation and experiment is obtained by treating the van der Waals forces as consisting of the following terms: 1) an attraction due to dispersion interaction, 2) a repulsion resulting from the close approach of the electron clouds of atoms not bound by valency forces, 3) the electrostatic interaction of the fixed charge distributions, and 4) specific intermolecular interactions such as hydrogen bonds.

Numerous and varied investigations during the last 30 years have shown that all these contributions can be described with adequate precision by assuming additivity of the interaction energy of multi-atomic molecules with respect to the interaction energies of their constituent atoms. This approximation allows us to express the interaction energy of two molecules (in the absence of specific bonding forces) as the sum

$$U = \frac{1}{2}\sum_{ij}(\varphi_{ij} + \psi_{ij}),$$

where ϕ_{ij} are the atom–atom potentials describing the first two of the above contributions, and ψ_{ij} are terms allowing for the interaction of the effective charges on the atoms (the atoms i and j being part of different molecules).

The van der Waals interaction energy within a single molecule can be described in a similar way. If the method of evaluating ϕ_{ij} and ψ_{ij} is known, the conformation of the molecules can be calculated (including the orientation of groups able to rotate round an ordinary bond, and perturbations caused by steric hindrance). Indeed, the first successful application of the atom–atom approximation was in the solution of conformational problems. This approach was pioneered by Hill[43,44] and Barton[45], who worked with compounds in which the effective charges on the atoms were so small that only the repulsion energy and the attraction from dispersion interaction needed to be considered. A detailed description of the many conformational calculations made by the atom–atom approximation is given in Dashevskii's monograph[46].

Summation over the molecules in pairs (i.e. calculation of the energy of interaction of one molecule, taken as the central molecule, with the whole of its surroundings) allows us to express the potential energy of the molecular crystal (U_Σ) in the atom–atom approximation. This quantity is approximately equal to the heat of sublimation extrapolated to the absolute zero (assuming that sublimation does not produce significant changes in the conformation of the molecules or in the energy of intramolecular vibrations). By minimising the quantity U_Σ, treated as a function of the parameters which characterise the relative position of the molecules, the structure of a molecular crystal can (in principle) be calculated theoretically, as stated above.

The ϕ_{ij} potentials are usually approximated by the Lennard-Jones "6–12" potential[47] or by the modified Buckingham "6–exp" potential[48]:

$$\varphi_{ij} = -A_{mn}r_{ij}^{-6} + B_{mn}r_{ij}^{-12},$$
$$\varphi_{ij} = -A_{mn}r_{ij}^{-6} + B_{mn}\exp(-\alpha_{mn}r_{ij}),$$

where the first term describes the attraction and the second the repulsion, the subscripts m and n refer to the types of atom, A, B, and α are empirical parameters, and r_{ij} is the interatomic distance.

In Ref. 49 the atom–atom potentials are expressed in a more general form (as "6–exp, D" potentials):

$$\varphi_{ij} = A\exp(-Br_{ij})/r_{ij}^{D} - C/r_{ij}^{6}.$$

If $D = 0$ this reduces to the "6–exp" potential, and if $B = 0$ and $D = 12$ it reduces to the "6–12" potential.

Recent papers often refer to a "repulsion potential", which we shall denote by "d–d_0". This potential, first proposed by Williams[50], is defined as

$$V_{ij} = \omega(d_0 - d_{ij})^2 \text{ for } d_{ij} < d_0;\ V = 0 \text{ for } d_{ij} > d_0.$$

Here d_{ij} is the interatomic distance, and d and ω are parameters depending on the nature of the interacting atoms. The use of this potential greatly simplifies the minimisation procedure by allowing the method of least squares to be used. The main shortcoming of the "d–d_0" potential is that the quantity $\sum_{ij} V_{ij}$ is not the energy of the structure: it cannot be compared with real physical quantities such as the heat of sublimation. Calculations by the "d–d_0" potential occupy a position intermediate between the geometric and the energy approach.

The method of selecting the appropriate parameters is very important in the application of atom–atom potentials. The usual selection criterion is good agreement between calculation and experiment for several model compounds and several quantities (various thermodynamic functions such as heats of sublimation, compressibility coefficients, components of the elasticity tensor, etc.). The chosen values of the parameters are then applied to other substances, not too different from the model substances. One of the most reliable and widely used methods of choosing the parameters relies on fitting the calculated crystal structure to the experimentally observed structure. This method is discussed in the next Section. The frequencies of intramolecular and intermolecular vibrations in crystals[26] have been used in recent work for optimising the parameters of atom–atom potentials.

Approximate quantum-mechanical formulae are occasionally used in parallel with the purely empirical approach. This is specially true of the parameters A, which can be calculated by the London formula[51] or by the Slater–Kirkwood formula[52], as in Refs. 53–55. In that work the repulsion parameters were found by minimising the potential at the equilibrium distance, which was selected empirically.

The first systematic selection of the parameters of the "6–exp" atom–atom potential in crystal chemistry is due to Kitaigorodskii and Mirskaya[56,57]. Since the parameters A, B, and α have no clear physical significance, these workers used formulae including characteristics of the potential curve such as r_0 (the equilibrium distance), ε (the depth of the potential well), and D (the second differential at the minimum). The advantage of this aproach is that the quantities r_0, ε, and D vary only within narrow limits, and they are sensitive to several specific properties (r_0 to the geometric parameters of the structure, ε to the heat of sublimation, and D to the vibration frequencies and to the elasticity tensor).

A unique feature of Kitaigorodskii's and Mirskaya's approach is their use of the "universal" curve

$$\varphi_{ij} = -0.119\,(r/r_0)^6 + 4.2\cdot 10^4 \exp(-13.6\,r/r_0),$$

obtained by assuming identical potential wells of −0.067 kcal mole^{-1} for the three main types of atom–atom interaction in organic crystals (C...C, C...H, and H...H). The expression also assumes that $r_0\alpha = 13.6$. If the equilibrium distances are known (and they are taken to be 3.8, 3.3, and 2.8 Å for C...C, C...H, and H...H respectively) the parameters A and α can easily be calculated. The parameter B is found to be constant for the three types of interaction.

Table 1. Parameters of the "6–exp" potential used by Kitaigorodskii et al.

Type of interaction	A, $\frac{\text{kcal}}{\text{mole}}\cdot$ Å^6	10^3B, kcal mole^{-1}	α, Å^{-1}	References
C...C	358	42.0	3.58	59
C...O	313.2	57.1	3.85	59
O...O	259.4	77.7	4.18	59
S...S	2346	235.0	3.49	60
S...C	847	99.4	3.54	60
N...N	259	42.0	3.78	61
N...O	256	57.0	3.98	61
C...C	421	71.6	3.68	90
C...H	118	18.6	3.94	90
H...H	29	4.9	4.29	90

Even these "universal" parameters gave an acceptable level of agreement between the calculated energy of the structure and the measured heat of sublimation. However subsequent work led the authors[58] to conclude that the best agreement with experiment is obtained by using atom–atom potential curves with minima of different depth (−0.067, −0.057, and −0.048 kcal mole^{-1} for C...C, C...H, and H...H respectively). The final values of the parameters obtained by Kitaigorodskii and coworkers for these three types of interaction are listed in Table 1 together with their later results[59–61] for interactions involving N, O, and S atoms.

Various combination rules are used to obtain the parameters of interactions between unlike atoms. Thus Scott and Scheraga[54], Hendrickson[62], and Kitaigorodskii and coworkers[59] obtained the parameter α_{mn} by the formula $\alpha_{mn} = (\alpha_m\alpha_n)^{1/2}$. Dashevskii and coworkers[63] relied on another empirical expression: $\alpha_{mn} = 2\alpha_m\alpha_n/(\alpha_m + \alpha_n)$. Similar combination rules were used by these workers for the parameters A_{mn} and B_{mn} in the equation for the "6–exp" potential. Theoretical justifications of the combination rules are given in Refs. 64–66.

Whereas early workers tended to ignore electrostatic interactions in crystals, arguing that their contribution to the energy of the structure was negligibly small[67–69], in more recent work this term is almost invariably included (albeit in different forms).

In principle there are two possible ways of calculating U_{el}, which characterises the electrostatic interaction of two molecules. The first consist in expanding the energy U_{el} in a series with respect to multipoles:

$$U_{el} = U^{(q,q)} + U^{(q,\mu)} + U^{(q,Q)} + \ldots U^{(\mu,\mu)} + U^{(\mu,Q)} + \ldots,$$

where q is the net charge of the molecules, μ is the dipole moment, and Q is the quadrupole moment. The quantity q is finite in charge-transfer molecular complexes, whereas for homomolecular crystals (i.e. crystals composed of identical molecules) $q = 0$ and the corresponding terms in the formula also vanish. For practical purposes the multipole expansion is used relatively rarely: on the one hand, the values of the higher-order multipoles are usually unknown, and on the other hand it is not easy to ascribe to point multipoles (and in particular dipoles) a definite position and orientation with respect to a molecule.

The second method of calculating U_{el} relies on the atom–atom approximation. The continuous distribution of electron density is replaced by a discrete distribution, and an effective point charge (localised near the nucleus) is assigned to each atom in the molecule. Then we can write

$$U_{el} = \sum_{ij} q_i q_j / r_{ij}.$$

The effective charges can be calculated by various quantum-mechanical methods. Some workers[70–72] use the simplest computational scheme, in which the effective atomic charge is treated as the sum of the π- and σ-charges (the former calculated by the simple Hückel method, the latter by the Del Re method[74]). Other workers have used more complex quantum-mechanical approximations[55,75]. As an alternative, the charges (as well as other parameters of the intermolecular interaction potentials) can be evaluated by fitting the optimum structure to the experimentally determined structure[76,77].

The components of the intermolecular interaction listed above contribute (though to varying extents) to the structure of all molecular crystals. In addition, we sometime meet specific intermolecular forces, which are always associated with the presence in the molecule of some particular atoms or atomic groups. These forces include hydrogen bonds, bonds of the metal–metal and metal–oxygen type, and other bonds found in crystals of some inner complex compounds. The energy of these interactions is quite difficult to calculate: a successful method of calculation has been developed (so far) only for the hydrogen bond.

Various procedures have been described for evaluating the hydrogen bond energy. Some workers[55,78,79] have used the "6–exp", "10–12", and "6–12" atom–atom potentials, assigning specially chosen parameters to the atoms taking part in the hydrogen bond, and allowing for the part of the hydrogen bond energy which appears as interaction between effective atomic charges. Other workers have used special empirical and semi-empirical functions: Stockmayer potentials[80–81], and Lippincott–Shroeder[82,83] or Morse[84] potentials.

Afonina and coworkers[85] have used all the above methods of allowing for the energy of the hydrogen bond in their calculation of the heats of sublimation of various organic compounds. The best agreement with experimental data was obtained by using the last two potentials.

One of the most interesting approaches in the current development of the atom–atom potential method is the work of Scheraga and coworkers[86–88], who treat the interaction between electrons and nuclei by assigning positive charges (located in the nucleus) of 1, 4, 5, and 6e to the H, C, N, and O atom respectively, while the electrons are placed in the bonds or in the directions occupied by unshared pairs. The distances between electrons and nuclei are used as the parameters of the model. The potential energy consists of coulombic terms of the q_iq_j/r_{ij} type, describing the interactions between electrons and nuclei, and terms which allow for the attraction and repulsion between electrons in terms of the "6–exp" potential. The parameters of these potential functions are chosen by least squares from a large fund of experimental data on various properties of the molecules and of the molecular crystals (dipole moments,

barriers to internal rotation, difference in energy of conformational isomers, lattice energies and lattice constants, etc.). The main advantage of this model is that special potentials are not needed to allow for H-bonds, and the barriers to internal rotation can be described without introducing torsional potentials[46].

IV. SELECTION OF THE ATOM–ATOM POTENTIAL PARAMETERS FROM CRYSTALLOGRAPHIC DATA

The parameters of the atom–atom interaction potentials can be determined from data on the molecular packing in the crystal by two methods. The first consists in finding the optimum packing for different values of the parameters (i.e. the packing corresponding to minimum energy). The best choice of parameters is taken to be the set which gives a calculated structure as nearly as possible identical to the experimentally observed structure. The second method relies on the following considerations. The experimental structure is assumed to be identical to the equilibrium structure. Hence the differentials of the energy at the experimental point should vanish, and therefore the parameters of the potential are chosen so as to keep the differentials of the potential equal to zero. This method of selection avoids the repetitive calculation of lattice sums† and thus offers a substantial saving in computer time.

The first of these approaches is used by Kitaigorodskii and coworkers, and also by Giglio, Liquori, and others.

As was mentioned in the previous Section, Kitaigorodskii uses a universal potential curve for C...C, C...H, and H...H interactions[56]. The parameters of this curve have been progressively modified in successive papers[58,89,90]. One-dimensional and multi-dimensional sections of the energy surface (U) were drawn for different values of the parameters of the potential curve for methane[56], adamantane[57], benzene[58], etc., and the best values of the parameters (for which the position of the energy minimum corresponds to the real structure) were identified in this way. The depth of the minimum was corrected in accordance with the known heat of sublimation. The set of parameters ultimately chosen gave excellent results in the calculation of the optimum packing in crystals of coronene[91], biphenyl[92], dibenzyl[92], and others.

The parameters of the potential functions describing interactions with oxygen[59], sulphur[60], and nitrogen[61] atoms were established in a similar way from data on the structure and heat of sublimation of CO_2, S_8, and N_2O. Numerical values of all the parameters recommended by Kitaigorodskii's team are listed in Table 1.

Giglio, Liquori, and others[93–97] used a different approach: they did not vary the parameters of the potential to search for the optimum packing, but they adopted sets of parameters previously suggested by various workers (in particular, for conformational analysis). The best values of the parameters for the "6–exp,D" potential are given in Table 2.

In the course of this work it was shown that the position of the minimum of the atom–atom potential curve plays an essential role in the search for the optimum packing: the other characteristics of the potential are relatively unimportant. However this conclusion cannot be extended uncritically to other physicochemical properties.

†The lattice sums are expressions of the type $\sum_{ij} 1/r_{ij}^{6}$, $\sum_{ij} 1/r_{ij}^{12}$, $\sum_{ij} 1/r_{ij}$, etc., in which the summation is taken over all the atoms in the structure.

The second of the above methods of selecting the parameters of C...C, C...H, and H...H interactions was first applied by Williams in the case of the "6–exp" potential. The experimental data used as a basis for the optimisation were the structures, heats of sublimation, and other constants of nine aromatic[69] and nine aliphatic and condensed hydrocarbons[68]. Using these data he wrote approximately 100 expressions equating the U_Σ values to heats of sublimation, the first differentials of energy to zero, and the second differentials to the elastic constants.

Table 2. Parameters of the potential used by Giglio et al.[93, 94,96,97,108]

Type of interaction	10^3A, kcal/mole · Å^6	B, Å^{-1}	C, kcal/mole · Å^6	D
C...C	301.0	0.0	327.0	12
C...H	48.8	2.040	125.0	6
H...H	6.6	4.080	49.2	0
S...S	220.8	3.62	1430.0	0
C...N	340.0	0.0	340.0	12
N...N	387.0	0.0	354.0	12
C...Cl	239.0	3.970	653	0
Cl...Cl	220.8	3.620	1430	0
H...Br	25.6	3.557	366.7	0
C...Br	149.0	1.517	945.8	6
N...Br	165.2	1.517	983.8	6
O...Br	140.9	1.517	989.3	6
Me...Br	133.5	3.181	2836.0	0
S...Br	123.0	3.327	1977.2	0
Br...Br	65.8	3.033	2733.8	0
H...I	43.4	3.540	527.8	0
C...I	246.0	1.500	1361.0	6
N...I	272.7	1.500	1415.6	6
O...I	232.6	1.500	1423.6	6
Me...I	219.9	3.164	4081.0	0
S...I	206.8	3.310	2845.2	0
Br...I	107.6	3.046	3934.0	0
I...I	174.2	2.999	5661.0	0
O...O	105.7	4.608	125.1	0
O...H	19.8	3.840	497.6	0
O...C	178.5	2.304	202.2	6
O...Me	170.2	3.969	796.2	6
Me...Me	273.9	3.329	2942.0	0
Me...C	287.9	1.665	1235.0	6
Me...H	31.9	3.200	2089.0	0
Me...O	170.2	3.969	796.2	6

By using least squares Willams selected several sets of the A and B parameters most consistent with these equations. For convenience in the minimisation procedure the α parameters were not varied in the calculation of the lattice sums. The parameter α_{CC} was taken to be 3.60 Å^{-1} from calculations of the compressibility of graphite[98], and the parameter α_{HH} was taken to be 3.74 Å^{-1} from a quantum-chemical calculation of the repulsion between two hydrogen molecules[99]. The sets of parameters were obtained independently for the aromatic and the non-aromatic hydrocarbons: four for each of these two series of compounds. The difference between the sets was that the parameters A_{CH} and B_{CH} (either singly or jointly) were either treated as independent or calculated by the combination rules. The best of these sets was chosen by calculating lattice constants and molecular packing arrangements for different sets of parameters in several aromatic or aliphatic hydrocarbons. It was found that all the hydrocarbon crystals examined could be described satisfactorily by a single set of parameters (listed in Table 3).

In his more recent work Williams has selected and tested a new set of parameters for the "6–exp" potential which allows for the electrostatic component[76,100] (following Warshel and Lifson[77], who first demonstrated the need to allow for

electrostatic interaction in hydrocarbons). The charges on the atoms were treated as parameters of the potential function, and were evaluated by the above method together with other parameters of the same series of compounds. The numerical values obtained are shown in Table 3. The contribution of the electrostatic component in the different hydrocarbons varies from 0 (for n-pentane) to 29% (for benzene). Only by allowing for the U_{el} term was Williams able to account for the polymorphic transition in benzene[100]. This suggests that even in hydrocarbons electrostatic forces are far from negligible. On the other hand the contribution of the electrostatic component to the energy of the benzene structure seems too high to be acceptable.

Table 3. Parameters of the "6–exp" potential used by Williams.

Type of interaction	A, $\frac{\text{kcal}}{\text{mole}} \cdot \text{Å}^6$	10^3B, $\frac{\text{kcal}}{\text{mole}}$	α, Å^{-1}	References
C...C	568	83.630	3.60	68
C...H	125	8.766	3.67	68
H...H	27.3	2.654	3.74	68
C...C	449	71.430	3.60	76
C...H	134.2	14.310	3.67	76
H...H	40.1	2.867	3.74	76

Notes: in Ref. 76 the parameters are given in kJ mole^{-1}; $q_H = q_C = 0.179$ e.s.u. [76]

Scheraga and coworkers used both the first and the second approach in their search for the parameters of the potential functions. They found a set of parameters describing the interaction of hydrocarbon molecules by the method of Williams, using as their experimental basis the heats of sublimation and structures of benzene measured at three temperatures[101].

More recently Scheraga and coworkers[55] used a wide range of compounds (including hydrocarbons, carboxylic acids, amines, and amides) to select and test a system of parameters to be used in calculations of the conformation of polypeptides and proteins. The energy of zero-valent interactions was calculated by using the "6–12" potential, the hydrogen bond energy by the "10–12" potential, and the U_{el} energy by Coulomb's law. The A coefficient, which characterises the attraction forces, was calculated by the Kirkwood–Müller formula in the "6–12" potential and by a quantum-mechanical formula in the "10–12" potential. The charges were calculated by the CNDO/2 method. Thus only the B parameter was varied, i.e. the parameter describing the repulsion between atoms not joined by valence bonds, and in particular between atoms taking part in hydrogen bonds.

The criterion for the validity of the parameters was the quantity σ, defined as

$$\sigma = \left[(1/N)\sum_{i=1}^{N}(l_i^{\text{calc}} - l_i^{\text{exper}})^2\right]^{1/2},$$

where $l_i = a, b, c, \alpha, \beta, \gamma$ are the lattice parameters and N is the number of these parameters. The search procedure included two independent (but interrelated) minimisations: 1) minimising the energy by varying the lattice parameters, and 2) minimising the σ value obtained in the previous calculation by varying the B coefficients, using the formula

$$\frac{\partial}{\partial B}\{[a^{\text{exper}} - a^{\text{calc}}]^2 + \ldots + [\gamma^{\text{exper}} - \gamma^{\text{calc}}]^2\} = 0.$$

Different parameters were selected for different types of nearest-neighbour environment: thus, H atoms bound to an aromatic ring, to an aliphatic chain, to the nitrogen of an amino group, to the oxygen of a hydroxyl group, etc. were considered to be different.

Table 4. Parameters of the "6–12" potential used by Momany, Scheraga, et al.[55]

Type of interaction	A, $\frac{\text{kcal}}{\text{mole}} \cdot \text{Å}^6$	10^3B, $\frac{\text{kcal}}{\text{mole}} \cdot \text{A}^{12}$
H...H (aliph.)	45.5	14.10
H...H (amino, amido)	45.5	8.43
H...H (arom.)	45.5	14.39
H...H (carboxy, carbonyl)	45.5	11.69
C...C (aliph.)	370.5	906.03
C...C (carboxy, carbonyl)	766.6	1048.98
C...C (atom.)	370.5	475.30
N...N (amido)	363.1	732.54
N...N (in H bond)	401.0	374.94
O...O (carbonyl, carboxy)	369.0	170.19
O...O (hydroxyl)	217.2	125.63
S...S (heterocyclic, sulpho group)	249.0	363.18

The parameters thus obtained (Table 4) were tested by calculating the packing and the energy of the structure for crystals of monomeric[102] and of polymeric amino-acids[103,104]. The authors stress that the results given by these parameters are satisfactory only if the charges on the atoms are calculated in the CNDO/2 approximation.

The two possible approaches to the selection of the atom–atom potential parameters are compared in a paper by Hagler and Lifson[105]. A serious drawback of the second approach is shown to be the non-equivalence of the optimisation of the potential parameters from the differentials of the energy and from the experimentally observed structure. Thus in the case of points on gently sloping regions of the potential energy surface the differentials can be small, and yet the distance from the minimum may still be large. For this reason these workers proposed a method[105] in which the exact values of the parameters are obtained directly from the structure whilst avoiding the need for repetitive calculations of lattice sums.

The authors[105] explain their method by defining the vector $\boldsymbol{a}$ whose components are the structure parameters. The special feature of the method is that the quantity $\Delta\boldsymbol{a} = \boldsymbol{a}_{\text{calc}} - \boldsymbol{a}_{\text{exper}}$ is obtained directly, by the Newton–Raphson method, of calculating $\boldsymbol{a}_{\text{calc}}$: $\Delta\boldsymbol{a} = -F(\boldsymbol{a}_{\text{exper}})^{-1}\nabla_{\boldsymbol{a}}U(\boldsymbol{a}_{\text{exper}})$, where F is the matrix of the second differentials $F_{\alpha\beta} = \partial^2 U/\partial a_\alpha \partial a_\beta$, $\nabla_{\boldsymbol{a}}U$ is a vector whose components are the differentials $\partial U/\partial a_\alpha$, and the numerical values of the differentials correspond to the experimentally determined structure.

The parameters of the potential, represented by the vector $\boldsymbol{p}$, are obtained by solving the equation

$$\delta\boldsymbol{p}^i = \boldsymbol{p}^i - \boldsymbol{p}^{i-1} = [(Z'Z)^{-1}Z'\Delta\boldsymbol{y}]^{i-1}$$

iteratively by least squares. In this equation $Z = \partial(F^{-1}\nabla U)/\partial\boldsymbol{p}$ is a matrix of the differentials of the deviations of the structure parameters (with respect to the parameters of the potential), and $\Delta\boldsymbol{y}$ is a vector of the deviation of the calculated from the experimental structure parameters.

In the first variant of the calculation the energy of the structure was described[106] by the formula

$$2U_{\Sigma}=-\Sigma A/r^6+\Sigma B/r^m+\Sigma qq'/r+2U_{H},$$

where m was taken to be 9 or 12. This formula includes a contribution from the hydrogen bonds (U_H), which was expressed by the Morse potential. However it was later shown that the hydrogen bond is adequately accounted for by the first three terms if the parameters of the potential and the charges are chosen for atoms taking part in hydrogen bond formation. The experimental material used in this calculation was a selection of structure data for eight amides, but heats of sublimation and dipole moments were also used in the minimisation procedure.

Table 5. Parameters of the potential used by Hagler, Lifson, et al.[106]

Type of interaction	A, $\frac{\text{kcal}}{\text{mole}}$ Å^6	10^3B, $\frac{\text{kcal}}{\text{mole}}\cdot$Å^{12}	q, e.s.u.***	A, $\frac{\text{kcal}}{\text{mole}}$ Å^6	10^3B, $\frac{\text{kcal}}{\text{mole}}\cdot$Å^{12}	q, e.s.u.***
	«6-12»			«6-9»		
H...H (att. to C)	32.9	1.15	0.10	15.0	0.445	0.11
O...O	502	275	—0.38	1410	45.8	—0.46
N...N	1230	2271	—0.28* —0.83**	2020	86.9	—0.26* —0.82**
C...C	532	1811	—	1230	38.9	—
C...C (in amides)	1340	3022	0.38	355	12.5	0.46
H...H(att. to N)	0	0	0.28* 0.41**	0	0	0.26* 0.41**

*In NH group; ** in NH_2 group, ***the CO, NH, NH_2, and CH_2 groups are assumed to be neutral.

The parameters of the potential functions selected in Ref.106 are listed in Table 5: we note that the "6–9" and the "6–12" potentials give equally good results in the calculation of equilibrium structures. The charges on the atoms obtained as parameters of the intermolecular interaction function were compared[106] with the charges found by quantum-mechanical calculations (*ab initio*, CNDO/2, and the Del Re method). The best agreement was obtained with the charges given by *ab initio* calculation.

The validity of the parameters thus obtained was tested by calculating the packing of molecules in ten crystalline amides[107]. For three of these the energy minimum was sought by varying every possible geometric parameter: only the number of molecules in the elementary cell was treated as known. The authors stress that this is the first reported calculation of this type.

Mirskaya and coworkers[90] compared the parameters of the potentials recommended by different authors for calculating the properties of crystalline hydrocarbons. Only those parameters having a clear physical significance were compared: the equilibrium distance r_0, the depth of the potential well ε, and the quantity $\lambda = r_0\alpha$ which characterises the steepness of the slopes towards the minimum for the "6-exp" potential. The authors point out[90] that the failure to ensure physical significance of the atom–atom potentials often leads to unrealistic potential curves. Thus the parameter $r_0^{HH} = 3.37$ obtained by Williams[68,69] is too high (when compared with the sum of the van der Waals radii). The values of ε^{CC} and r_0^{CH} obtained in Ref.77 are clearly too high. Momany and coworkers[101] obtained a curve for the C...C interaction without a minimum, and curves for the C...H and H...H interaction with excessively deep minima.

Table 6. Comparison of the characteristics of the potential curves proposed by various authors for hydrocarbon crystals[90] (ε in kcal mole^{-1}, r_0 in Å).

C...C			C...H			H...H			Refs.
ε	r_0	λ	ε	r_0	λ	ε	r_0	λ	
0.080	3.80	14.0	0.049	3.30	13.0	0.030	2.80	12.0	90
0.067	3.80	13.6	0.067	3.30	13.6	0.067	2.80	13.6	89
0.095	3.88	13.97	0.048	3.31	12.1	0.010	3.37	12.6	68,69
*	*	«6-12»	0.259	2.73	«6-12»	0.423	2.61	«6-12»	101
0.185	3.62	«6-9»	—	—	—	0.003	3.55	«6-9»	77

*No minimum.

Subsequently[55,106] these same workers[77,101] reconsidered their recommended potential parameters and compared r_0 and ε values (Tables 7 and 8) as had been done in Ref.90. We see from these Tables that the discrepancy between the r_0 values for the curves proposed by different authors is much smaller than the discrepancy between the ε values. One reason for the large differences between the ε values is that the overall energy of the intermolecular interaction (which alone can be compared directly with experiment) depends not only on ε but also on the effective charges on the atoms, which vary quite markedly according to the method of calculation and are even ignored altogether in some cases. It follows that the methods of calculating the component of the energy which is determined by the "6–exp", "6–12", etc. potentials, and the method of calculating the electrostatic component, should be mutually consistent.

Table 7. Comparison of the characteristics of the potential curves proposed in Refs.106, 109, and 110 (ε in kcal mole^{-1}, r_0 in Å).

ε	r_0	Refs.	ε	r_0	Refs.	ε	r_0	Refs.
H...H (attached to C)			C...C (in amides)			N...N		
0.0025	3.54	106	0.042	3.75	106	0.161	4.01	106
0.038	2.75	106	0.148	4.06	106	0.167	3.93	106
0.122	2.4	109	0.11	3.4	109	0.20	3.1	109
0.076	2.6	110	0.138	3.6	110	0.212	3.3	110
C...C			O...O			H...H (attached to N)		
0.184	3.62	106	0.198	3.65	106	0.0	0.0	106
0.039	4.35	106	0.228	3.21	106	0.0	0.0	106
0.11	3.4	109	0.23	3.04	109	0.122	2.4	109
0.138	3.6	110	0.172	3.2	110	0.076	0.26	110

V. TABULATION OF THEORETICAL CALCULATIONS OF MOLECULAR PACKING

In this Section we shall try to present as fully as possible, in tabular form (Tables 9–16), all the results obtained in theoretical calculations of crystal structures using atom–atom potentials. These investigations began in 1961, when

Kitaigorodskii proposed this method of identifying the energy minimum in a crystal. Since then, and up to 1977, the number of papers published on this topic has risen to 180.

Table 8. Comparison of the characteristics of the potential curves proposed by various authors (ε in kcal mole^{-1}, r_0 in Å).

ε	r_0	Refs.	ε	r_0	Refs.	ε	r_0	Refs.
H...H (aliph.)			C...C (aliph.)			O...O (carbonyl, carboxyl)		
0.037	2.92	55	0.038	4.12	55	0.200	3.12	55
0.0045	2.936	111	0.196	4.228	111	0.230[365]	3.00	111
0.0025	3.548	77	0.185	3.616	77	0.325	3.10	261
0.033	3.36	261	0.049	4.16	261	0.124[59]	3.25	262
0.060	2.80	262	0.060	3.80	262	0.106	3.32	263
0.010	3.37	68	0.095	3.88	68	N...N (amino)		
0.027	3.08	263	S...S			0.107	3.51	55
C...C (arom.)			0.043	3.78	55	0.194	3.60	111
0.073	3.70	55	0.361	3.91	261	0.165	3.52	261
0.095	3.90	261	0.333[60]	3.90	262	0.076	3.80	263
0.095	3.88	68				0.081	3.60	264

Table 9. Publications by Kitaigorodskii and coworkers on molecular packing calculations.

Year	Compound	Adjustable parameters	Refs.	Remarks
1961	Methane[a]	a	56	—
1961	Methane, adamantane	a	57	—
1964	Hydrocarbons (6 compounds)[a]	a, ψ	89	ΔH
1968	Benzene[a]	a, ψ	112	—
1969	Naphthalene, anthracene	a, ψ	113	a ($t°$)
1969	Naphthalene	ψ, X	114	ν ($t°$)
1969	CO_2	a	59	Q
1970	Coronene	a, ψ	91	ΔH
1971	Naphthalene, anthracene, biphenyl	ψ, X	115	ν, ν ($t°$)
1971	S8(rhombic), CS_2	a, ψ	60	ΔH
1970, 1971	C(Ph)4, Si(Ph)4, Sn(Ph)4, Pb(Ph)4[d]	a, ψ, φ	116, 117	—
1972	N_2O, α-N_2, hexamethylene-tetramine[e]	a, ψ	61	Q, ΔH
1972	3,6-Diphenyl-s-tetrazine	ψ, φ	118	ΔH
1972	Biphenyl, dibenzyl	a, ψ, φ	92	ΔH
1972	p-Diethynylbenzene	ψ	119	Xsa
1974	Naphthalene[a]	—	90	ΔH, el. const.
1975	Acenaphthene, tolane, biphenyl*	SC a, ψ, X	120	—
1975	Benzene	ψ, X	41	A
1976	Adamantane	ψ, X	38	A, polymorph.
1976	Coumarin	a, ψ, X	121	ΔH
1976	Naphthalene, anthracene	ψ, X	42	A
1976	Binary acenaphthene–α-nitronaphthalene system	ψ, X, φ	122	—

*The "6–12" potential was used in this calculation, the "6–exp" in all the others. New parameters used for: (a) C, H, (b) O, (c) S, (d) Si, Sn, Pb, (e) N.

The most important contributions to this area of research came from the teams of Kitaigorodskii, Williams, Giglio, Simonetti, Scheraga, Lifson, Sarko, and Zugenmaier. The work of these groups accounts for more than 50% of the published material, and is presented in Tables 9–15. Publications from other laboratories are listed in chronological order in Table 16.

It is clear from the Tables that the number of papers dealing with this topic has risen steeply in recent years: approximately 60 papers between 1961 and 1970, as compared with over 100 papers between 1971 and 1977. The greatest number of publications appeared in 1974–1975. Whereas the early papers dealt with crystals consisting of molecules containing a small number of atoms (halogens, methane, benzene), and a limited number (one or two) of types of atom, the scope of the more recent papers has become much wider.

Table 10. Publications by Williams and coworkers on molecular packing calculations.

Year	Compound	Adjustable parameters	Refs.	Remarks
1966	Aromatic hydrocarbons (9 compounds)[a]		69	—
1966	Dibenzoylmethane*	ψ, X	8	Xsa
1967	n-Hexane, n-pentane, and other hydrocarbons (9 compounds)[a]	ψ, X	68	—
1968	Benzene, naphthalene, phenanthrene[a]*	ψ	123	—
1969	3,4-Dihydro-2,4,6-triphenyl-s-tetrazin-1,2(2H)-yl*	ψ, X	124	Xsa
1969	Aromatic hydrocarbons (4 compounds)*	ψ, X, φ	50	—
1972	p,p'-Bitolyl	ψ, X, φ	125	q
1973	2,4,6-Triphenylverdazil*	ψ, X, φ	126	Xsa
1974	18 hydrocarbons[a]	a	76	q
1975	Benzene (2 modifications)	a, ψ, X	100	q, polymorphic
1977	18 hydrocarbons[a]	ψ, X	127	q

*"$d-d_0$" potential: in all the other calculations the "6–exp" potential was used.

[a]New parameters used for C and H.

Table 11. Publications by Giglio and coworkers on molecular packing calculations.

Year	Compound	Adjustable parameters	Refs.	Remarks
1967	Hexamethylbenzene	ψ	128	—
1967	5-α-Androstan-3,17-dione	ψX	129	—
1968	Adamantane[a]	a, ψ	93	—
1968	S8(rhombic)*[b]	a	94	—
1969	$(SO_3)_n$*	a, φ	95	—
1969	Dimethylglyoxime**	ψ	80	H-b
1970	Ethylene, deutero-ethylene*	ψ, X, φ	130	ν
1970	N_2, dicyanogen, octachlorocyclobutane[c]	a	96	—
1970	Diketopiperazine**	ψ	131	H-b
1970	Hexabromomethylbenzene, iodoform[d]	a, ψ	97	—
1971	N,N'-Dicyclohexylurea*	ψ, X, φ	132	H-b, Xsa
1972	N-Methylacetamide	ψ, X	133	H-b
1972	Bromoform	SC a, ψ, X	134	μ
1972	Complexes of desoxycholinic acid with p-diiodobenzene and phenanthrene	ψ, X, φ	135	Xsa
1973	5-α-Androstan-3,17-dione*	ψ, X	108	Xsa
1974	Poly(fluoroethylene), polyethylene*	SC ψ, φ	136	—
1974	Coumarin*	ψ, X	137	Xsa
1977	Benzene, naphthalene, anthracene, phenanthrene[a]	a, ψ, X	138	ΔH

*The "6–exp, D" potential was used, **"6–12" potential (in all other calculations the "6–exp" potential was used). New parameters used for: (a) C, H, (b) S, (c) C, N, Cl, (d) Br, I.

At present most of the workers in this field are concerned with amides, mono- and poly(amino-acids), and other compounds of relevance to developing methods of calculation for complex, biologically important substances such as polypeptides and proteins. At the same time metal–organic and inorganic substances are beginning to be studied by the atom–atom potential method.

As the range of compounds being studied becomes wider, suitable parameters of the potentials have to be chosen. Papers dealing with this problem are mentioned in the Notes of the Tables.

Table 12. Publications by Simonetti and coworkers on molecular packing calculations.

Year	Compound	Adjustable parameters	Refs.	Remarks
1967	2-Bromo-1,1-diphenylprop-1-ene***	φ	139	φfree
1967	2-Bromo-1,1-ditolylethylene	φ	140	—
1968	Biphenyl	ψ, φ	141	—
1969	*p,p'*-Bitolyl	ψ, φ	142	—
1971	1,1-Di(*p*-nitrophenyl)ethylene*	φ	143	*q*, φfree
1971	Polyethylene*	*a*, ψ	75	*q*, φfree
1971	11,11-Difluoro-1,6-methano[10]annulene**	*X*	144	Xsa
1972	1,6:8,13-Butan-1,4-diylidene[14]annulene*	ψ	145, 146	*q*, φfree, Xsa
1972	1,6:8,13-Propan-1,3-diylidene[14]annulene*	ψ	147	*q*, φfree, Xsa
1973	*p*-Nitrobiphenyl*	ψ, φ	148	*q*, φfree
1973	Naphthalene, anthracene, pyrene, etc. (9 compounds)	ψ, *X*	149	ν
1975	Anthracene, adamantane, dibenzo-1,4-cycloocta-3,7-diene**	*a*	27	*A*, ν
1975	Hydrocarbons, molecules containing N and O (25 compounds)	ψ, *X*	150	reorient.
1976	F-substituted aromatic compounds (5 compounds)[a]	ψ, *X*	151	Δ*H*, ν

*"6–12" and "6–exp" potentials used; **a special potential was used in this calculation, the "6–exp" potential in all other calculations; ***form of the potential not stated.

[a]New parameter for the potential of F.

Table 13. Publications by Scheraga and coworkers on molecular packing calculations.

Year	Compound	Adjustable parameters	Refs.	Remarks
1968	Benzene[a]	*a*	101	*a* (*t*°)
1971	Poly(*L*-alanine), poly(β-benzyl-*L*-aspartate)	*a*, ψ, φ	103	*q*
1974	Amino-acids (14 compounds)[b]	*a*, φ	102	*q*
1974	Hydrocarbons, carboxylic acids, amines, amides (14 compounds)	*a*	55	*q*
1974	Poly[β-(*p*-chlorobenzyl)-*L*-aspartate]	*a*, ψ, *X*, φ	104	*q*, *A*
1975	Hydrocarbons, alcohols, amines, ice (8 compounds)*[c]	*a*, φ	86	*q*, μ, ν
1975	n-Hexane, n-octane, methylamine, methanol, α-*D*-glucose*	*a*, φ	88	*q*
1975	Acetic and formic acid	*a*, φ	152	*q*, μ, ε

*The "6–exp" potential was used in the approximation of the electron–nucleus interaction model; in all other calculations the "6–12" potential was used.
New parameters for the potentials of: (a) C, H, (b) C, H, N, O, S, (c) C, H, N, O.

It is clear from Tables 9–16 that the "6–exp" and "6–12" potentials have been used most frequently. The "6–exp, *D*" potential often appears in the papers from Giglio's laboratory. More recently some workers have successfully used the "d–d_0" potential proposed by Williams. All these types of potential are described in Section III. Special potentials of a non-standard type are only rarely used.

The complexity of the calculations reported can be judged by the column headed "Adjustable Parameters" in the Tables. Most of the authors have treated the space group, the number of molecules in the cell, and the type of position taken up by the molecules in the cell as known (from experimental data) when seeking to optimise the packing of the structure: in other words, they have assumed a given structure class. However some workers have considered different structure classes: this is indicated by the abbreviation SC in the Adjustable Parameters column. The following abbreviations are also used in that column to indicate the structure parameters which were varied during the optimisation procedure: *a*—the parameters of the elementary cell, ψ—the Euler angles which characterise the orientation of the molecules, *X*—the coordinates of the centres of gravity of the molecules, and ϕ—parameters describing the conformation of the molecules (usually the angular rotations about single bonds).

Table 14. Publications by Lifson and coworkers on molecular packing calculations.

Year	Substance	Potential	Adjustable parameters	Ref.	Remarks
1969	α-N_2	6-12	ψ, *X*	153	ν
1970	α-N_2^a	6-12, 6-exp	ψ, *X*, φ	154	*Q*, ν
1970	Alkanes (13 compounds)[b]	6-12, 6-9, 6-exp	*a*, ψ, *X*, φ	77	*q*, Δ*H*, ν
1971	n-Hexane	6-9, 6-12, 6-exp	• ψ, *X*	155	*q*, ν
1974	Benzene, biphenyl, 9,10-trans-β-ionylidene-γ-crotonic acid	6-12, 6-9, 6-exp	SC *a*, ψ, *X*, φ	156	ν
1974	Chalcones (4 compounds)	6-exp	*a*, φ	157	—
1974	Amides (6 compounds)[c]	6-9	*a*, ψ, *X*	105	*q*
1974	Amides (9 compounds)[c]	6-9, 6-12	*a*	106	*q*, μ, H-b, Δ*H*
1974	Amides (10 compounds)	6-9, 6-12	SC *a*, ψ, *X*	107	*q*
1975	Naphthalene, benzene	6-exp	*a*, ψ, *X*	158	ν
1975	α-N_2, γ-N_2^a	6-12	ψ, *X*, φ	159	Δ*H*, ν, ν (*t*°)
1975	Urea, formamide, adipamide	6-9, 6-12	*a*, ψ, *X*	160	*q*, H-b, ν
1976	Ice (hexagonal)	modified 6-exp	*a*, ψ, *X*	161	*q*
1976	*N*-Methylamide, amides, peptides	6-9, 6-12	SC, *a*, ψ, *X*, φ	162	—

New parameters for the potentials of (a) N, (b) CH, (c) C, H, N, O.

Table 15. Publications by Sarko, Zugenmaier, and coworkers on molecular packing calculations.

Year	Compound	Adjustable parameters	Refs.	Remarks
1972	6-monosaccharides (α and β glucose, etc.)	ψ, *X*	163	H-b
1973	B-Amylose.H_2O	SC *a*, ψ, *X*, φ	164	H-b, Xsa
1974	Cellulose I	SC *a*, ψ, *X*, φ	165	H-b
1974	Mannan	ψ, *X*, φ	166	—
1974	Dimethylsulphoxide–amylose complex	ψ, *X*	167	Xsa
1976	Cellulose II	*a*, ψ, *X*, φ	168	H-b, Xsa
1976	Cellulose III_1	*a*, ψ, φ	169	H-b
1976	V-Amylose	ψ, *X*	170	H-b, Xsa, φfree
1977	β-*D*-Glucone acetate	ψ, *X*	171	Xsa, φfree

*New parameters for the potentials of C, H, O. The "d–d_0" potential was used in all calculations.

In the early work the number of adjustable parameters was usually small, but as computer techniques become more generally available the complexity of the calculations increased. The record for the number of parameters varied in the calculations is held by Scheraga's group, who treated

all the parameters listed above as adjustable and took only the number of molecules in the cell as given.

Table 16.

Substance	Adjustable parameters	Refs.	Remarks
1	2	3	4
	1962		
Chlorine, iodine[I]	SC *a*, ψ	172	—
	1964		
Methane	SC *a*, ψ, φ	173	*q*
Chlorine[I]	SC *a*, ψ	174	*Q*
	1965		
Naphthalene	ψ	175	μ, *Q*
	1966		
Polyethylene	*a*, ψ	176	—
β,β-Dimethyladipic acid	ψ	9	—
	1967		
Chlorine[I]	SC *a*, ψ	177	*q*
Benzene[IV,a]	ψ	178	ν
Naphthalene, anthracene	ψ, *X*	179,180,181	ν
	1968		
$(CH_2O)_n$	ψ	182	ν
Chlorine, fluorine[I]	SC *a*, ψ	183	*q*, *Q*
$(CH_2O)_n$[b]	*a*, ψ	184	—
Benzene[V]	*a*	185	*Q*
C_2N_2[I]	ψ, *X*	186	*Q*, ν
	1969		
1,3,5,7-Tetramethylocta-1,3,5,7-tetraene	ψ	187	—
Ethylene[IV]	ψ, *X*	188	ν
Benzene	ψ	189	ν
Benzene[IV]	ψ, *X*	190	ν
Chlorine[I,IV]	ψ	191	*q*, ν
Chlorine	ψ	192	—
	1970		
Benzene, deuterobenzene	ψ	193	ν
α-N_2[I]	ψ, *X*	194	*q*, ν
Acenaphthene	ψ	63,195	ν
Deutero-anthracene	ψ, *X*	196	ν
Naphthalene	ψ, *X*	197	ν
Formic acid[IV,b]	—	198	*q*
Anthracene	ψ, *X*	199	ν
Polyethylene	*a*, φ	200	—
	1971		
p-Dichlorobenzene, *p*-dibromobenzene[II]	ψ	201	—
Acetylene[IV]	ψ	202	*Q*
Methane	SC ψ, *X*	203	Δ*H*, polymorph.
α-O_2, β-O_2[I]	ψ, φ	204	*Q*, ν (t°)
α-, γ-N_2; α-, γ-CO[I,IV]	SC *a*, φ	205	*Q*, μ, ν, polymorph.
CO_2[I,c]	ψ, *X*	206	ν (t°)
Adamantane	*a*, ψ	207	Δ*H*, reorient., polymorph.
	1972		
Cyclobutane	SC *a*	208	—
Planar molecules	ψ, *X*	209	*q*
Iodoform, chloroform, bromoform	SC	210	μ, Xsa
Biphenyl	ψ, *X*	211	ν
Trans-dichloroethane	ψ	212	
	1972		
Polyethylene[VI,a]	*a*, ψ	213	—
α-Chitin[III]	ψ, *X*, φ	214	Xsa
Benzene, naphthalene	ψ, *X*	215	ν
	1973		
Chloro-substituted benzenes (3 compounds)[d]	ψ, *X*	216,217	Δ*H*, ν
Benzene, deuterobenzene	ψ, *X*	218,219	μ, ν
Triphenylphosphine	φ	220	φ_{free}
Ethylene[VI]	SC ψ	221	ν
Hexamethylenetetramine	ψ, φ	222	ν
Acenaphthylene	ψ	223	—
Benzene, SO_2	ψ	224	*q*
N-Methylacetamide	ψ, *X*	225	*q*, H-b
Mucondinitrile and 8 organic complexes[II]	ψ	226	reorient.
	1974		
Hexachlorobenzene[I]	*a*, ψ	227	*q*, ν
Aromatic compounds (8 compounds)	ψ	228	Δ*H*, reorient.
Tetraphenylsilane[I]	ψ, φ	229	*q*, Δ*H*, ν
Cl_2, Br_2[I,V,VI]	ψ, *X*	230	ν, ν (t°)
H_2, N_2, O_2, F_2, Cl_2, Br_2, I_2[I]	SC *a*, ψ, *X*	231	*Q*
α-O_2[I]	SC ψ, *X*	232	—
α-N_2, γ-N_2[e]	*a*, ψ	233	ν
Methane	SC *a*, ψ	234	ν

Table 16 (contd.).

Substance	Adjustable parameters	Refs.	Remarks
1	2	3	4
	1975		
CH_4, CO_2, C_6H_6, $C_6H_5NO_2$	*a*, ψ, *X*	235	*q*, Δ*H*
n-Butane	*a*, ψ, *X*	236	ν
Pyridazine derivatives (2 compounds)	ψ	237	*q*, μ
Durol	ψ, φ	238	ν, Δ*H*
	1976		
Imidazole, pyrazine, urea, cyanuric acid[I]	ψ, *X*	239	ν
Biphenylene	*a*, ψ	240	ν, Δ*H*
Adrenaline	*a*, ψ, *X*, φ	241	*q*, H-b, φ_{free}
Anthracene	SC *a*, ψ	242	reorient.
Hydroquinone clathrates[I]	ψ, *X*	243	*q*
Hexamethylenetetramine, (α, β)	ψ	244	reorient.
α-CO[I,c]	ψ, *X*, φ	245	*Q*, ν
Hexachlorobenzene	ψ, *X*	246	μ, ν
CO_2, N_2, C_6H_6[I,IV]	*a*, ψ	247	*Q*, Δ*H*
Methane, adamantane, 2,2-paracyclophane, 3,3-paracyclophane	*a*, ψ	248	*a* (t°) reorient., polymorph.
Benzene	ψ, *X*, φ	249	ν
Hexaphenylbenzene, triphenylbenzene, triphenyltriazine	*a*, φ	250	φ_{free}
Phenoselenazine[V]	ψ, *X*, φ	251	—
	1977		
n-Alkanes (5 compounds)	ψ, *X*	252	Δ*H*, reorient., polymorph
$Sb(Ph)_5$, $P(Ph)_5$, $As(Ph)_5$	SC ψ, φ	253,254	*q*
	1977		
$M(Ph)_5 \cdot \frac{1}{2}C_6H_{12}$ (M = P, As, Sb)	SC *a*, ψ, *X*	255	*q*
Acetic acid	SC ψ	256	*q*, H-b
TCNQM-phenanthroline[II]	ψ	257	reorient., Xsa
2-Methyl-5,8-dihydroxy-1,4-naphthaquinone[III]	ψ, *X*, φ	258	Xsa
α-N_2[I,IV,e]	ψ, *X*	259	*Q*, ν, ν (t°)
Formic acid	ψ	260	*q*, *Q*

Notes. The following potentials were used: (I) "6–12", (II) "6–exp,*D*", (III) "*d*–d_0", (IV) a specially defined potential, (V) "6–exp" and "*d*–d_0", (VI) "6–exp" and "6–12" (in all other cases the "6–exp" potential was used). New parameters for the potentials of: (a) C, H, (b) C, H, O, (c) C, O, (d) C, H, Cl, (e) N, (f) C, H,N.

The column headed "Remarks" gives some additional information on the method of calculation or on the purpose of the investigation. The following abbreviations are used: *q*, μ, and *Q* denote allowance for the electrostatic interactions in the monopole, dipole–dipole, and quadrupole–quadrupole approximation respectively, ε denotes allowance for the dielectric constant in the calculation of the electrostatic component, H-b shows that the energy of the hydrogen bond has been allowed for, Δ*H* that the calculated results have been compared with the experimental heat of sublimation, el.const. that the results have been compared with the experimental elastic constants of the crystal, reorient. that the reorientation of molecules in the crystals has been considered, Xsa that the optimum structure was calculated in the course of an X-ray structural analysis, polymorph. that the work was aimed at interpreting a polymorphic transformation, ϕ_{free} that the conformation of the molecule in the crystal has been compared with the calculated conformation of the free molecules, *a*(t°) that the temperature dependence of the lattice parameters has been calculated, *A* that the thermodynamic functions have been calculated, ν that the vibration frequencies in the crystals have been calculated, and ν(t°) that the temperature dependence of the frequency has been calculated.

We note that a discussion of calculated frequencies of internal and external molecular vibrations lies outside the scope of this review. Special review articles have appeared on this topic[26,266]. Work on the calculation of frequencies

is included in the Tables only in so far as it involves minimisation of the intermolecular interaction energy by varying the structure parameters.

In most of the work listed in Tables 9–16 the structure class of the crystals under study is taken from X-ray diffraction data, i.e. the problem of optimising the packing of the molecules is solved for a given structure class. However some workers have formulated the problem more widely, and have treated the structure class as a variable. A brief outline of publications in which packing arrangements for different structure classes are compared is given below.

Brock and Ibers[253,254] tried to account for the square-pyramidal coordination of antimony in $Sb(C_6H_5)_5$ (structure class $P\bar{1}$, $Z = 2(1)$) as compared with the trigonal-bipyramid coordination found in $P(C_6H_5)_5$ and $As(C_6H_5)_5$ (structure class Cc, $Z = 4(1)$). For each of the three compounds the potential energy of the crystal structure was minimised for a coordination polyhedron taken either as a tetragonal pyramid in the class $P\bar{1}$, $Z = 2(1)$, or as a trigonal bipyramid in the class Cc, $Z = 4(1)$. The calculation was satisfactorily consistent with experiment, but only after allowing for the electrostatic component.

Kitaigorodskii and coworkers[120] studied acenaphthene (structure class $Pcm2_1$, $Z = 4(m,m)$), biphenylene ($P2_2/a$, $Z = 6(1,\bar{1})$), and tolane ($P2_1/a$, $Z = 4(1,1)$) to explain the existence of quasi-heteromolecular crystal structures, in which identical molecules can occupy more than one system of equivalent positions. To this end they calculated the optimum packing of acenaphthene molecules in the $P2_1/a$, $Z = 4(1)$ structure class, and of biphenylene and tolane in the $P2_1/a$, $Z = 2(\bar{1})$ structure class, i.e. they examined the normal packing arrangements in which all the molecules are symmetrically equivalent. Only in the case of acenaphthene was the potential energy of the real structure lower than the energy of the hypothetical packing arrangement. For biphenylene and tolane the energies of the real and the hypothetical packing were found to be almost identical.

The aim of Derissen and Smit[256] was to explain the specific behaviour of acetic acid during crystallisation. Unlike most of the other carboxylic acids, acetic acid forms a structure (structure class $Pna2_1$, $Z = 4(1)$) in which the molecules are connected by hydrogen bonds in infinite chains (rather than in dimers). The most likely alternative to the real structure of acetic acid was taken to be that of fluoroacetic acid ($P2_1/c$, $Z = 4(1)$). Minimisation of the potential energy for this structure class gave two minima of similar depth. Their energy was practically identical to that of the real structure. Thus the authors[256] could not reach any firm conclusion on the reasons for the anomalous structure of crystalline acetic acid. However they correctly point out[256], like other workers[120], that this type of problem cannot be finally resolved without calculating the free energy. In all probability the lack of success of a number of investigations[172,174,177,183] of the crystal structure of chlorine is also due to the use of the potential energy (instead of the free energy) of the structure in the minimisation procedure.

We shall now turn to a more detailed discussion of some special aspects of the calculation of the energy of molecular packing, noted in the "Remarks" column of Tables 9–16.

1. Comparison of the Conformation of the Free Molecule and the Conformation of the Molecule in the Crystal

If the molecule contains atomic groups able to rotate about an ordinary bond the crystal field may be sufficient to affect the conformation when such a molecule is introduced into a crystal. This effect has along been recognised in comparisons of X-ray diffraction results with the results of analytical methods sensitive to the geometry of "free" molecules (electron diffraction of vapours, and microwave spectroscopy).

Minimisation of the energy of zero-valent interactions in the atom–atom approximation allows us to interpret and to predict the influence of a crystal field on molecular conformation. The classical work in this area was contributed by various authors[92,141,125], who calculated the conformation of biphenyl molecules in the vapour and in the crystalline phase. In complete agreement with experiment, the calculations indicated a planar structure for the molecule in the crystal and a non-planar conformation (with an angle between the phenyl rings between 30° and 42° according to different authors) in the free state.

In a more recent paper of this type[250] the energy of the free molecule and the energy of the crystal structure are calculated as a function of the angle of rotation of the phenyl rings about the ordinary bond for hexaphenylbenzene, 1,3,5-triphenylbenzene, and 1,3,5-triphenyltriazine. The result of the calculation is that the isolated molecule has a higher symmetry, and that the rotation angles of the phenyl rings are slightly altered (by less than 10°) when the molecules are introduced into a crystal.

Calculations of molecular conformation in a crystal can be used to establish the location of atoms or atomic groups not detected with sufficient precision by X-ray diffraction. The calculation of the coordinates of hydrogen atoms in methyl groups is an example of this type of work[162,267].

2. Application of Optimum Packing Calculations in X-ray Diffraction Analysis

In this work an initial model of the molecule is usually assumed, based on standard bond lengths and bond angles, and supplemented if necessary by conformational analysis. Data on the structure class and on the elementary cell parameters are obtained from X-ray diffraction. The distribution of the molecules within the cell corresponding to a minimum energy is obtained from that information. If more than one distribution is found to be possible the R-factor is calculated in each case, and the structure corresponding to the lowest R-factor is identified by the standard methods of X-ray analysis. This method has been used, for example, in Williams' calculations of the structure of organic compounds containing nitrogen heterocyclic rings[124,126]. Simonetta and coworkers[145–147], having calculated the conformation of several derivatives of annulene, established their packing in the crystal to within $R \cong 5–8\%$. Similarly, Giglio and coworkers identified the structures of N,N'-dicyclohexylurea[132], 5α-androstan-3,17-dione[108], coumarin[137], and other compounds. The second structure in this list could not be determined by conventional methods of X-ray analysis.

The search for optimum packing as a means of determining structure is particularly valuable in the case of polymers. Perfect crystals, suitable for X-ray structural analysis, are seldom formed by polymers. By minimising the energy of the crystal structure we can build a model of the polymer which is then modified or confirmed by X-ray diffraction results.

A good example of this method of evaluating polymer crystal structures is given by the work of Sarko, Zugenmaier, and others (Table 15) on the crystal structure of carbohydrates and polysaccharides. These workers used the "$d–d_0$" potential (see above), with parameters chosen on the basis of six model monosaccharides[163]. This potential allowed them to calculate the effect of hydrogen bonds as well as ordinary intermolecular interactions. The packing of two model chains was considered in the work on the structure of

mannans[166]: these models gave very similar energy terms, and only by interpreting i.r. spectral data could one of them be chosen as the more likely.

The structure of different modifications of a material as important as cellulose could not be established until calculations of packing were applied to the problem. The first step in this type of work is a conformational analysis of the free molecule. Choosing the most probable conformations, and using experimental data on the space group and on the parameters of the elementary cell, 185 initial models were assembled. Minimisation of the energy reduced this number to 24 variants, from which the packing arrangements with the largest number of hydrogen bonds were chosen. The model was further refined by using experimental values of the structure amplitudes. It was shown that cellulose I consists of parallel chains and has a triclinic (and not monoclinic, as previously thought) unit cell. The *R*-factor of this structure was 29%. The modification known as cellulose II was characterised to an *R* value of 15.1%: it consists of antiparallel chains and contains a greater number of hydrogen bonds, which explains is greater stability. For the cellulose III modification the *R*-factor was 20.3%: in this modification the chains are parallel, as in modification I. Thus the polymorphic transformations in cellulose are now fully characterised.

3. Calculation of Thermodynamic Functions and Interpretation of Polymorphism

Methods of identifying the optimum packing by minimising the free energy were described in Section II. The problem of evaluating the thermodynamic functions is often encountered in various aspects of this type of work (not only in the calculation of the optimum structure). Several workers have calculated thermodynamic quantities through the frequency distribution functions. Thus in a study of crystalline benzene[190] the zero-point vibration energy and the specific heat for the range 60–220 K are calculated; the heat of sublimation at 0 K has also been obtained[77] from calculations of the optimum crystal structure, of the vibration frequencies, and of the molecular conformation in the gas and the crystalline phase.

Thermodynamic functions have also been calculated[35,36] through the configuration integral on the basis of the cell model. Thus the free energy, the specific heat, and the entropy at different temperatures have been obtained for naphthalene, benzene, and anthracene crystals.

One of the most important and interesting applications of the calculation of thermodynamic quantities is the explanation and prediction of polymorphism in molecular crystals. The simplest way of interpreting polymorphism is to demonstrate the presence of two minima, of similar depth, in the potential energy surface. Various attempts have been made[207,224] to account for polymorphism in this way, often successfully. Nevertheless the method is not universal because several minima of comparable depth can be found on the potential surface, and not all of these correspond to real modifications.

A strict interpretation of polymorphism requires calculation of the free energy. Pertsin and Kitaigorodskii[37,38] used the atom–atom potential method and the cell model to calculate the entropy and the free energy of benzene and adamantane as a function of temperature and pressure. At each point the free energy was minimised with respect to the structure parameters. The calculation was carried out for two modifications of each compound (treating the structure class as known): the intersection of the two free energy curves thus obtained gave the polymorphic transformation. In this way the phase transition temperature of adamantane was obtained, in excellent agreement with experiment. In the case of benzene the free energy isotherms intersected in the negative pressure region: the authors point out that the change in free energy with pressure is small, and comparable with the error of the calculation. However it is important to note that even in this case it was possible to obtain at least a qualitative prediction of the polymorphic transformation induced by changes in pressure.

4. Molecular Reorientation and Orientational Disorder

The symmetry or pseudo-symmetry present in some molecules can produce minima of identical (or similar) depth in the potential energy surface of the crystal for different values of the Euler angles. If the barriers separating these minima are low, reorientation is possible in the crystal (a sudden rotation of the molecule with a negligibly small effect on the position of the centre of gravity). On the other hand if the barrier is fairly high, and the molecule lies in substantially different positions before and after the change in orientation, orientational disorder can occur with molecules of suitable shape.

Reorientation can be observed experimentally through the NMR spectra, from which the height of the barrier can also be calculated. Orientational disorder is detected from X-ray diffraction data. However it should be noted that dynamic reorientation and static orientational disorder are almost impossible to distinguish by X-ray diffraction. Therefore published reports of orientational disorder should be accepted with caution.

This uncertainty can often be avoided by calculating the height of the reorientation barrier. In the case of planar molecules the simplest method of calculating the barrier height is the following. The molecule is rotated about an axis passing through its centre of gravity and normal to the plane of the molecule. The other molecules are considered to be rigidly fixed in the positions indicated by X-ray structural analysis. The plot of intermolecular interaction energy against angle of rotation gives the most favourable orientations and the height of the barrier opposing the orientational transitions.

Calculations of this type have been reported for benzene[67], for polycyclic aromatic molecules (naphthalene, coronene, pyrene, etc.)[228], and for a group of planar molecules including derivatives of benzene and naphthalene and some heterocycles[150]. The authors[150] point out the difference between: 1) crystals in which reorientation is easy (benzene, hexamethylbenzene, thiophen), 2) crystals in which reorientation is hindered (hexachlorobenzene), and 3) crystals in which reorientation is impossible (2-bromonaphthalene). This classification correctly reflects the qualitative conclusions obtained from NMR spectra. However not all the calculated reorientation barriers agree quantitatively with the experimental values.

Similar calculations have been carried out for organic molecular complexes[223,257], but unfortunately no allowance was made for the electrostatic component, which in this case can be expected to play an important role.

Calculations[226] on the TCE–naphthalene and TCE-paracyclophane complexes (where TCE is tetracyanoethylene) have shown the existence of the TCE molecule in two positions of similar energy differing by a 90° rotation of the molecule in its own plane. The barrier between these positions is unsurmountable in practice. This suggests the possibility of orientational disorder in these complexes, a conclusion which is consistent with X-ray diffraction data for the latter

complex[268], in whose crystals 25% of the molecules occupy one of the possible positions and 75% the other. However in the case of the TCE–naphthalene complex X-ray diffraction gives no evidence of orientational disorder[269].

The energy curve describing the rotation of the naphthalene molecule (in its own plane) in the naphthalene–TCE and naphthalene–TCB complexes (where TCB is tetracyanobenzene) has two minima separated by an angle of ~35° and by a barrier whose height (~3 kcal mole^{-1}) is much lower than the corresponding barrier for the TCE molecule. X-ray diffraction studies[269–271] have indicated the presence of disorder in these crystals, corresponding exactly to the calculated disorder, but with a lower barrier, which therefore does not exclude the possibility of dynamic reorientation.

The plots of energy against rotation angle for anthracene molecules in complexes with TCB and tetracyanoquinonedimethane show only one minimum. However this minimum is quite broad, and the molecules can perform large-amplitude librations in their own plane. This conclusion is consistent with X-ray results.

A calculation[244] of the reorientation barriers in crystals of adamantane (α and β modifications) and of hexamethylenetetramine was complicated by the absence of a direction which could be identified with the axis of rotation of the molecule. The authors considered two possible directions as the axis of rotation, corresponding to the diad and triad symmetry axes of the molecule, and two possible positions of the neighbouring molecules. The reorientation barrier of the molecules in the β modification was found to be higher than in the high-temperature (α) modification. Molecular rotation in hexamethylenetetramine crystals is strongly hindered by the intermolecular hydrogen bonds.

REFERENCES

1. R.Mason, in "Perspectives in Structural Chemistry", Vol.3 (J.D.Dunitz and J.A.Ibers, Editors), Wiley, New York, 1970, p.58.
2. A.I.Kitaigorodsky and K.V.Mirskaya, Materials Res.Bull., 7, 1271 (1972).
3. M.Simonetta, Acc.Chem.Res., 7, 345 (1974).
4. H.A.Scheraga, "Peptides, Polypeptides and Proteins", Symposium Proceedings, Israel, New York, 1974, p.47.
5. A.I.Kitaigorodskii, Uspekhi Fiz.Nauk, 127, 391 (1979).
6. A.I.Kitaigorodskii, "Organicheskaya Kristallokhimiya" (Organic Crystal Chemistry), Izd.Akad.Nauk SSSR, Moscow, 1955.
7. D.E.Williams, Science, 147, 605 (1965).
8. D.E.Williams, Acta Cryst., 21, 340 (1966).
9. G.Avitabile, P.Corradini, P.Ganis, and E.Martuscelli, Ricerca Scient., 36, 681 (1966).
10. I.M.Gel'fand, E.B.Vul, S.L.Ginzburg, and Yu.G.Fedorov, "Metod Ovragov v Zadachakh Rentgenostrukturnogo Analiza" (The Gully Method in Problems of X-ray Structural Analysis), Izd. Nauka, Moscow, 1966.
11. S.L.Ginzburg and M.G.Neigauz, Zhur.Strukturnoi Khim., 10, 877 (1969).
12. A.I.Kitaigorodskii, Kristallografiya, 2, 456 (1957).
13. A.I.Kitaigorodskii, Kristallografiya, 2, 646 (1957).
14. E.Segerman, Acta Cryst., 19, 789 (1965).
15. P.M.Zorkii and M.A.Porai-Koshits, Kristallografiya, 6, 655 (1961).
16. P.M.Zorkii and M.A.Porai-Koshits, Kristallografiya, 12, 989 (1967).
17. P.M.Zorkii and M.A.Porai-Koshits, Symposium "Sovremennye Problemy Fizicheskoi Khimii" (Modern Problems in Physical Chemistry), Vol.1, Izd.Moskov. Univ., 1968, p.98.
18. P.M.Zorkii, M.A.Porai-Koshits, L.M.Prezman, and G.P.Murav'eva, Zhur.Strukturnoi Khim., 10, 633 (1969).
19. L.M.Prezman and P.M.Zorkii, Zhur.Strukturnoi Khim., 12, 1044 (1971).
20. P.M.Zorkii, M.A.Porai-Koshits, and V.S.Psalidas, Zhur.Strukturnoi Khim., 7, 577 (1966).
21. P.M.Zorkii, M.A.Porai-Koshits, and S.N.Sveshnikova, Zhur.Strukturnoi Khim., 7, 752 (1966).
22. Yu.V.Zefirov and P.M.Zorkii, Zhur.Strukturnoi Khim., 15, 118 (1974).
23. Yu.V.Zefirov and P.M.Zorkii, Zhur.Strukturnoi Khim., 17, 745 (1976).
24. M.Born and K.Huang, "Dynamical Theory of Crystal Lattices" (Translated into Russian), Moscow, 1958.
25. A.I.Kitaigorodskii, Kristallografiya, 7, 195 (1962).
26. N.N.Afonina and P.M.Zorkii, "Itogi Nauki i Tekhniki, Seriya Kristallokhimiya" (Advances in Science and Technology. Crystal Chemistry Series), Izd.VINITI Akad.Nauk SSSR, Moscow, 1974, p.149.
27. G.Filippini, C.M.Gramaccioli, and M.Simonetta, Chem.Phys.Letters, 35, 17 (1975).
28. I.Z.Fisher, "Statisticheskaya Teoriya Zhidkostei" (Statistical Theory of Liquids), Fizmatgiz, Moscow, 1961.
29. M.L.Klein and R.D.Murphy, Phys.Rev., 6, 2433 (1972).
30. T.G.Gibbons, M.L.Klein, and R.D.Murphy, Chem. Phys.Letters, 18, 325 (1973).
31. M.L.Klein and R.D.Murphy, Chem.Phys.Letters, 29, 463 (1974).
32. T.G.Gibbons and M.L.Klein, J.Chem.Phys., 60, 112 (1974).
33. J.A.Barker, "Lattice Theories of the Liquid State", Pergamon, Oxford–London–New York–Paris, 1963.
34. A.C.Holt, W.G.Hoover, S.G.Gray, and D.R.Shortle, Phys.(Utr.), 49, 61 (1970).
35. A.J.Pertsin, V.V.Nauchitel, and A.I.Kitaigorodsky, Mol.Cryst.Liquid Cryst., 31, 205 (1975).
36. A.I.Pertsin and A.I.Kitaigorodskii, Kristallografiya, 21, 287 (1976).
37. A.I.Pertsin and A.I.Kitaigorodskii, "Tezisy Dokladov Tretego Simpoziuma Mezhmolekulyarnoe Vzaimodeistvie i Konformatsii Molekul" (Extended Abstracts of the Third Symposium on Intermolecular Interaction and Conformation of Molecules), Pushchino, 1976, p.17.
38. A.J.Pertsin and A.I.Kitaigorodsky, Molecular Phys., 32, 1781 (1976).
39. P.M.Zorkii, Kristallografiya, 13, 26 (1968).
40. P.M.Zorkii and V.K.Bel'skii, Symposium "Sovremennye Problemy Fizicheskoi Khimii" (Modern Problems in Physical Chemistry), Vol.4, Izd.Moskov.Univ., 1970, p.379.
41. P.M.Zorkii and V.K.Bel'skii, Zhur.Strukturnoi Khim., 13, 305 (1972).
42. V.K.Bel'skii and A.V.Dzyavchenko, Zhur.Strukturnoi Khim., 16, 437 (1975).
43. T.L.Hill, J.Chem.Phys., 14, 465 (1946).
44. T.L.Hill, J.Chem.Phys., 16, 399 (1948).
45. D.H.Barton, J.Chem.Soc., 340 (1948).
46. V.G.Dashevskii, "Konformatsii Organicheskikh Molekul" (Conformations of Organic Molecules), Izd.Khimiya, Moscow, 1974.
47. J.E.Lennard-Jones, Proc.Roy.Soc., A106, 441, 463, 709 (1924).

48. J.O.Hirschfelder, C.F.Curtiss, and R.B.Bird, "The Molecular Theory of Gases and Liquids" (Translated into Russian), Inostr.Lit., 1961.
49. J.L.De Coen, G.Elefabte, A.M.Liquori, and A.Damiani, Nature, 216, 910 (1967).
50. D.E.Williams, Acta Cryst., A25, 464 (1969).
51. F.London, Z.phys.Chem., B11, 222, 236 (1930).
52. J.Slater and J.Kirkwood, Phys.Rev., 37, 682 (1931).
53. V.I.Poltev and B.I.Sukhorukov, Zhur.Strukturnoi Khim., 9, 298 (1968).
54. R.A.Scott and H.A.Scheraga, J.Chem.Phys., 42, 2209 (1965).
55. F.A.Momany, L.M.Carruthers, R.F.McGuire, and H.A.Scheraga, J.Phys.Chem., 78, 1595 (1974).
56. A.I.Kitaigorodskii, Dokl.Akad.Nauk SSSR, 137, 116 (1961).
57. A.I.Kitaigorodskii and K.V.Mirskaya, Kristallografiya, 6, 507 (1961).
58. A.I.Kitaigorodskii, K.V.Mirskaya, and A.B.Tovbis, Kristallografiya, 13, 255 (1968).
59. A.I.Kitaigorodskii, K.V.Mirskaya, and V.V.Nauchitel', Kristallografiya, 14, 900 (1969).
60. V.V.Nauchitel' and K.V.Mirskaya, Kristallografiya, 16, 1025 (1971).
61. K.V.Mirskaya and V.V.Nauchitel', Kristallografiya, 17, 73 (1972).
62. J.B.Hendrickson, J.Amer.Chem.Soc., 83, 4537 (1961).
63. V.G.Dashevskii, Yu.T.Struchkov, and Z.A.Akopyan, Zhur.Strukturnoi Khim., 7, 594 (1966).
64. H.L.Kramer and D.R.Herschbach, J.Chem.Phys., 53, 2792 (1970).
65. P.T.Sicora, J.Phys.B: Atom.Molec.Phys., 3, 1457 (1970).
66. K.V.Mirskaya, Tetrahedron, 29, 679 (1973).
67. A.I.Kitaigorodskii, "Molekulyarnye Kristally" (Molecular Crystals), Izd.Nauka, Moscow, 1971.
68. D.E.Williams, J.Chem.Phys., 47, 4680 (1967).
69. D.E.Williams, J.Chem.Phys., 45, 3770 (1966).
70. I.A.Il'icheva and V.I.Poltev, Zhur.Strukturnoi Khim., 16, 375 (1975).
71. H.De Voe and I.Tinoco, J.Molec.Biol., 4, 500 (1962).
72. Yu.V.Zefirov, P.M.Zorkii, and S.G.Lazareva, Zhur.Fiz.Khim., 45, 460 (1971)[Russ.J.Phys.Chem., No.2 (1971)].
73. P.M.Zorkii, S.G.Lazareva, and Yu.V.Zefirov, Kristallografiya, 15, 698 (1970).
74. G.Del Re, J.Chem.Soc., 4031 (1958).
75. G.Morosi and M.Simonetta, Chem.Phys.Letters, 8, 358 (1971).
76. D.E.Williams, Acta Cryst., A30, 71 (1974).
77. A.Warshel and S.Lifson, J.Chem.Phys., 53, 582 (1970).
78. V.I.Poltev, "Tezisy Dokladov Pervogo Vsesoyuznogo Soveshchaniya po Organicheskoi Kristallokhimii" (Extended Abstracts of the First All-Union Conference on Organic Crystal Chemistry), Riga, 1975, p.107.
79. D.Poland and H.A.Scheraga, Biochemistry, 6, 3791 (1967).
80. W.H.Stockmayer, J.Chem.Phys., 9, 398 (1941).
81. E.Giglio, Nature, 222, 339 (1969).
82. E.R.Lippincott and R.Shroeder, J.Chem.Phys., 23, 1099 (1955).
83. R.Shroeder and E.R.Lippincott, J.Phys.Chem., 6, 921 (1957).
84. E.M.Popov, V.G.Dashevskii, G.M.Lipkind, and S.F.Arkhipova, Molek.Biologiya, 2, 612 (1968).
85. N.N.Afonina, L.N.Kuleshova, and P.M.Zorkii, Vestnik Moskov.Univ., Dep.No.1372-78 (1978).
86. L.L.Shipman, A.W.Burgess, and H.A.Scheraga, Proc.Nat.Acad.Sci.USA, 72, 534 (1975).
87. A.W.Burgess, L.L.Shipman, R.A.Nemenoff, and H.A.Scheraga, J.Amer.Chem.Soc., 98, 23 (1976).
88. A.W.Burgess, L.L.Shipman, and H.A.Scheraga, Proc.Nat.Acad.Sci.USA, 72, 854 (1975).
89. A.I.Kitaigorodskii and K.V.Mirskaya, Kristallografiya, 9, 174 (1964).
90. K.V.Mirskaya, I.E.Kozlova, and V.F.Bereznitskaya, Phys.Status Solidi, 62, 291 (1974).
91. A.I.Kitaigorodskii, K.V.Mirskaya, and V.F.Bereznitskaya, Kristallografiya, 15, 405 (1970).
92. V.F.Bereznitskaya, A.I.Kitaigorodskii, V.M.Kozhin, I.E.Kozlova, and K.V.Mirskaya, Zhur.Fiz.Khim., 46, 2492 (1972)[Russ.J.Phys.Chem., No.10 (1972)].
93. A.M.Liquori, E.Giglio, and L.Mazzarella, Nuovo Cimento, 55B, 476 (1968).
94. E.Giglio, A.M.Liquori, and L.Mazzarella, Nuovo Cimento, 56B, 57 (1968).
95. E.Giglio, A.M.Liquori, and L.Mazzarella, Nuovo Cimento, Ser.I, 1, 135 (1969).
96. A.Di Nola and E.Giglio, Acta Cryst., A26, 144 (1970).
97. E.Giglio, Z.Kristallogr., 131, 385 (1970).
98. A.D.Crowell, J.Chem.Phys., 29, 44 (1958).
99. D.E.Williams, J.Chem.Phys., 43, 4424 (1965).
100. D.Hall and D.E.Williams, Acta Cryst., A31, 56 (1975).
101. F.A.Momany, G.Vandercooi, and H.A.Scheraga, Proc.Nat.Acad.Sci.USA, 61, 429 (1968).
102. F.A.Momany, L.M.Carruthers, and H.A.Scheraga, J.Phys.Chem., 78, 1621 (1974).
103. R.F.McGuire, G.Vandercooi, F.A.Momany, R.T.Ingwall, G.M.Crippen, N.Lotan, R.W.Tuttle, K.L.Kashuba, and H.A.Scheraga, Macromolecules, 4, 112 (1971).
104. Yi-Chang Fu, R.F.McGuire, and H.A.Scheraga, Macromolecules, 7, 468 (1974).
105. A.T.Hagler and S.Lifson, Acta Cryst., B30, 1336 (1974).
106. A.T.Hagler, E.Huler, and S.Lifson, J.Amer.Chem. Soc., 96, 5319 (1974).
107. A.T.Hagler and S.Lifson, J.Amer.Chem.Soc., 96, 5327 (1974).
108. V.M.Coiro, E.Giglio, A.Lucano, and R.Puliti, Acta Cryst., B29, 1404 (1973).
109. H.A.Scheraga, Adv.Phys.Org.Chem., 6, 103 (1968).
110. D.A.Brant, W.G.Miller, and P.J.Flory, J.Mol.Biol., 23, 47 (1967).
111. S.Lifson and A.Warshel, J.Chem.Phys., 49, 5116 (1968).
112. A.I.Kitaigorodskii, K.V.Mirskaya, and A.B.Tovbis, Kristallografiya, 13, 225 (1968).
113. K.V.Mirskaya and I.E.Kozlova, Kristallografiya, 14, 412 (1969).
114. A.I.Kitaigorodskii and E.I.Mukhtarov, Kristallografiya, 14, 784 (1969).
115. A.I.Kitaigorodskii and E.I.Mukhtarov, Optika i Spektrosk., 31, 706 (1971).
116. N.A.Ahmed, A.I.Kitaigorodskii, and K.V.Mirskaya, Acta Cryst., B27, 867 (1971).
117. N.A.Akhmed and G.G.Aleksandrov, Zhur.Strukturnoi Khim., 11, 891 (1970).
118. N.A.Ahmed and A.I.Kitaigorodsky, Acta Cryst., B28, 738 (1972).
119. N.A.Ahmed, A.I.Kitaigorodsky, and M.I.Sirota, Acta Cryst., B28, 2875 (1972).

120. A.I.Kitaigorodskii, A.I.Pertsin, and I.E.Kozlova, Kristallografiya, 20, 1035 (1975).
121. A.I.Kitaigorodskii, R.M.Myasnikova, I.E.Kozlova, and A.I.Pershin, Kristallografiya, 21, 511 (1976).
122. R.M.Myasnikova, I.E.Kozlova, A.I.Pertsin, and L.G.Radchenko, Kristallografiya, 21, 964 (1976).
123. D.E.Williams, Science, **159**, 645 (1968).
124. D.E.Williams, J.Amer.Chem.Soc., 91, 1243 (1969).
125. D.E.Williams, Acta Cryst., **A28**, 629 (1972).
126. D.E.Williams, Acta Cryst., **B29**, 96 (1973).
127. T.L.Starr and D.E.Williams, Acta Cryst., **A133**, 771 (1977).
128. E.Giglio and A.M.Liquori, Acta Cryst., 22, 437 (1967).
129. A.Damiani, E.Giglio, A.M.Liquori, and L.Mazzarella, Nature, **215**, 1167 (1967).
130. G.Taddei and E.Giglio, J.Chem.Phys., **53**, 2768 (1970).
131. P.Giacomello and E.Giglio, Acta Cryst., **A26**, 324 (1970).
132. V.M.Coiro, P.Giacomello, and E.Giglio, Acta Cryst., B27, 2112 (1971).
133. M.Dentini, P.De Santis, S.Morosetti, and P.Piantonida, Z.Kristallogr., **136**, 305 (1972).
134. V.M.Coiro, E.Giglio, and C.Quagliata, Acta Cryst., B29, 3601 (1972).
135. S.C.De Sanctis, E.Giglio, V.Pavel, and C.Quagliata, Acta Cryst., **B28**, 3656 (1972).
136. L.D.Hario and E.Giglio, Acta Cryst., **B30**, 372 (1974).
137. E.Gavuzzo, E.Mazza, and E.Giglio, Acta Cryst., **B30**, 1351 (1974).
138. G.Taddei, R.Righini, and P.Manzelli, Acta Cryst., **A33**, 626 (1977).
139. G.L.Casalone, C.Mariani, A.Mugnoli, and M.Simonetta, Theor.Chim.Acta, 8, 228 (1967).
140. G.L.Casalone, C.Mariani, A.Mugnoli, and Simonetta, Acta Cryst., 22, 228 (1967).
141. G.L.Casalone, C.Mariani, A.Mugnoli, and M.Simonetta, Mol.Phys., **15**, 339 (1968).
142. G.L.Casalone, C.Mariani, A.Mugnoli, and M.Simonetta, Acta Cryst., **B25**, 1741 (1969).
143. G.L.Casalone and M.Simonetta, J.Chem.Soc.B, 1180 (1971).
144. C.M.Gramaccioli and M.Simonetta, Acta Cryst., **B27**, 2231 (1971).
145. C.M.Gramaccioli, A.Mugnoli, and M.Simonetta, Chem.Comm., 973 (1971).
146. C.M.Gramaccioli, A.Mugnoli, T.Pilati, M.Raimondi, and M.Simonetta, Acta Cryst., **B28**, 2365 (1972).
147. A.Gavezzotti, A.Mugnoli, M.Raimondi, and M.Simonetta, J.Chem.Soc.Perkins Trans.II, 425 (1972).
148. G.Casalone, A.Gavezzotti, and M.Simonetta, J.Chem. Soc.Perkins Trans.II, 342 (1973).
149. G.Filippini, C.M.Gramaccioli, M.Simonetta, and G.B.Suffritti, J.Chem.Phys., **59**, 5088 (1973).
150. A.Gavezzotti and M.Simonetta, Acta Cryst., **A31**, 645 (1975).
151. G.Filippini, C.M.Gramaccioli, M.Simonetta, C.B.Suffritti, and O.Sala, Chem.Phys.Letters, **39**, 14 (1976).
152. F.A.Momany, "Environment Effects on Molecular Structure and Properties", Proc.VIII Symp., Jerusalem, 1975, Dordrecht–Boston, 1976, p.437.
153. O.Schepp and A.Ron, Discuss.Faraday Soc., **26**, 1353 (1969).
154. T.S.Kuan, A.Warshel, and O.Schepp, J.Chem.Phys., 52, 3012 (1970).
155. A.Warshel, J.Chem.Phys., **54**, 5324 (1971).
156. E.Huler and A.Warshel, Acta Cryst., **B30**, 1822 (1974).
157. A.Warshel, E.Huler, D.Rabinovich, and Z.Shakkea, J.Mol.Struct., 23, 175 (1974).
158. E.Huler and A.Warshel, J.Chem.Phys., 8, 239 (1975).
159. E.Huler and A.Zunger, Phys.Rev.B: Solid State, 12, 5878 (1975).
160. E.Huler, Chem.Phys.Letters, **33**, 566 (1975).
161. E.Huler and A.Zunger, J.Chem.Phys., **13**, 433 (1976).
162. A.T.Hagler, L.Leiserowitz, and M.Tuval, J.Amer. Chem.Soc., **98**, 4600 (1976).
163. P.Zugenmaier and A.Sarko, Acta Cryst., **B28**, 3158 (1972).
164. P.Zugenmaier and A.Sarko, Biopolymers, **12**, 435 (1973).
165. A.Sarko and R.Muggli, Macromolecules, 7, 486 (1974).
166. P.Zugenmaier, Biopolymers, **13**, 1127 (1974).
167. N.T.Winter and A.Sarko, Biopolymers, **13**, 1461 (1974).
168. A.Sarko and J.Southwick, Macromolecules, **9**, 851 (1976).
169. A.Sarko and J.Southwick, Macromolecules, **9**, 957 (1976).
170. T.L.Bluhm and A.Sarko, Biopolymers, 16, 2067 (1977).
171. P.Zugenmaier and A.Sarko, Biopolymers, **15**, 2121 (1976).
172. K.Jamasaki, J.Phys.Soc.Japan, 17, 1262 (1962).
173. S.Kimel, A.Ron, and D.F.Horning, J.Chem.Phys., **40**, 3351 (1964).
174. S.C.Nyburg, J.Chem.Phys., **40**, 2493 (1964).
175. D.P.Craig, R.Mason, P.Pauling, and D.P.Santry, Proc.Roy.Soc., **A286**, 98 (1965).
176. A.Adajima and T.Maeda, J.Polymer Sci., **C-15**, 55 (1966).
177. J.H.Hiller and S.A.Rice, J.Chem.Phys., **46**, 3881 (1967).
178. I.Harada and T.Simanouchi, J.Chem.Phys., 46, 2708 (1967).
179. G.S.Pawley, Phys.Status Solidi, 20, 347 (1967).
180. P.Weulersse, Compt.rend., **B264**, 327 (1976).
181. P.Weulersse, Compt.rend., **B268**, 1440 (1969).
182. V.Z.Kompaniets, E.F.Oleinik, and N.S.Enikolopyan, Zhur.Strukturnoi Khim., 9, 322 (1968).
183. S.C.Nyburg, J.Chem.Phys., **48**, 4890 (1968).
184. C.Corradini and G.Avitabile, Europ.Polymer J., **4**, 385 (1968).
185. A.I.Rae and R.Mason, Proc.Roy.Soc., **A304**, 487 (1968).
186. P.M.Richardson and E.R.Nixon, J.Chem.Phys., 49, 4276 (1968).
187. G.Avitabile, P.Ganis, and V.Petraccone, J.Chem. Phys., **73**, 2378 (1969).
188. M.Brith and A.Ron, J.Chem.Phys., **50**, 3053 (1969).
189. D.A.Oliver and S.H.Walmsley, Mol.Phys., 17, 617 (1969).
190. M.Nakamura and T.Miyazawa, J.Chem.Phys., **51**, 3146 (1969).
191. M.Suzuki, T.Yokoyama, and M.Ito, J.Chem.Phys., **50**, 3392 (1969).
192. R.Weyland and O.Dideberg, Bull.Soc.roy.Sci. Liège, **38**, 533 (1969).
193. E.R.Bernstein, J.Chem.Phys., **52**, 4701 (1970).
194. M.C.Donkersloot and S.H.Walmsley, Mol.Phys., **19**, 183 (1970).

195. T.Luty, J.A.Janik, A.Bajorek, J.Matkaniec, J.Domoslawsky, and J.M.Janik [Rept] Inst.fiz.jadr. Krakwie, No.724 (1970).
196. U.A.Lutz and W.Halg, Solid State Comm., 8, 165 (1970).
197. G.S.Pawley and S.J.Cyrin, J.Chem.Phys., **52**, 4073 (1970).
198. W.P.Miniccozzi and M.T.Stroot, J.Compt.Phys., 6, 95 (1970).
199. P.Weulersse, Acta Cryst., A26, 628 (1970).
200. G.Wobster and S.Blasenbrey, Kolloid-Z.u.Z.Polymere, **241**, 985 (1970).
201. G.Bandoli, D.A.Clemente, U.Croatto, and C.Panatoni, Gazzetta, **101**, 99 (1971).
202. M.Hashimoto, M.Hashimoto, and T.Isobe, Bull.Chem. Soc.Japan, **44**, 649 (1971).
203. M.Hashimoto and M.Hashimoto, Bull.Chem.Soc.Japan, **44**, 2272 (1971).
204. J.C.Laufer and C.E.Leroi, J.Chem.Phys., **55**, 993 (1971).
205. J.C.Raich and R.L.Mills, J.Chem.Phys., 55, 1811 (1971).
206. M.Suzuki and O.Schnepp, J.Chem.Phys., 55, 5349 (1971).
207. P.-J.Wu, L.Hsu, and D.A.Dows, J.Chem.Phys., **54**, 2714 (1971).
208. E.Castellucci, M.G.Mugliorini, and P.Manzelli, Acta Cryst., A28, 432 (1972).
209. F.Cser, "Hungarian Diffraction Conference, Abstracts of Contributed Papers" 6, Siófok, Hungary, 1972.
210. T.Kawaguchi, K.Takashina, T.Tanaka, and T.Wotanabé, Acta Cryst., B28, 967 (1972).
211. T.Luty, Mol.Cryst.Liquid Cryst., 17, 327 (1972).
212. P.Mancelli and G.Taddei, Chem.Phys.Letters, 13, 132 (1972).
213. R.L.McCullough and P.H.Zindermeyer, Kolloid-Z.u. Z.Polymer, **250**, 440 (1972).
214. P.Nageshwar and C.Eamakrishnan, Indian J.Pure Appl.Phys., 10, 501 (1972).
215. G.Taddei, H.Bonadeo, and S.Califano, Chem.Phys. Letters, 13, 136 (1972).
216. H.Bonadeo and E.D'Alessio, "Rendiconto Scientifico Internazionale "Enrico Fermi"", Varenna sul Lago di Como, 1972, New York–London, 1975, p.136.
217. H.Bonadeo and E.D'Alessio, Chem.Phys.Letters, **19**, 117 (1973).
218. H.Bonadeo and G.Taddei, J.Chem.Phys., **58**, 979 (1973).
219. G.Taddei, H.Bonadeo, M.P.Marzocchi, and S.Califano, J.Chem.Phys., **28**, 966 (1973).
220. C.P.Brock and J.A.Ibers, Acta Cryst., **B29**, 2426 (1973).
221. G.R.Eliot and G.E.Leroi, J.Chem.Phys., **59**, 1217 (1973).
222. G.Dolling, G.S.Pawley, and B.M.Powell, Proc.Roy. Soc., **A333**, 363 (1973).
223. J.M.Morris, Austral.J.Chem., **26**, 649 (1973).
224. G.N.Ramachandran, K.P.Sarathy, and A.S.Kolaskar, Z.Kristallogr., **138**, 299 (1973).
225. G.N.Ramachandran, K.P.Sarathy, and A.S.Kolaskar, Z.Naturforsch., **28a**, 643 (1973).
226. U.Shumueli and I.Goldberg, Acta Cryst., **B29**, 2466 (1973).
227. J.B.Bates and W.R.Busing, J.Chem.Phys., **60**, 2414 (1974).
228. P.K.Boyd, C.A.Fyfe, and D.A.Wright, J.Phys. Chem.Solids, **35**, 1355 (1974).
229. F.Cser, L.Párkányi, and P.Hencsei, Magyar Kém. Folyóirat, 80, 259 (1974).
230. G.G.Dumas, F.Vovelle, and J.-P.Viennot, Mol. Phys., 28, 1345 (1974).
231. C.A.English and J.A.Venables, Proc.Roy.Soc., A340, 57 (1974).
232. C.A.English and J.A.Venables, Proc.Roy.Soc., A340, 81 (1974).
233. T.Luty and G.S.Pawley, Chem.Phys.Letters, 28, 593 (1974).
234. T.Wasiutynsky and T.Luty, Acta Phys.Polon., A45, 551 (1974).
235. J.Caillet and P.Claverie, Acta Cryst., A31, 448 (1975).
236. M.L.Cangeloni and V.Schettino, Mol.Cryst.Liquid Cryst., 31, 219 (1975).
237. L.Fanfani, M.Tomassini, P.F.Zanazzi, and A.R.Zanzari, Acta Cryst., B31, 1740 (1975).
238. M.Sanguer and J.C.Messager, Mol.Cryst.Liquid Cryst., **29**, 285 (1975).
239. S.Besnainou and D.L.Cummings, J.Mol.Struct., 34, 131 (1976).
240. E.Burgos, H.Bonadeo, and E.D'Alessio, J.Chem. Phys., 65, 2460 (1976).
241. J.Caillet, P.Claverie, and B.Pullman, Acta Cryst., B32, 2740 (1976).
242. D.P.Craig, J.F.Ogilvie, and P.A.Reynolds, J.Chem. Soc., Faraday Trans.II, 1603 (1976).
243. P.Dansas and P.Sixou, Mol.Phys., 31, 1297 (1976).
244. C.A.Fyfe and D.Harold-Smith, Canad.J.Chem., 54, 769 (1976).
245. B.O.Hall and H.M.James, Phys.Rev.B: Solid State, 13, 3590 (1976).
246. T.Luty and A.Mierzejensky, "Proceedings of the Fifth International Conference on Raman Spectroscopy Freiburg, 1976", Freiburg–Breisgau, 1976, p.518.
247. T.B.MacRury, W.A.Stelle, and B.J.Berne, J.Chem. Phys., **64**, 1288 (1976).
248. K.Mirsky, Acta Cryst., A32, 199 (1976).
249. N.Neto, G.Taddei, S.Califano, and S.H.Walmsley, Mol.Phys., 31, 457 (1976).
250. Vasantha Pattabhi, Pramana J.Phys., 6, 299 (1976).
251. P.Villares, R.Jimenez-Gray, A.Conole, and R.Marguez, Acta Cryst., B32, 2293 (1976).
252. D.H.Bonsor and D.Bloor, J.Materials Sci., 12, 1552 (1977).
253. C.P.Brock, Acta Cryst., A33, 193 (1977).
254. C.P.Brock and J.A.Ibers, Acta Cryst., A32, 38 (1976).
255. C.P.Brock, Acta Cryst., A33, 898 (1977).
256. J.L.Derissen and P.H.Smit, Acta Cryst., A33, 230 (1977).
257. I.Goldberg and U.Shmueli, Acta Cryst., B33, 2189 (1977).
258. P.D.Cradwick, D.Hall, and M.K.Wood, Acta Cryst., B33, 2380 (1977).
259. S.Romano, Z.Naturforsch., **32a**, 485 (1977).
260. P.H.Smit, J.L.Derissen, and F.B.van Duijmeveldt, J.Chem.Phys., **67**, 274 (1977).
261. D.R.Ferro and J.Hermans, Biopolymers, 11, 105 (1972).
262. A.I.Kitaigorodskii, Symposium "Advances in Structure Research by Diffraction Methods, Brunswock", Vol.3 (R.Brill and R.Masson, Editors), Braunshweigh, 1970, p.173.
263. M.Oobatake and T.Ooi, Progr.Theor.Phys., **48**, 2132 (1972).

264. N.C.Parsonage and R.C.Pemberton, Trans.Faraday Soc., 63, 311 (1967).
265. A.Warshel, M.Levitt, and S.Lifson, J.Mol.Spectrosc., 33, 84 (1970).
266. T.Luty, Post.fiz., 24, 435 (1973).
267. N.N.Afonina and P.M.Zorkii, Zhur.Strukturnoi Khim., 17, 18 (1976).
268. J.Bernstein and K.N.Trueblood, Acta Cryst., B27, 2078 (1971).
269. R.M.Williams and S.C.Wallwork, Acta Cryst., 22, 899 (1967).
270. F.H.Herbstein, "Perspectives in Structural Chemistry", Vol.4, New York, 1971, pp.166–395.
271. S.Kumakura, F.Ivasaki, and Y.Saito, Bull.Chem. Soc.Japan, 40, 1826 (1967).

Lomonosov Moscow State University
Chemistry Faculty
Institute of Element–Organic
Compounds of the USSR Academy
of Sciences

Translated from *Uspekhi Khimii*, 49, 998-1013 (1980) U.D.C. 541.183 : 547.279.1 + 547.279.3 + 547.732 : 543.422

Mechanism of the Adsorption of Organic Sulphur Compounds by Oxides and Zeolites

N.K.Lyapina, V.I.Lygin, and A.D.Ulendeeva

Recent views on the mechanism of the separation of organic sulphur compounds by adsorption on oxides and on zeolites are discussed. 137 references

CONTENTS

I. Introduction 526
II. Adsorption methods of separation and purification 526
III. Isotherms and heats of adsorption 527
IV. Spectroscopic study of adsorption 529
V. Quantum-chemical calculations of adsorption complexes 531

I. INTRODUCTION

Interest in organic sulphur compounds has increased in recent years, mainly because of the increased importance of the extraction and treatment of sulphur- and high-sulphur-bearing petroleum and natural gas, of the extensive use of hydro- and thermocatalytic processes, and of the more stringent requirements for high-purity petroleum products produced by our increasing awareness of the need to combat atmospheric pollution.

At present the chemistry of natural organo-sulphur compounds (and in particular those associated with petroleum deposits) is being developed in two main directions: 1) improvements and developments in the methods of decomposing organo-sulphur compounds in order to produce high-quality fuels and oils[1,2], and 2) developments in the separation[3,4] and in the practical exploitation[5-7] of organic sulphur compounds. The latter activities offer the greatest interest in the chemistry of organic sulphur compounds, because they relate directly to the most basic problems of petroleum refining: to obtain high-quality products, to protect the environment from contamination, and to optimise our usage of natural resources. In recent years this work has become even more important because of the wide use of organic sulphur compounds isolated from petroleum products as special solvents, as very efficient media for the extraction of precious metals, as flotation reagents, as physiologically active materials, etc.[5,6]. In some cases[7] the prospect of replacing currently used, expensive synthetic products by naturally occurring organic sulphur compounds has been convincingly demonstrated.

Organic sulphur compounds found in petroleum include sulphides, disulphides, mercaptans, and thiophens[3]. The separation of these compounds, dissolved in multi-component mixtures of petroleum hydrocarbons, is laborious and difficult. Therefore much of the current research is aimed at effective methods of concentrating and separating organic sulphur compounds. Adsorption chromatography is one of the most promising methods of separating complex mixtures, and is widely used in this work[8,9].

Methods of controlling the surface properties of adsorbents by chemical modification have attracted a great deal of attention[8,9], and the theory of intermolecular interactions has been further developed[10]. However still further developments are needed in the chemistry of organic sulphur compounds. The main achievements in the past few years have been the development of new methods of separating complex mixtures on pure and on mixed oxides with variously modified surfaces. This review aims to discuss recent publications on the separation of natural and model systems on oxide adsorbents and on zeolites (including organic sulphur compounds). Studies of the mechanism of adsorption of sulphur-containing organic molecules by thermodynamic, spectral, and quantum-chemical methods will be specially considered.

II. ADSORPTION METHODS OF SEPARATION AND PURIFICATION

Both synthetic (zeolites, silica gels) and naturally occurring sorbents (fuller's earths, bauxites, other ores) are used in adsorption methods for the industrial production of oils, purification of gases from sulphur compounds, and separation of aromatic hydrocarbons from the products of the dehydrogenation of light petroleum fractions[11-13]. However these adsorbents have insufficient selectivity. Aromatic hydrocarbons, which are valuable constituents of fuels, are removed from the distillates together with the organic sulphur compounds. Hence one of the most important current problems is to develop adsorbents able to separate aromatic hydrocarbons selectively from organic sulphur compounds.

In the purification of fuels it is important not only to remove the sulphur compounds but also to desorb them without decomposition, in order to exploit any possible practical application. Recently discovered possibilities in the application of sulphur compounds from petroleum have shifted the problem into the area of very fine differentiations. It is essential to be able to identify the organic sulphur compounds, and to establish their structure, both by classifying them into groups (sulphides, disulphides, thiophens, mercaptans) and by identifying the individual members of a homologous series. The ideal solution is to use adsorbents with an activity related to the functional properties of the sulphur atom in different compounds. On the whole, oxide adsorbents offer most of the features needed for the separation of organic sulphur compounds, while zeolites have a number of advantages for more complete separation and purification[14-17].

The selectivity of adsorbents has been studied on synthetic mixtures of hydrocarbons and organic sulphur compounds, and also on various petroleum fractions. It has been shown that organic sulphur compounds are adsorbed on silica gel less strongly than nitrogen and oxygen compounds of analogous structure[18,19], but more strongly than paraffin–naphthene hydrocarbons or aromatic hydrocarbons[20]. The adsorbability of compounds in these classes decreases in the sequence:

nitrogen-containing, oxygen-containing, sulphur-containing compounds, aromatic hydrocarbons, paraffin–naphthene hydrocarbons. Within the organic sulphur compounds class the adsorption affinity increases in the sequence thiophens, aliphatic thiols, aliphatic disulphides, aromatic and cyclic thiols, aliphatic and cyclic sulphides[20,21]. Within each homologous series the adsorption affinity of the organic sulphur compounds decreases as the molecular weight increases.

Synthetic sorbents (silica gels, alumina gels, alumina-silicas, Mg, Fe, Cr, Al, Mo silicates) have been used successfully in the separation of the paraffin–naphthene part of petroleum fractions[22]. However the aromatic hydrocarbons are eluted together with the organic sulphur compounds. Extensive work[22-24] on the choice of adsorbents, eluents, and conditions for the separation of aromatic hydrocarbons from organic sulphur compounds has resulted in a modest enrichment of the chromatographic fractions in organic sulphur compounds, though the proportion of aromatic hydrocarbons in these fractions remains as high as 40–70%.[25] The difficulty of separating organic sulphur compounds from aromatic hydrocarbons is due partly to the similarity in the adsorption affinities of the two classes[21,24] and partly to the possibility of interactions between molecules in these classes[26,27]. Furthermore it has been shown that the conjugation of π-electrons with the unshared electron pairs of the hetero-atom can assist the separation (by adsorption) of a mixture of organic sulphides and sulphur-containing compounds of the aromatic type with a sulphur atom in the ring (thiophens). It is reported[21,28] that these mixtures can be separated fairly cleanly into sulphides and thiophens by repeated chromatography on silica gel.

Some success has been reported also in the separation of sulphides with normal and iso structures[29].

The influence of the surface chemistry of silica gel on the adsorption of organic sulphur compounds has been studied by several workers[30-38]. It has been shown that an increase in the concentration of water from 6 to 10 wt.% produces an almost total loss of the adsorption capacity of silica gel for organic sulphur compounds. Finely porous silica gels are more selective towards organic sulphur compounds than silica gels with larger pores[30]. Because of their greater selectivity, and of their greater surface area, finely porous silica gels offer a greater concentration and a higher yield of sulphur in the chromatographic fractions.

In spite of their greater surface area, silica gels and alumina gels have been found[33-38] to be inferior to alumina-silicas and to natural sorbents in their specific desulphurisation value. The adsorption capacity of silica gel towards organic sulphur compounds is markedly increased by deposition on the silica gel surface of iron[39] or nickel[33] oxides, nickel sulphide and phenyltrichlorosilane[32], or mercury acetate[40].

A comparative study of the adsorption capacity of metal silicates (Mg, Fe, Hg, Cr, Al, Mo) with different metal oxide to silica ratios towards organic sulphur compounds has shown that the most effective adsorbent is chromium silicate[32]. Up to 99.6% of the organic sulphur compounds from an oil fraction can be adsorbed on chromium silicate. Unfortunately the surface compounds undergo catalytic changes on the chromium silicate surface. Catalytic changes in the organic sulphur compounds have been observed also in the desulphurisation of fuels on alumina–silica catalysts[35,36,41-47]. Furthermore hydrogen bond formation between the SH group of mercaptans and the surface hydroxyl groups has been suggested[34].

On changing from adsorption on silica gel to adsorption on alumina an inversion of the relative adsorption affinities of organic sulphur compounds and aromatic hydrocarbons has been observed[48]. Unlike the selectivity of silica gel[49-52] towards organic sulphur compounds, that of alumina increases steeply with the temperature of the preliminary heat treatment[53]. With alumina baked at 700 °C up to 93% of the organic sulphur compounds could be removed from an oil fraction. Sulphides[54] and thiophens[55] can be separated more fully from petroleum fractions by successive chromatographic treatments on silica gel and on alumina.

Naturally occurring sorbents and alumina–silicas are used mainly for desulphurising petroleum products and natural gases[13,32-35]. The desulphurising power of bauxite can be increased by working at a higher adsorption temperature, which assists the chemisorption and the catalytic changes of the organic sulphur compounds. It has been shown[34] that sulphides and disulphides are fully desorbed from the bauxite surface, whereas mercaptans are oxidised to disulphides. The latter reaction is observed also on zeolites[13].

The use of manganese and iron ores[56] and of tripoli earth[18] for desulphurising petroleum products in the liquid and the vapour phase has shown that the adsorption capacity of these materials towards organic sulphur compounds is relatively low. In some cases the effectiveness of the natural sorbent tripoli earth has been improved by acid–alkali activation.

Zeolites can be used to purify petroleum products from sulphur-containing constituents and to separate these impurities[57,58]. However this method of sulphur removal is most widely used for gaseous media[13,59,60]. Natural gas can be purified from hydrogen sulphide and other sulphur gases on zeolites.

Several variants of analytical and preparative gas–liquid chromatography[3,23,24,61] are used for identifying and classifying into groups the organic sulphur compounds obtained from petroleum products. The method offers effective separation into groups in the case of the low-molecular-weight organic sulphur compounds obtained from benzine and kerosine distillates[62-64]. However the results are directly applicable to the analysis of heavier fractions, because of the volatility of the liquid phase at the relatively high temperatures used in the chromatographic analysis. In this context the correct choice of adsorbent for analysis and preparative separation by liquid–adsorption chromatography is most important[65,66].

The method of chromatography in a thin layer of adsorbent has been widely used to monitor rate and extent of reaction in the synthesis of sulphides[67] and in studies of the reactions and transformations of sulphides[67,68].

III. ISOTHERMS AND HEATS OF ADSORPTION

The isotherms and the heats of adsorption provide important information on the mechanism of the interaction of organic sulphur compounds with the adsorbent surface. Adsorption isotherms have been measured mainly for low-molecular aliphatic sulphides[35,50-52,69], some aromatic (diphenyl and dibenzyl) sulphides[36], and thiophen[70-72] on silica gels, on mixed oxides, and on zeolites and naturally occurring sorbents.

A detailed study has been made[70-72] of the isotherm for the adsorption of thiophen from solutions in heptane and in benzene. As shown in Fig.1, in the low-coverage region the adsorption of thiophen by 13X zeolite is an order of magnitude greater than adsorption by silica gel or alumina. The difference on the adsorption of thiophen on silica gel and on alumina is relatively small.

A study of the adsorption isotherms of thiophen and of benzene on silica gel, alumina gel, and alumina[70] showed that the adsorption of thiophen (for the same relative pressure) is greater (by ~10%). The difference in adsorption is ascribed to the smaller size of the thiophen molecule (38 Å^2, as compared with 41 Å^2 for the benzene molecule). However the difference between the specific interaction energies of thiophen

(2.3 kcal mole^{-1}) and benzene (1.7 kcal mole^{-1}) with the silica surface suggests that the adsorption may be affected also by the interaction of the hydroxyl groups with the sulphur atom.

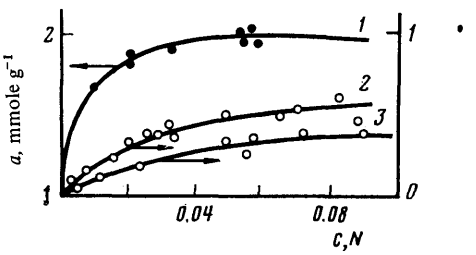


Figure 1. Isotherms for the adsorption of thiophen from hepaten on: *1*) 13X zeolite, *2*) silica gel, and *3*) aluminium oxide (*c* is the equilibrium concentration, *a* is the adsorption).

The influence of the chemistry of the adsorbent surface on the type of interaction can be studied by comparing the heats of adsorption of thiophen on mixed oxides, on silica gel, and on naturally occurring sorbents[49,74,75]. The cobalt–molybdenum oxide catalyst gives the highest interaction energy for thiophen molecules (15.5 kcal mole^{-1}, as compared with 8.4 kcal mole^{-1} on silica gel). Changes in the chemistry of the catalyst surface (by sulphidation) and of the silica gel (by dehydroxylation) are always accompanied by changes in heat of adsorption. However the largest effect is observed after sulphidation of the cobalt–molybdenum oxide catalyst: the heat of adsorption of thiophen on a sulphidised sample (6.6 kcal mole^{-1}) is close to the value obtained for a dehydroxylated sample of silica (6.1 kcal mole^{-1}).[49]

The effect of dehydroxylation of Aerosil[49] and silica gel surfaces[50–52] on the interaction energy of adsorbed molecules has been observed also for other classes of sulphur compounds. Progressive dehydroxylation of an Aerosil surface (by heating the sample at 300, 500, and 900 °C) lowers the heats of adsorption of sulphides, disulphides, and thiophens. By increasing the level of dehydroxylation of the surface we can decrease the sensitivity of the heat of adsorption to the chemical properties of the adsorbed molecules, confirming the important contribution of the sulphur atom to the specific interaction energy with the hydroxyl groups.

The nature of the interaction of organic sulphur compounds with the OH groups of the silica surface is reflected by the specific component of the heat of adsorption ΔQ.[49] Relatively low values of ΔQ (2.3–4.8 kcal mole^{-1}) suggest interaction through a hydrogen bond. Saturated aliphatic hydrocarbons have almost identical specific interaction energies (3.9–4.4 kcal mole^{-1}), somewhat lower than the specific interaction energy of cyclic sulphides (4.8 kcal mole^{-1}). It is interesting to note that disulphides have a specific interaction energy (3.0–3.2 kcal mole^{-1}) 1.5 times lower than that of sulphides. Even lower ΔQ values (2.6–2.2 kcal mole^{-1}) are reported[76] for compounds of the thiophen series, suggesting that the contribution of the sulphur atom to the interaction is weakened by the conjugation of its unshared electron pairs with the π-electrons of the thiophen ring.

The effect of dehydroxylation of the silica gel surface (by baking the sample at 200 and 500 °C) on the adsorption of low-molecular sulphur compounds has been studied by Ross and coworkers[50–52]. The fast desorption of hydrogen sulphide from the surface confirms that adsorption is physical, as reported also in Refs.69 and 77. The adsorption of methyl and ethyl mercaptan, and of dimethyl sulphide, is also reversible[50]. The energy of the specific interaction of methyl mercaptan with the hydroxyl groups of silica gel is ~2.2 kcal mole^{-1}.[50]

It has been suggested that the difference in the nature of the interactions of SO_2,[50] H_2S, CH_3SH, C_2H_5SH, and $(CH_3)_2S$[51,52] with the silica gel surface is determined by the symmetry and the character of the spatial localisation of the orbits occupied by the unshared electron pairs. This explanation is consistent with the formation of complexes of methyl mercaptan and dimethyl sulphide with diborane [$CH_3SH.BH_3$; $(CH_3)_2S.BH_3$]. This type of complex is not formed by hydrogen sulphide[78].

When organic sulphur compounds are adsorbed on silica gel at 150 °C the initial heat of adsorption is fairly high[51] (>30 kcal mole^{-1}): this is probably due to the presence of impurities, undergoing surface reactions.

The adsorption of methyl mercaptan, ethyl mercaptan, dimethyl sulphide, and hydrogen sulphide on γ-Al_2O_3 baked at 700 °C has been studied[79] at 150 °C. Hydrogen sulphide is adsorbed less readily than the other compounds. Unlike the adsorption of methyl and ethyl mercaptan and dimethyl sulphide, the adsorption of hydrogen sulphide leaves a residue of elemental sulphur on the γ-Al_2O_3 surface, which proves the reality of surface decomposition reactions.

The heat of adsorption of hydrogen sulphide falls from 31.5 to 16.3 kcal mole^{-1} as the surface coverage is increased from 0.05 to 0.34 mmole m^{-2}. Similar variations were observed for the adsorption of hydrogen sulphide on γ-Al_2O_3 at 300 and 464 °C, when the heat of adsorption was 25 and 38 kcal mole^{-1} for surface loadings of 0.17 and 0.114 mmole m^{-2} respectively[80]. The heats of adsorption (Q, kcal mole^{-1}) of organic sulphur compounds on silica gel[52] and alumina[79] surfaces dehydroxylated at different temperatures are listed below (for a surface coverage of 1.4 mmole m^{-2}):

t, °C	Silica gel			γ-Al_2O_3
	240	550	700	700
Hydrogen sulphide	9.8	7.3	5.8	16.8
Methyl mercaptan	11.5	10.5	6.5	16.5
Ethyl mercaptan	12.3	11.7	9.7	18.4
Dimethyl sulphide	17.5	14.7	12.3	20.7

The higher heats of adsorption on γ-Al_2O_3 than on silica gel (at the same coverage) are ascribed to the interaction of the organic sulphur compounds with both the surface hydroxyl groups and the Lewis-acid centres of γ-Al_2O_3.

Gal'pern and coworkers[32] describe a comparative study of the adsorption of dibenzyl sulphide, diisopentyl sulphide, and biphenyl from solutions in iso-octane on a magnesium silicate adsorbent and on coarsely porous silica gel modified by nickel sulphide and phenyltrichlorosilane. The largest difference in the adsorptions of the sulphides and of biphenyl was observed on silica gel coated with a layer of nickel sulphide[32]. The largest increase in the adsorption capacity of tripoli earth[18] for dibutyl sulphide was achieved by acid–base activation (with a mixture of 12% NaOH and 20% HCl) of the surface of the naturally occurring sorbent.

Studies of the adsorption isotherms of organic sulphur compounds on zeolites have shown that the nature of the interaction is determined by the geometric and by the chemical structure of both the adsorbed molecules and the zeolite surface. It is reported[13,81] that hydrogen sulphide and mercaptans can be removed by CaA zeolites, and cyclic organo-sulphur compounds by type X zeolites: the difference is due mainly to steric hindrance during adsorption. The largest effect on the amount of adsorption is produced by the

type and extent of cation exchange. Thus it is shown[17] that the adsorption of sulphur compounds is more extensive on zeolites containing alkaline-earth metal cations than on NaY zeolite. However the adsorption does not increase regularly as the Na^+ cations are replaced by univalent and bivalent metal cations[82-86]. The amount of exchange giving optimum adsorption depends on the type of molecule being adsorbed, and for organic sulphur compounds (ethyl propyl sulphide, di-n-butyl sulphide, thiophen, alkyl mercaptan, thiophenol) the optimum varies between 25 and 70%.

The increased adsorption capacity of zeolites as a result of ion exchange is due to the creation on the zeolite surface of a distribution of cations with different charges which is favourable to adsorption. The adsorption capacity of NaA and NaX zeolites and their magnesium-substituted samples can be increased also by pre-adsorption of a controlled amount (between 1 and 3.5 wt.%) of H_2O, NH_3, or CH_3NH_2.[15,87] The exchangeable cations are located in different sites of the zeolite network, and site exchange is possible during adsorption[88,89].

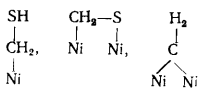
The activity of zeolites towards organic sulphur compounds is substantially increased by decationation of the zeolite[90]. In this case the activity increases monotonically with the extent of decationation. By using this type of sample thiophen can be extracted almost quantitatively from dilute solutions in benzene.

IV. SPECTROSCOPIC STUDY OF ADSORPTION

The optical method most widely used to study the hydroxyl covering of oxide surfaces and its role in adsorption interactions is infrared spectroscopy[91-93]. It was first applied to studies of the adsorption mechanism of organic sulphur compounds by Eyring and Wadsworth[94], who explained the spectra of n-hexyl mercaptan on zinc oxide, sulphide, and silicate, and also on willemite ($ZnSiO_4$), by postulating the surface reaction

$$-Zn-OH + HSR \rightarrow -Zn-SR + H_2O.$$

From the spectra of hydrogen sulphide, methyl mercaptan, ethyl mercaptan, and diethyl sulphide adsorbed on nickel (20%) supported on silica gel it was concluded[95] that surface compounds of the following types are formed:



Analogous structures were proposed for chemisorbed ethyl mercaptan and diethyl sulphide.

The interaction of sulphides, disulphides, mercaptans, and thiophens with the surface hydroxyl groups of silica samples baked at 200 and 500 °C has been investigated by infrared spectroscopy[96-99]. It was found that the organic sulphur compounds interact with the hydroxyl groups of the silica surface, as shown by the decreased intensity and the shift of the absorption band at 3750 cm^{-1} (which characterises the stretching vibrations of the free OH groups). For the sulphides the absorption band of the perturbed OH groups lies at 3320–3390 cm^{-1}, for the mercaptans at 3310–3475 cm^{-1}, for the disulphides at 3340–3530 cm^{-1}, and for the thiophens at 3600–3630 cm^{-1}.

The smallest shifts in the absorption band for the stretching vibrations of the surface hydroxyl groups are observed after adsorption of compounds of the thiophen series (thiophen, 3-propylthiophen, 2,5-diethylthiophen, which give shifts of 116, 140, and 150 cm^{-1} respectively). These small values suggest a weak participation in adsorption interaction by the sulphur atom, due to the conjugation of its unshared electron pairs with the π-electrons of the thiophen ring.

It has also been shown that organic sulphur compounds of the aromatic type can interact with hydroxyl groups both through the unshared electron pairs of the sulphur and through the π-electron system. The absorption band at 3640 cm^{-1} characterises the interaction of the OH groups with the benzene ring, and the absorption band at 3550 cm^{-1} their interaction with the sulphur atom of thiophenol (Fig. 2). The shift of the absorption band of the surface hydroxyl groups increases in the same sequence as the specific interaction energy[49]. In homologous series of organic sulphur compounds the quantity $\Delta\nu_{OH}$ varies in direct proportion to the ionisation potential. The observed spectral[97-99] and energy parameters[49] of the adsorption process lead to the conclusion that organic sulphur compounds can be arranged in the following series as regards their affinity towards hydrogen bond formation with surface hydroxyl groups: sulphides > mercaptans > disulphides > thiophens.

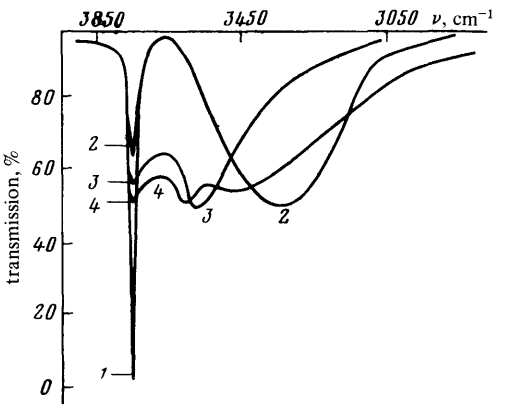


Figure 2. Changes in the spectrum of the surface hydroxyl groups of Aerosil (*1*) caused by the adsorption of organic sulphur compounds: *2*) dipropyl sulphide, *3*) thiophen, *4*) thiophenol (spectrum *1* was obtained after vacuum baking the sample for 5 h at 500 °C).

We should note that organic sulphur compounds behave as weaker donors than oxygen compounds of the same structure when forming hydrogen bonds with surface hydroxyl groups. This effect can be ascribed (as in the formation of hydrogen bonds with proton-donating solvents[100,101]) to the difference in electronic structure between the sulphur and the oxygen atom.

The i.r. spectra of sulphides, disulphides, mercaptans, and thiophens adsorbed on alumina[96,102-106] or on mixed oxides (Al_2O_3, NiO, MoO_3)[95,106-108] show that surface reactions can occur in parallel with the physisorption of organic sulphur compounds as a result of the formation of co-ordination bonds with the electronically unsaturated surface centres through the sulphur atom.

It has been shown also[97,105] that organic sulphur compounds adsorbed on alumina can interact with the hydroxyl groups of the surface through the formation of a hydrogen bond. The changes in frequency of the OH absorption bands ($\Delta\nu_{OH}$,

cm^{-1}) caused by adsorption on silica and on alumina are listed below:

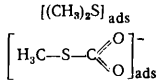
Compound	Thiophan	Dimethyl sulphide	Dimethyl disulphide	Thiophenol	Thiophen
SiO_2[49]	415	369	215	200	116
γ-Al_2O_3[66]	180	130	120	130	100

The shifts in the absorption bands of the structural hydroxyl groups produced by the adsorption of aliphatic and cyclic sulphides and disulphides and of aliphatic mercaptans on alumina are less substantial than the shifts produced in silica. We note that the shift $\Delta\nu_{Al-OH}$ is less sensitive to the state of the sulphur atom in the molecule. Thus on changing from thiophan to thiophen the shift changes by ~3.6 for adsorption on silica and only by 1.8 for adsorption on alumina, which may be explained, as in the case of the adsorption of ethers[91], by the amphoteric nature of the groups in aluminium oxide. However, in contrast to adsorption on pure silica, we observe the formation of surface compounds containing CH_2 and CH_3 groups (with absorption bands at 2890, 2950, and 2988 cm^{-1}).

Analogous spectral changes in the region 2700–3200 cm^{-1} are observed during the interaction of thiophen with the surface of nickel[95], montmorillonite[76], cobalt molybdate, and molybdenum or germanium sulphide[107,108], and also zeolites of type HY,[109] NaX, CaX,[110] NaY, CaY, and CuNaY.[111,112]

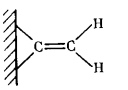
The spectra of sulphides, mercaptans, disulphides, and thiophens adsorbed on alumina[102-106,112,113] and on the oxides of molybdenum, manganese, vanadium, and chromium[114,115] show absorption bands in the region of 1290–1600 cm^{-1} (with maxima at 1290, 1470, 1495, and 1600 cm^{-1}) even at 20 °C. The appearance of these bands is believed to result from the formation of thiocarbonate and thiocarboxylic acid groups on the surface[93,116,117], and of groups with an oxidised sulphur atom (see Table). The absorption bands at 1290, 1495, and 1600 cm^{-1} persist in the spectrum at high desorption temperatures (400–500 °C), demonstrating the high thermal stability of these surface compounds.

Structures formed by the adsorption of dimethyl sulphide on metal oxides (Si, Al, Mo, Cr, Mn, V).[114]

Structure No.	Structure	Formation temp., °C	Decomposition temp., °C
(I)	$[(CH_3)_2S]_{ads}$	20	100–150
(II)		20	450
(III)	$[(CH_3)_2SO]_{ads}$	20	150–200
(IV)	$[(CH_3)_2SO_2]_{ads}$	20	150–200
(V)	$[CH_3SO_3]^-_{ads}$	20–150	450
(VI)	$[HCOO]^-_{ads}$	20–250	450
(VII)	$(SO_4)^{2-}$	150	400–500

The breakdown of the surface structures produced by chemisorbed organic sulphur compounds yields hydrogen sulphide and unsaturated hydrocarbons. Thus on raising the desorption temperature of thiophen adsorbed on ultramarine[119] we observe the appearance of a new spectral band at 2630 cm^{-1} (for desorption at 100 °C), which splits into two bands (2500 and 2650 cm^{-1}) for desorption at 200 °C, accompanied by a new absorption band at 2690 cm^{-1}, characteristic of adsorbed hydrogen sulphide (2679 cm^{-1}). All three absorption bands disappear at 300 °C. Similar adsorption bands were observed[108] during the desorption of thiophen, water, and hydrogen adsorbed on MoS_2 and GeS. It is suggested[108,119] that the absorption bands at 2500–2700 cm^{-1} correspond to the vibrations of the S–H bonds of surface compounds. The appearance of absorption bands at 2850, 2960, and 3045 cm^{-1} is ascribed to the formation of but-1-ene or but-2-ene.

The absorption bands at 3050, 3140, and 3150 in the spectrum are assigned to HC ≡ CH surface groups, or to the structure



Davydova and coworkers[114,115] observed the oxidation of dimethyl sulphide on molybdenum, manganese, vanadium and chromium oxides in the presence of surface oxygen. The evidence was the appearance in the spectrum (Fig. 3) of absorption bands at 1045, 1145, and 1320 cm^{-1}, typical of the stretching vibrations of the SO group in adsorbed dimethyl sulphoxide[120] and dimethyl sulphone[121] [structures (III) and (IV)]. Raising the adsorption temperature (to 150 °C) caused the formation of surface structures [(V) and (VII)] with a sulphur atom in a higher state of oxidation, as shown by the appearance of absorption bands at 1045, 1145, and 1275 cm^{-1}, characteristic of the vibrations of the S–O bond in sulphites, sulphates, and sulphonates[122] [structure (VII)]. The formation of absorption bands at 1360 and 1380 cm^{-1} (stable up to 450–500 °C) in the spectrum of dimethyl sulphide adsorbed on chromium oxide at 250 °C is ascribed to formate ions on the surface [structure (VI)].

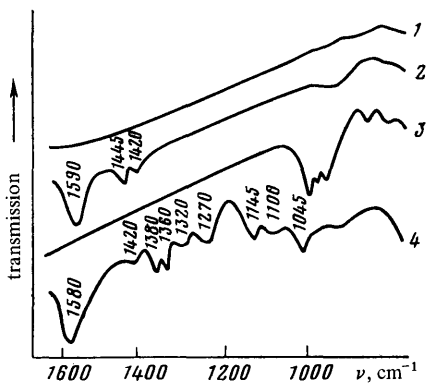


Figure 3. I.r. absorption spectra of chromium oxide: *1*) activated in vacuum at 250 °C, *2*) after adsorption of dimethyl sulphide at 250 °C, *3*) activated in oxygen at 250 °C, *4*) adsorption of dimethyl sulphide at 250 °C on a sample activated in oxygen.

Thiocarboxylate and thiocarbonate groups, and groups with an oxidised sulphur atom, are formed also during the adsorption of sulphur compounds on alumina, and on NaY, CaY, NaCay, and CuNaY zeolites[110-112,123,124]. The adsorption of thiophen on zeolites with exchanged cations of the transition metals produces complex compounds[110]. More

extensive decomposition of the sulphur-containing molecules occurs when the univalent cation is replaced by a bivalent cation. It is found[109,123] that the adsorption mechanism is strongly influenced by the protonic acidity of the zeolite. Thus on HY zeolite[109,123] (but not on NaY zeolite) thiophen undergoes chemical reactions involving the breaking of C–S bonds and the formation of surface compounds containing S–H bonds (2380 cm^{-1}) and unsaturated (3100 cm^{-1}) or saturated (2800–3000 cm^{-1}) C–H bonds. These results are relevant to our understanding of the mechanism of catalytic hydrodesulphurisation processes for organic sulphur compounds.

In recent years adsorption and spectra methods have been combined to demonstrate the important role of impurity centres during adsorption on silicas[91,125,126]. These results help us to understand the mechanism of adsorption, because technical grades of siliceous adsorbents always contain impurities of aluminium, iron, and other oxides. The effect of aluminium, boron, cadmium, titanium, and iron oxides on the interaction of organic sulphur compounds with silica has been studied in detail[96,127,128]: it was found that the sulphur compounds interact by the hydrogen bond mechanism with the silanol hydroxyl groups and with OH groups bound to impurity metal atoms. Furthermore the presence of impurity centres leads to chemisorption and to the formation of surface complexes, with partial decomposition of the sulphur compound.

U.v. spectroscopy has been used[129,130] for the analysis of charged forms of adsorbed molecules such as carbonium ions. We have studied[131] the u.v. spectra of thiopehn, thiophan, thiophenol, benzothiophen, 2- and 3-methylbenzothiophens, and 2-methyl-2,3-dihydrobenzothiophen adsorbed on alumina and on alumina-silica. Adsorption of these molecules on alumina does not produce any charged forms up to 300 °C, but charged forms are produced by adsorption on alumina–silica at temperatures above 100 °C.

V. QUANTUM-CHEMICAL CALCULATIONS OF ADSORPTION COMPLEXES

The methods of quantum chemistry are being used increasingly in the study of adsorption mechanisms[132–134]. In this approach the conventional semi-empirical procedures of quantum chemistry are applied to calculations on models which include an adsorbed molecule and an atom from the adsorbent surface (cluster).

Relying on the simple Hückel method, Stodoiski and coworkers[135] used the interaction between organic sulphur compounds and a transition metal surface to calculate adsorption models, allowing for the possible formation of surface structures without dissociation of the adsorbed molecules and also for the formation of sulphide layers by the reactions

$$R{-}S + M \rightarrow M \ldots S{-}R, \quad (1)$$

$$R{-}S + M \rightarrow R + MS, \quad (2)$$

where R is a hydrocarbon radical and M is a metal atom.

It was found that the stability of the S–M bond decreases as the electronegativity of the metal increases. The reaction between the organic sulphur compound and metals was shown to weaken the C–S bond and to strengthen the adjacent C–C bond. A significantly large decrease in the population of the C–S bond indicates the possibility of dissociation of the adsorbed molecules. By calculating the energy of reaction (2) it was shown that dissociation is most likely with thiophenol, hexamethylene sulphide, and vinyl mercaptan.

We have also used[136] the extended Hückel method in calculations on adsorption complexes containing hydroxyl groups, modelling the interaction of thiophen and dimethyl sulphide with oxide surfaces. The change in the properties of the hydroxyl group on different oxide surfaces was modelled by assigning a predetermined charge to the hydroxyl group. The CNDO/2 method was used[137] to show that the charge on the proton can be correlated with the acidic properties of the hydroxyl groups. Recent calculations[136] have shown that better agreement with experimental data[49,96,97] can be expected for models including uncharged hydroxyl groups.

The substantial stabilisation and strong change in the charge on the sulphur atom in the complexes produced by thiophen and dimethyl sulphide with a positively charged hydroxyl group are ascribed to the formation of bonds with charge transfer from the sulphur atom towards the hydroxyl group. In the model complexes between dimethyl sulphide and the hydroxyl group the weakening of the O–H bond is more marked than in the corresponding thiophen complexes. These results are consistent with the more substantial shift of the surface hydroxyl absorption band at 3750 cm^{-1} [96,97] and with the greater specific interaction energy for the adsorption of dimethyl sulphide on silica (360 cm^{-1} and 3.2 kcal $mole^{-1}$ respectively) as compared with the adsorption of thiophen (120 cm^{-1} and 2.3 kcal $mole^{-1}$ respectively). The calculations suggest that interaction of the organic sulphur compounds with two surface hydroxyl groups may be preferred on energy grounds. Hence a planar orientation of the molecules on the silica surface is probably the most favourable.

---oOo---

Thus adsorption-chromatographic methods will be used increasingly for the separation of naturally occurring organic sulphur compounds without changing their structure, and also for developing new methods of classifying these compounds by group (sulphides, disulphides, mercaptans, thiophens) and according to structural features within a homologous series.

The solution of important problems in the chemistry of the sulphur compounds occurring in petroleum depends on a correct understanding of the mechanism by which organic sulphur compounds interact with adsorbents of different types: this understanding is needed in the search for new modifying additives for inorganic sorbents, aimed at increasing their efficiency and at extending the practical utilisation of sulphur compounds from petroleum in the national economy.

This review has shown that the application of thermodynamic and spectral methods (together with quantum-chemical calculations) to adsorption studies can assist our understanding of the interactions taking place on the surface.

REFERENCES

1. V.Z.Minaev, M.A.Lur'e, B.N.Matveev, V.G.Lipovich, and I.V.Kalechits, "Kataliticheskie Prevrashcheniya Uglevodorodov" (Catalytic Transformations of Hydrocarbons), Izd.Irkutsk.Univ., 1976, p.3.
2. S.A.Giller, Symposium "Izuchenie i Ispol'zovanie Geteroatomnykh Komponentov Sernistykh Neftei" (Study and Utilisation of the Hetero-atomic Components of Sulphur-bearing Petroleum), Izd.Zinatne, Riga, 1976, p.6.
3. G.D.Gal'pern, Uspekhi Khim., **45**, 1395 (1976)[Russ. Chem.Rev., No.8 (1976)].
4. G.D.Gal'pern, Internat.J.Sulphur.Chem., **B6**, 115 (1971).

5. Yu.E.Nikitin, Yu.I.Murinov, N.K.Lyapina, V.G.Ben'kovskii, N.I.Antipov, V.I.Boldin, P.S.Vlasov, A.K.Ivanov, V.V.Bulantsev, and V.A.Mikhailov, USSR P. 397 514/1973; Byull.Izobr., No.37 (1973).
6. Yu.E.Nikitin, N.L.Egutkin, Yu.I.Murinov, and N.K.Lyapina, USSR P. 466 182/1974; Byull.Izobr., No.13 (1975).
7. Yu.E.Nikitin, Yu.I.Murinov, A.M.Rozen, N.Z.Mineeva, A.A.Gavrilova, A.G.Kartavtseva, A.P.Kapina, and N.L.Egutkin, Symposium "Khimiya i Fizikokhimiya Monomerov" (Chemistry and Physical Chemistry of Monomers), Izd.Bashkirsk.Filiala Akad.Nauk SSSR, Ufa, 1975, p.141.
8. Ya.I.Yashin and A.V.Kiselev, "Gazoadsorbtsionnaya Khromatografiya" (Gas Adsorption Chromatography), Izd.Nauka, Moscow, 1967.
9. N.N.Avgul', A.V.Kiselev, and D.P.Poshkus, "Adsorbtsiya Gazov i Parov na Odnorodnykh Poverkhnostyakh" (Adsorption of Gases and Vapours on Homogeneous Surfaces), Izd.Khimiya, Moscow, 1975.
10. E.A.Flood (Editor), "The Gas–Solid Interface" [Arnold, 1967] (Translated into Russian), Izd.Mir, 1970.
11. V.N.Zrelov and G.I.Kichkin, "Khromatografiya v Neftyanoi i Neftekhimicheskoi Promyshlennosti" (Chromatography in the Petroleum and Petrochemicals Industry), GNTINGL, Moscow, 1963.
12. "Adsorbenty Dlya Analiza i Razdeleniya Nefteproduktov" (Adsorbents for the Analysis and Separation of Petroleum Products), Izd.Fan, Tashkent, 1970.
13. N.V.Kel'tsev, "Osnovy Adsorbtsionnoi Tekhniki" (Fundamentals of Adsorption Technology), Izd. Khimiya, Moscow, 1976.
14. E.A.Aripov, D.A.Usmanova, and Yu.A.El'tekov, Symposium "Adsorbenty, Ikh Poluchenie, Svoistva, i Primenenie" (Adsorbents: Their Production, Properties, and Applications), Izd.Nauka, Leningrad, 1971, p.128.
15. W.Friedrich and B.Karl-Heinz, Chem.Techn., **26**, 707 (1974).
16. E.I.Shcherbina, V.A.Yakubovich, and L.I.Mikhal'skaya, Neftekhimiya, **47**, 151 (1977).
17. B.Karl-Heinz and W.Friedrich, Z.Chem., **14**, 344 (1974).
18. V.T.Bykov, G.N.Vasilenko, G.A.Krizhanenko, V.N.Telesheva, and B.T.Gerasimov, "Organicheskie Soedineniya Sery" (Organic Sulphur Compounds). Vol.1, Izd.Zinatne, Riga, 1976, p.107.
19. G.A.Rumyantseva, N.N.Gryazev, and M.N.Rakhlevskaya, "Organicheskie Soedineniya Sery" (Organic Sulphur Compounds), Vol.1, Izd.Zinatne, Riga, 1976, p.114.
20. D.Haresnape, F.A.Fidler, and R.A.Lowry, Ind. Eng.Chem., **41**, 2691 (1949).
21. H.Prinzler and R.Ochler, Chem.Techn., **15**, 31 (1963).
22. I.U.Numanov and I.M.Nasyrov, "Geteroatomnye Komponenty Neftei Tadzhikskoi Depressii" (Heteroatomic Components of Petroleum from the Tadzhik Depression), Izd.Donish, Dushanbe, 1973, p.22.
23. D.K.Zhestkov and G.D.Gal'pern, Symposium "Metody Analiza Organicheskikh Soedinenii Nefti, Ikh Smesei, i Proizvodnykh" (Methods of Analysis of Organic Compounds from Petroleum. Their Mixture, and Derivatives), Izd.Nauka, Moscow, 1969, p.28.
24. E.N.Karaulova, "Khimiya Sul'fidov" (Chemistry of Sulphides), Izd.Nauka, Moscow, 1970.
25. E.I.Skripnik, K.P.Sorokina, and V.I.Dolganov, Symposium "Khimiya Seraorganicheskikh Soedinenii Soderzhashchikhsya v Neftyakh i Nefteproduktakh" (Chemistry of Organic Sulphur Compounds Found in Petroleum and Petroleum Products), Vol.6, Izd. Khimiya, Moscow, 1964, p.48.
26. I.A.Rubinshtein, Yu.A.Markov, and S.E.Krein, Neftekhimiya, **13**, 280 (1973).
27. Yu.A.Markov, I.A.Rubinshtein, E.A.Popova, and S.E.Krein, Symposium "Organicheskie Soedineniya Sery" (Organic Sulphur Compounds), Vol.1, Izd. Zinatne, Riga, 1976, p.195.
28. R.D.Obolentsev, N.K.Lyapina, G.V.Galeeva, and and V.N.Tazeeva, Neftekhimiya, **10**, 110 (1970).
29. R.D.Obolentsev, B.V.Aivazov, and S.V.Netupskaya, Dokl.Akad.Nauk SSSR, **106**, 283 (1956).
30. R.D.Obolentsev, B.V.Aivazov, and K.V.Titova, Symposium "Khimiya Sera- i Azotorganicheskikh Soedinenii Soderzhashchikhsya v Neftyakh i Nefteproduktakh" (Chemistry of Sulphur- and Nitrogen-containing Organic Compounds Found in Petroleum and Petroleum Products), Izd.Bashkirsk.Filiala Akad.Nauk SSSR, Ufa, 1960, p.211.
31. P.I.Sanin, E.A.D'yachkova, and N.I.Komissarova, Symposium "Khimiya Seraorganicheskikh Soedinenii Soderzhashchikhsya v Neftyakh i Nefteproduktakh" (Chemistry of Organic Sulphur Compounds Found in Petroleum and Petroleum Products), Vol.2, Izd.Akad, Nauk SSSR, Moscow, 1959, p.125.
32. G.D.Gal'pern, V.N.Karicheva, and A.S.Nekrasova, Symposium "Khimiya Sera- i Azotorganicheskikh Soedinenii Soderzhashchikhsya v Neftyakh i Nefteproduktakh" (Chemistry of Sulphur- and Nitrogen-containing Organic Compounds Found in Petroleum and Petroleum Products), Vol.3, Izd.Bashkirsk. Filiala Akad.Nauk SSSR, Ufa, 1960, p.219.
33. "Issledovanie Protsessov Adsorbtsionnoi i Kataliticheskoi Ochistki Nefteproduktov v Prisutstvii Poristykh Tel" (Studies of the Adsorption and Catalytic Purification of Petroleum Products in the Presence of Porous Bodies), Izd.Saratovsk.Univ., 1965, No.1.
34. L.M.Belavinskaya, B.M.Gikht, N.N.Gryazev, K.A.Dmitrieva, V.B.Perfilova, N.M.Shubina, and V.K.Shchitikova, Symposium "Khimiya Seraorganicheskikh Soedinenii Soderzhashchikhsya v Neftyakh i Nefteproduktakh" (Chemistry of Organic Sulphur Compounds Found in Petroleum and Petroleum Products), Vol.8, Izd.Vysshaya Shkola, Moscow, 1968, p.370.
35. N.N.Gryazev and M.N.Rakhlevskaya, Zhur.Fiz.Khim., **41**, 622 (1967)[Russ.J.Phys.Chem., No.3 (1967)].
36. N.N.Gryazev and G.G.Sidorenko, Symposium "Khimiya Seraorganicheskikh Soedinenii Soderzhashchikhsya v Neftyakh i Nefteproduktakh" (Chemistry of Organic Sulphur Compounds Found in Petroleum and Petroleum Products), Vol.7, Izd.Khimiya, 1964, p.205.
37. B.M.Gikht, N.N.Gryazev, V.Ya.Karyakina, I.V.Larionov, S.M.Myakushina, V.B.Perfilova, S.I.Orlov, and V.K.Shchitikov, Symposium "Khimiya Seraorganicheskikh Soedinenii Soderzhashchikhsya v Neftyakh i Nefteproduktakh" (Chemistry of Organic Sulphur Compounds Found in Petroleum and Petroleum Products), Vol.7, Izd.Khimiya, 1964, p.200.

38. N.N.Gryazev, V.B.Perfilova, and M.N.Rakhlevskaya, Symposium "Khimiya Seraorganicheskikh Soedinenii Soderzhashchikhsya v Neftyakh i Nefteproduktakh" (Chemistry of Organic Sulphur Compounds Found in Petroleum and Petroleum Products), Vol.9, Izd. Vysshaya Shkola, Moscow, 1972, p.415.
39. K.Wehner and G.Seidel, Chem.Techn., **15**, 276 (1963).
40. W.L.Orr, Analyt.Chem., **38**, 1558 (1963).
41. M.A.Mardanov, Zh.I.Gasanova, A.Ya.Isaev, and E.V.Grigoryan, Trudy Inst.Neftekhim.Protsessov Akad.Nauk AzerbSSR, **8**, 304 (1977).
42. I.N.Diyarov, N.L.Solodova, and N.P.Vasil'eva, Symposium "Khimicheskaya Tekhnologiya Pererabotki Nefti i Gaza" (Chemical Technology of Petroleum and Gas Refining), No.4, Kazan', 1976, p.28.
43. K.Kessel , H.Deringer, and P.Radusch, BRD P.1 470 588/1976.
44. N.Iomiti and Makoto, Meiden Dzikho, No.130, 8 (1976).
45. R.Ikawa, Sulphuric Acid and Ind., 30, 10 (1977).
46. G.E.Samoilenko and Z.V.Vorontsova, Symposium "Metallurgiya i Koksokhimiya" (Metallurgy and Coke Chemistry), No.37, 1974, p.39.
47. M. Zdražil, Coll.Czech.Chem.Comm., **42**, 1484 (1977).
48. H.E.Lumpkin and B.H.Jonson, Analyt.Chem., **26**, 1719 (1954).
49. V.I.Lygin, N.K.Lyapina, and A.D.Ulendeeva, Neftekhimiya, **15**, 474 (1975).
50. W.J.Jones and R.A.Ross, J.Chem.Soc., **A**, 1787 (1968).
51. W.J.Jones and R.A.Ross, J.Chem.Soc., **A**, 1021 (1967).
52. R.W.Glass and R.A.Ross, J.Phys.Chem., 77, 2571 (1973).
53. J.L.Jezl and A.P.Stuart, Ind.Eng.Chem., **50**, 943 (1958).
54. A.A.Rozhdestvenskaya, B.B.Krol', L.G.Zherdeva, and N.N.Kucheryavaya, Symposium "Khimiya Seraorganicheskikh Soedinenii Soderzhashchikhsya v Neftyakh i Nefteproduktakh" (Chemistry of Organic Sulphur Compounds Found in Petroleum and Petroleum Products), Vol.8, Izd.Vysshaya Shkola, 1968, p.348.
55. M.A.Parfenova, N.K.Lyapina, E.S.Brodskii, and T.S.Nikitina, Neftekhimiya, 17, 156 (1977).
56. V.T.Chagunava and E.R.Dzneladze, Symposium "Khimiya Seraorganicheskikh Soedinenii Soderzhashchikhsya v Neftyakh i Nefteproduktakh" (Chemistry of Organic Sulphur Compounds Found in Petroleum and Petroleum Products), Vol.5, Gostoptekhizdat, Moscow, 1963, p.113.
57. Yu.A.El'tekov, L.I.Piguzova, and V.N.Novikova, Symposium "Khimiya Seraorganicheskikh Soedinenii Soderzhashchikhsya v Neftyakh i Nefteproduktakh" (Chemistry of Organic Sulphur Compounds Found in Petroleum and Petroleum Products), Vol.7, Izd. Khimiya, Moscow–Leningrad, 1964, p.173.
58. L.I.Mikhal'skaya and V.A.Yakubovich, Symposium "Khimiya i Khimicheskaya Tekhnologiya" (Chemistry and Chemical Technology), No.9, Izd.Vysheish. Shkola, Minsk, 1975, p.64.
59. G.A.Sharkin, M.L.Dantsig, G.A.Dantsig, V.N.Men'shov, V.I.Yakerson, L.P.Fominskii, E.V.Gorozhanin, G.P.Cherkasov, and Z.M.Mosolova, USSR P.527 201 (1974); Byull.Izobr., No.33, 1975.
60. I.M.Starshov, G.Ya.Rovanova, R.G.Galeeva, and R.G.Sharafutdinov, Symposium "Neftepererabotka i Neftekhimiya" (Petroleum Refining and Petroleum Chemistry), No.5, 1975, p.34.
61. W.Bruning and A.Bruning, Anais Assoc.brasil.Quím., **28**, 61 (1972).
62. T.I.Allilueva, Thesis, Ufa, 1969.
63. R.D.Obolentsev, T.I.Allilueva, S.S.Krivolapov, and L.G.Gapich, Symposium "Khimiya Seraorganicheskikh Soedinenii Soderzhashchikhsya v Neftyakh i Nefteproduktakh" (Chemistry of Organic Sulphur Compounds Found in Petroleum and Petroleum Products), Vol.7, Izd.Khimiya, Moscow–Leningrad, 1964, p.243.
64. S.L.Gusinskaya and O.A.Beiko, Neftekhimiya, **16**, 602 (1976).
65. O.A.Beiko, Neftekhimiya, **16**, 596 (1976).
66. V.P.Yakimova, Gigiena i Sanitariya, **5**, 55 (1977).
67. E.N.Karaulova, Symposium "Metody Analiza Organicheskikh Soedinenii Nefti, Ikh Smesei, i Proizvodnykh" (Methods of Analysis of Organic Compounds from Petroleum, Their Mixtures, and Derivatives), Izd.Nauka, Moscow, 1969, p.76.
68. V.I.Dronov, V.A.Snegotskaya, L.P.Ivanova, D.P.Voronchikhina, and N.N.Bannikova, Symposium "Khimiya Seraorganicheskikh Soedinenii Soderzhashchikhsya v Neftyakh i Nefteproduktakh" (Chemistry of Organic Compounds Found in Petroleum and Petroleum Products), Vol.9, Izd.Vysshaya Shkola, Moscow, 1972, p.218.
69. E.B.Miller, US P. 2 784 804/1957; Chem.Abs., **51**, 8413 (1957).
70. A.V.Kiselev, V.N.Semenova, and Yu.A.El'tekov, Kinetika i Kataliz, **3**, 937 (1962).
71. Yu.A.El'tekov and V.N.Semenova, Symposium "Khimiya Seraorganicheskikh Soedinenii Soderzhashchikhsya v Neftyakh i Nefteproduktakh" (Chemistry of Organic Sulphur Compounds Found in Petroleum and Petroleum Products), Vol.6, Izd.Khimiya, Moscow, 1964, p.243.
72. E.A.Agronomov and Yu.S.Mardashev, Vestnik Moskov.Univ., **3**, 197 (1958).
73. V.Ya.Davydov, A.V.Kiselev, and V.I.Lygin, Dokl. Akad.Nauk SSSR, **147**, 131 (1962).
74. V.I.Erofeev and V.V.An, "Tezisy Dokladov XIV Nauchnoi Sessii po Khimii i Tekhnologii Organicheskikh Soedinenii Sery i Sernistykh Neftei" (Abstracts of Papers Presented to the Fourteenth Scientific Session on the Chemistry and Technology of Sulphur Compounds and of Sulphur-bearing Petroleum), Izd.Zinatne, Riga, 1976, p.200.
75. Ya.D.Zel'venskii and I.G.Sarshivili, Zhur.Prikl. Khim., **29**, 833 (1956).
76. R.Cloos, D.Varde Poel, and J.P.Camerlynck, Nature, Phys.Sci., **243**, 54 (1973).
77. W.Stober, Kolloid, Z.–Z.Polym., **145**, 17 (1956).
78. A.B.Burg, Symposium "Organic Sulphur Compounds" (N.Kharasch, Editor), Pergamon, London, 1961, p.30.
79. R.W.Glass and R.A.Ross, J.Phys.Chem., 77, 2576 (1973).
80. A.J.de Rosset, C.G.Finstrom, and C.J.Adams, J. Catalysis, **1**, 235 (1962).
81. F.Wolf and K.H.Bergk, Chem.Techn., **26**, 361 (1974).
82. E.Wolf, W.Höse, and H.Fürtig, Chem.Techn., 27, 362 (1973).
83. F.Wolf, J.Junge, and K.Pilchowski, Z.Chem., **15**, 75 (1975).
84. L.I.Mikhal'skaya and V.A.Yakubovich, Symposium, "Khimiya i Khimicheskaya Tekhnologiya" (Chemistry and Chemical Technology), No.10, Izd.Vysheish. Shkola, Minsk, 1976, p.69.

85. A.V.Kiselev, Yu.A.El'tekov, and V.N.Novikova, Neftekhimiya, **5**, 136 (1965).
86. E.A.Aripov, A.V.Kiselev, D.A.Usmanova, and Yu.A.El'tekov, Kolloid.Zhur.. **36**, 742 (1974).
87. F.Wolf, W.Höse, and H.Fürtig, Chem.Techn.. **27**, 541 (1975).
88. S.S.D'yakonov, A.V.Kiselev, N.M.Kuz'menko, and V.I.Lygin, Zhur.Fiz.Khim., **49**, 3173 (1975)[Russ. J.Phys.Chem., No.12 (1975)].
89. D.Dombrovskii, S.S.D'yakonov, A.V.Kiselev, and V.I.Lygin, Kinetika i Kataliz, **19**, 1067 (1978).
90. S.A.Levina, I.F.Bondarev, and L.S.Ivashchenko, Kolloid Zhur., **33**, 858 (1971).
91. A.V.Kiselev and V.I.Lygin, "Infrakrasnye Spektry Poverkhnostnykh Soedinenii i Adsorbirovannykh Veshchestv" (Infrared Spectra of Surface Compounds and Adsorbed Substances), Izd.Nauka, Moscow, 1972.
92. V.V.Platonov, N.E.Tret'yakov, and V.N.Filimonov, Symposium "Uspekhi Fotoniki" (Advances in Photonics), Izd.Leningrad.Univ., No.2, 1971, p.92.
93. L.Little, "Infrared Spectra of Adsorbed Molecules" (Translated into Russian), Izd.Mir, Moscow, 1969.
94. E.M.Eyring and M.E.Wadsworth, Mining Eng., **5**, 531 (1956).
95. G.Blyholder and D.O.Bowen, J.Phys.Chem., **66**, 1288 (1962).
96. A.D.Ulendeeva, Thesis, Ufa, 1978.
97. V.I.Lygin, N.K.Lyapina, and A.D.Ulendeeva, Zhur.Fiz.Khim., **50**, 2032 (1976)[Russ.J.Phys.Chem., No.8 (1976)].
98. A.D.Ulendeeva, "Khimiya Vysokomolekulyarnykh Soedinenii i Neftekhimiya" (The Chemistry of High-molecular Compounds and Petroleum Chemistry), Izd. Bashkir.Filiala Akad.Nauk SSSR, Ufa, 1973, p.25.
99. A.D.Ulendeeva, V.I.Lygin, N.K.Lyapina, and M.I.Zibaeva, Symposium "Khimiya i Fizika Nefti i Neftekhimicheskii Sintez" (Chemistry and Physics of Petroleum, and Petrochemical Synthesis), Izd. Bashkir.Filiala Akad.Nauk SSSR, Ufa, 1976, p.141.
100. I.V.Zuika and Yu.A.Bankovskii, Uspekhi Khim., **42**, 39 (1973)[Russ.Chem.Rev., No.1 (1973)].
101. V.K.Pogorelyi, Uspekhi Khim., **46**, 602 (1977) [Russ.Chem.Rev., No.4 (1977)].
102. V.I.Lygin, N.K.Lyapina, and A.D.Ulendeeva, "Tezisy Dokladov XIV Nauchnoi Sessii po Khimii i Tekhnologii Organicheskikh Soedinenii Sery i Sernistykh Neftei" (Abstracts of Papers Presented to the Fourteenth Scientific Session on the Chemistry and Technology of Organic Sulphur Compounds and Sulphur-bearing Petroleum), Izd.Zinatne, Riga, 1976, p.321.
103. N.K.Lyapina and A.D.Ulendeeva, "Tezisy Dokladov Chetvertoi Vsesoyuznoi Shkoly-seminara" (Abstracts of Papers Presented to the Fourth All-Union Schools Seminar), Izd.Akad.Nauk ArmSSR, Erevan, 1976, p.14.
104. G.Sh.Talipov, U.B.Khakimov, A.M.Ganiev, G.M.Til'-dingersh, and M.N.Mansurova, "Tezisy Dokladov Chetvertoi Vsesoyuznoi Shkoly-seminara" (Abstracts of Papers Presented to the Fourth All-Union Schools Seminar), Izd.Akad.Nauk ArmSSR, Erevan, 1976, p.13.
105. U.B.Khakimov, G.Sh.Talipov, Yu.M.Shchekochikhin, and A.S.Sultanov, Kinetika i Kataliz, **17**, 155 (1976).
106. A.S.Sultanov, U.B.Khakimov, G.Sh.Talipov, and Yu.M.Shchekochikhin, React.Kinet.Catal.Letters, **2**, 243 (1975).
107. D.E.Nicolson, Analyt.Chem., 34, 340 (1962).
108. P.Ratnasamy and J.J.Fripiat, Trans.Faraday Soc., **66**, 2897 (1970).
109. V.I.Lygin, B.V.Romanovskii, K.V.Topchieva, and Kho Shi Tkhoang, Zhur.Fiz.Khim., **42**, 289 (1968) [Russ.J.Phys.Chem., No.1 (1968)].
110. A.A.Vol'tsov, V.I.Lygin, N.K.Lyapina, and A.D.Ulendeeva, Kinetika i Kataliz, **20**, 253 (1979); **20**, 978 (1979).
111. A.A.Vol'tsov, N.K.Lyapina, and A.D.Ulendeeva, "Tezisy Dokladov Pyatoi Vsesoyuznoi Shkoly-seminara" (Abstracts of Papers Presented to the Fifth All-Union Schools Seminar), Irkutsk, 1978, p.29.
112. A.V.Deo, I.G.Dalla Lana, and H.W.Habgood, J. Catalysis, **21**, 270 (1971).
113. J.C.Lavalley, J.Travert, D.Laroche, and O.Saur, Compt.rend., C**285**, 385 (1977).
114. E.M.Davydova, Thesis, Novosibirsk, 1974.
115. E.M.Davydova, Yu.M.Shchekochikhin, and V.A.Mashkina, Kinetika i Kataliz, 11, 1615 (1970).
116. R.A.Nyquist and W.J.Potts, Spectrochim.Acta, 17, 679 (1961).
117. R.A.Nyquist and W.J.Potts, Spectrochim.Acta, **15**, 514 (1959).
118. P.A.Miller and C.H.Wilkins, Analyt.Chem., **24**, 1253 (1952).
119. P.Ratnasamy, Curr.Sci. (India), **41**, 118 (1972).
120. T.Cairng, J.Eglenton, and D.T.Gibson, Spectrochim.Acta, 20, 31 (1964).
121. W.R.Feaihel and J.E.Katon, Spectrochim.Acta, **20**, 1099 (1964).
122. G.Lundel and A.Murr, Naturforsch., **21a**, 1640 (1966).
123. B.A.Deangelis and G.Appierto, J.Colloid Interface Sci., **53**, 14 (1975).
124. H.Forster and M.Schuldt, J.Colloid Interface Sci., **52**, 380 (1975).
125. A.V.Kiselev, B.V.Kuznetsov, and Yu.S.Nikitin, Kinetika i Kataliz, **11**, 500 (1970).
126. V.M.Kiryutenko, A.V.Kiselev, and V.I.Lygin, and K.L.Shchepalin, Kinetika i Kataliz, **15**, 1584 (1974).
127. V.I.Lygin, N.K.Lyapina, and A.D.Ulendeeva, Zhur. Fiz.Khim., **50**, 2657 (1976)[Russ.J.Phys.Chem., No.10 (1976)].
128. V.I.Lygin, N.K.Lyapina, and A.D.Ulendeeva, "Neftekhimicheskii Sintez i Tekhnicheskii Progress (Tezisy Dokladov)" [The Petrochemical Synthesis and Advances in Technology (Abstracts)], Ufa, 1976, p.45.
129. G.N.Asmolov and O.V.Krylov, Symposium "Problemy Kinetiki i Kataliza" (Problems in Kinetics and Catalysis), Vol.16, Izd.Nauka, Moscow, 1975, p.78.
130. Kh.Dimitrov, N.A.Zubareva, V.I.Lygin, and N.Topalova, Kinetika i Kataliz, **18**, 1501 (1977).
131. V.I.Lygin, E.A.Karakhanov, N.A.Zubareva, M.V.Vagabov, G.G.Akhmetova, and A.Sh.Ramazanov, Vestnik Moskov.Univ., Khimiya, 604 (1978).
132. H.Dunken and V.I.Lygin, "Quantenchemie der Adsorption an Festkorperoberflächen", Verl. Grundstoffindustrie, Leipzig, 1978.
133. A.P.Zeif, Symposium, "Elementarny Fizikokhimicheskie Protsessy na Poverkhnosti Monokristallicheskikh Poluprovodnikov" (Elementary Physicochemical Processes on the Surface of Monocrystalline Semiconductors), Izd.Nauka, Novosibirsk, 1975, p.9.
134. V.I.Lygin and V.A.Seregina, Vestnik Moskov.Univ., Khimiya, 515 (1976).

135. R.Stodolski, J.Petkow, and H.H.Dunken, Wiss.Z. Friedrich-Schiller Univ., Jena, Math.-Nat.R., 1, 89 (1971).
136. V.I.Lygin, A.D.Ulendeeva, V.T.Ben'kovskii, and N.K.Lyapina, Dokl.Akad.Nauk SSSR, **233**, 420 (1977).
137. I.A.Lygina and V.I.Lygin, Dokl.Akad.Nauk SSSR, **231**, 137 (1976).

Bashkir Branch of the USSR Academy of Sciences, Institute of Chemistry, Ufa

Lomonosov Moscow State University, Chemistry Faculty

Translated from *Uspekhi Khimii*, **49**, 1014-1038 (1980) U.D.C. 541.135

The Electrochemistry of Hydroxide Melts

O.G.Zarubitskii

The results of the study of electrode potentials and processes in molten alkalis have been analysed. The influence of acid-base equilibrium on the mechanism and kinetics of the reactions which take place at indifferent electrodes in hydroxide melts between 200 and 500 °C has been demonstrated. The results of the study of the decomposition voltage and the electrochemical transformations at the cathode and anode when direct current is passed through these electrolytes have been examined. The bibliography contains 85 references.

CONTENTS

I. Introduction 536
II. Equilibria in hydroxide melts 536
III. Electrode potentials in alkali melts 538
IV. Electrode processes 540

I. INTRODUCTION

Hydroxide melts exhibit specific physicochemical properties, which distinguish these media as a special class of high-temperature electrolytes. The electrolysis of molten alkalis is distinguished by a number of characteristic features. It was in the study of the electrolysis of hydroxide melts that the phenomenon of metal transport from the cathode to the anode was first observed[1]. Review articles and widely known monographs[2-4] devoted to ionic melts, however, contain practically no information on the chemistry and electrochemistry of molten alkali metal hydroxides. The study of the electrochemistry of alkali melts has been particularly intensive over the last 10–15 years in connection with the promising possibilities provided by their application in various branches of the new technology. The present review is devoted chiefly to an analysis and generalisation of work carried out in recent years, and the electrochemical properties of "pure" alkalis are examined.

II. EQUILIBRIA IN HYDROXIDE MELTS

In the molten state, alkalis are dissociated[5] to give the cations Li^+, Na^+, K^+, Rb^+, and Cs^+, and hydroxide ions OH^-. Recent work[5-16] has established that in molten alkalis there exist a number of oxygen-containing ions (O^{2-}, O_2^{2-}, O_2^-) and molecules (O_2, H_2O). The solubility of molecular oxygen is low[7]. At the same time, it reacts with the melt according to the scheme

$$2NaOH + 0.5O_2 \rightleftarrows Na_2O_2 + H_2O \cdot$$

Rahmel and Krueger[17] were able to determine the solubility of oxygen in NaOH by a gravimetric method. At an oxygen pressure of 1 atm, the equilibrium concentration of O_2 in the melt increases with temperature, and amounts to 0.8 cm^3 and 4.2 cm^3 per cm^3 NaOH at 350 °C and 500 °C respectively. The same authors[17] obtained experimental isotherms giving the change in the concentration of water in a sodium hydroxide melt at different pressures of H_2O in the atmosphere above the electrolyte. There is a linear relationship between the increase in the water vapour pressure above the melt and the increase in the mass of the melt Δm, that is Henry's law is obeyed.

$$\Delta m = k p_{H_2O}.$$

The constant k changes with temperature according to the Van't Hoff equation

$$\lg(k/k_0) = A/T,$$

where k_0 and A are constants, equal to 2.88×10^{-7} mg g^{-1} $mmHg^{-1}$ and 3.21×10^{-3} K respectively. This equilibrium is established in 2–3 h.

The principal chemical reactions taking place with the participation of oxygen-containing species are described[6] by the following equations

$$O^{2-} + 0.5O_2 \rightleftarrows O_2^{2-}, \quad (1)$$

$$O_2^{2-} + H_2O \rightleftarrows 2OH^- + 0.5O_2, \quad (2)$$

$$2O_2^- + H_2O \rightleftarrows 2OH^- + 1.5O_2, \quad (3)$$

$$O_2 + O_2^{2-} \rightleftarrows 2O_2^-, \quad (4)$$

$$3O_2 + 2O^{2-} \rightleftarrows 4O_2^-. \quad (5)$$

Of the three simple oxygen anions (O^{2-}, O_2^{2-}, O_2^-), the O^{2-} ion is the most highly reduced species[7]. It cannot coexist with water. The peroxide ion O_2^{2-} is an ampholyte; it is reduced to O^{2-} or oxidised to O_2. The superoxide ion O_2^- also exhibits amphoteric properties; it is an oxidising agent with respect to O_2^{2-}, and a reducing agent with respect to O_2. Sodium oxide and peroxide, and also gaseous oxygen, are relatively sparingly soluble in the NaOH–KOH eutectic at 227°.[7] According to the data of Lux and coworkers[18], however, the action of dry oxygen (1 atm, 410 °C) for 5–16 h (as far as complete equilibration) leads to the formation, in the melt, of 3 mass % Na_2O_2 in NaOH, 54 mass % K_2O_2 (or 22 mass % KO_2) in KOH, 137 mass % Rb_2O_2 (or 57 mass % RbO_2) in RbOH, and 165 mass % Cs_2O_2 (or 64 mass % CsO_2) in CsOH. In LiOH, the formation of Li_2O_2 and LiO_2 was not detected. The equilibria for the formation of peroxides and superoxides, for example Eqns.(2) and (3), indicates that the concentrations of O_2^{2-} and O_2^- should show a definite dependence on the partial pressures of oxygen and water vapour above the melt. This was confirmed experimentally by Lux and coworkers[18], and it was shown that NaOH contains the peroxide Na_2O_2 in solution, whereas in KOH, RbOH, and CsOH the superoxides KO_2, RbO_2, and CsO_2 predominate.

Appropriate experiments[18] established that in molten NaOH the reaction with oxygen takes place according to Eqn.(2), since the following relationships derived from it are obeyed:

$$c_{O_2^{2-}} = k' p_{O_2}^{1/4} \text{ for } p_{H_2O}/c_{OH^-}^2 = \text{const}$$

$$c_{O_2^{2-}} = k'' c_{OH^-}^2 / p_{H_2O} \text{ for } p_{O_2} = \text{const.}$$

Oxygen reacts with KOH, RbOH, and CsOH according to Eqn.(3), as indicated by the fact that the following relationships are obeyed:

$$c_{O_2^-} = k_1 p_{O_2}^{3/4} \text{ for } p_{H_2O}/c_{OH^-}^2 = \text{const}$$

and

$$c_{O_2^-} = k c_{OH^-} / p_{H_2O}^{1/2} \text{ for } p_{O_2} = \text{const.}$$

With increase in temperature, the concentration of higher oxygen compounds of the alkali metals increases[18] ($p_{O_2} = 0.94$ atm, $p_{H_2O} = 0$ mmHg, $\tau = 4$–5 h):

t, °C	360	410	460	510
Concentration of Na_2O_2 in NaOH, mass %	1.70	2.19	2.60	3.65
Concentration of KO_2 in KOH, mass %	—	21.97	26.49	31.88

The efficiency of the formation of peroxides and superoxides in the reaction of hydroxides with atomic oxygen, generated in a glow discharge:

Alkali	Concentration, mass %		
	peroxide	superoxide	hydroxide
NaOH	31.4	11.4	57.2
KOH	нет	80.5	19.2

is considerably greater than that in the O_2–molten NaOH or KOH systems.

The chemical properties of molten alkalis, used as solvents, are related chiefly to the properties of the OH^- ions, which dissociate according to the equation[5–9]:

$$2OH^- \rightleftarrows H_2O + O^{2-} . \qquad (6)$$

The constant for this equilibrium is equal to the product of the activities of H_2O and O^{2-}, and corresponds to the product of the concentrations of the components in the given dilute solution:

$$K_i = [H_2O][O^{2-}]. \qquad (7)$$

The concentration of OH^- ions is taken as constant, since the degree of dissociation according to Eqn.(6) is small. The ionic product (7) has a definite value for a given mixture of alkalis and a given temperature. For the NaOH–KOH eutectic at 227 °C, it is given by[7] $pK = -\lg K = 11.5 \pm 0.7$.

Eqn.(7) can be used to determine[5] the acid–base properties of molten alkalis. Just as in aqueous solution the H_3O^+ ion is a complex proton, solvated by a molecule of the solvent H_2O, so in molten hydroxides it is also possible to regard H_2O as a complex, that is a compound of the proton H^+ with the ions of the solvent OH^-. Thus in hydroxide melts, H_2O is the most "acidic" species, and O^{2-} the most "basic".

By analogy with the pH scale in water, it is possible[5] to introduce for molten alkalis an analogous scale, which Goret called the pH_2O scale ($pH_2O = -\lg [H_2O]$). The value of the ionic product $pK_i = -\lg K_i$ determines the range of pH_2O values which can be achieved in a given medium. If $[H_2O] = 1$, then $pH_2O = 0$, and the concentration of O^{2-} ions is very low, since

$$pH_2O = pK_i + \lg[O^{2-}],$$
$$pO^{2-} = 11.5 - pH_2O.$$

Neutrality of the medium corresponds to the pure anhydrous eutectic mixture KOH–NaOH at 227 °C, where $pH_2O = pO^{2-} = 1/2\ pK_i = 5.75$. Molten alkalis rich in water correspond to "acidic" media, and those rich in O^{2-} ions correspond to "basic" media. It is possible to change the acidity of a medium by introducing non-dried alkalis or alkali metal oxides (Na_2O, KO_2, etc.). In the examination of acid–base equilibria in hydroxide melts, it is assumed[5] that in these media, all compounds (ions) which facilitate the appearance of water behave as "acids". The examination of the behaviour of metal cations is of particular interest in this connection. For these, the following phenomena may be observed, depending on the magnitude of pH_2O.

1) In a very acidic medium (rich in water), strong acceptors of O^{2-} ions form complex oxides, for example the cations Ni^{2+}, Pt^{2+}, and Al^{3+} give the sparingly soluble oxides NiO, PtO, and Al_2O_3. Oxygen-containing species such as CO_2 and PO_3^- behave as acids and form CO_3^{2-} and PO_4^{3-} ions:

$$CO_2 + 2OH^- \rightarrow CO_3^{2-} + H_2O ,$$

$$PO_3^- + 2OH^- \rightarrow PO_4^{3-} + H_2O .$$

On going to more basic media (with the removal of water), higher complex compounds may be formed. Thus alumina is more soluble in a dehydrated medium and is transferred to the melt in the presence of the O^{2-} ion by the reaction

$$Al_2O_3 + O^{2-} \rightarrow 2AlO_2^- .$$

In molten alkalis, in addition to equilibria (1)–(5), dissociation according to the equation[14,19,20]

$$2MOH \rightleftarrows M_2O + H_2O \qquad (8)$$

is observed. Since M_2O is a strong O^{2-} donor, reactions (8) and (6) are displaced to the left.

Table 1. Calculated dissociation constants K^* of molten alkalis at different temperatures[14] (the hypothetical values corresponding to temperatures below the solidification temperature are given in brackets).

t, °C	LiOH	NaOH	KOH	RbOH	CsOH
227	(7.0)	(13.1)	(17.7)	(18.6)	(18.9)
350	(4.3)	9.7	13.1	13.7	14
400	(3.5)	8.5	11.8	12.3	12.5
477	2.5	7.4	10.3	10.5	10.8
577	1.8	6.2	8.8	8.7	9.0
723	1.1	5.0	7.1	6.8	7.0

By applying the law of mass action to equilibria of type (8), it is possible to obtain different values of the dissociation constants, depending on the method of expressing the activities of the components[14]. If the standard states of MOH, M_2O, and H_2O are taken as the liquid hydroxide, the pure solid oxide, and water dissolved at a vapour pressure of 1 atm respectively, then

$$a_{M_2O} p_{H_2O} / a_{MOH}^2 = K^* .$$

If $a_{MOH} = 1$, then

$$p a_{M_2O} - \lg p_{H_2O} = -\lg K^* = p K^* .$$

The values of pK^* for different alkalis have been calculated[14]

from thermochemical data using the equation

$$2.3RT\,\mathrm{p}K^{\bullet} = \mu^{\bullet}_{M_2O} + \mu^{\bullet}_{H_2O} - 2\mu^{\bullet}_{MOH}$$

and are given in Table 1.

The degree of dissociation of alkalis at a given temperature increases with decrease in the radius of the cation: LiOH dissociates when the alkali is melted; KOH, RbOH, and CsOH are less extensively dissociated, and NaOH occupies an intermediate position.

For analytical calculations, the preferred definition of the constant pK is

$$\mathrm{p}K = \mathrm{pO^{2-}} + \mathrm{pH_2O},$$

when the standard state is taken as the solution having O^{2-} and H_2O concentrations equal to unity. The experimental determination of pK presents considerable difficulty, however. Its value has been determined only for the KOH–NaOH eutectic mixture[7]. The values of pK for NaOH at different temperatures have been calculated[14] using published data[17,21–23] on equilibrium in the NaOH–Na_2O and NaOH–H_2O systems:

t, °C	360	420	500	600	700
pK	8.75	7.50	6.25	5.00	4.0

These calculated data have been confirmed[15] by potentiometric measurements.

III. ELECTRODE POTENTIALS IN ALKALI MELTS

As described above, various oxygen-containing ions may be present in hydroxide melts when the atmosphere above them contains O_2 and H_2O. These ions are involved in the electrode equilibria, which are characterised by definite potentials and influence the characteristics of technical electrolysis or the operation of a galvanic cell.

Antropov and Tkalenko[24,25] compiled nine equations (Table 2) corresponding to possible redox systems involving oxygen-containing anions. Using thermochemical data, they calculated the standard potentials of the reactions represented in Table 2 in NaOH, KOH, and LiOH melts relative to the reference electrode M/M^+, where M is the corresponding alkali metal. These calculations were used to construct the plots of the potential against the acidity of the medium, analysis of which showed that in these hydroxide melts ($c_{H_2O} > 0.01\%$), the potential-determining system is system 1 (Table 2). In particular, in an NaOH melt, the potential of the oxygen electrode is determined by system 1 at values of $pH_2O < 4.75$, and by system 5 at values of $pH_2O > 4.75$; in a KOH melt, the potential-determining system is system 1 at values of $pH_2O < 2.2$, and system 4 at values of $pH_2O > 2.2$. The E–pH_2O diagram for LiOH does not show regions corresponding to the preferential formation of the peroxide or superoxide. The calculated values[25] of the concentrations of active oxygen in mole litre^{-1} in NaOH and KOH melts at $p_{H_2O} = 1$, $p_{O_2} = 0.2$, and $T = 700$ K are given below:

Melt	Peroxide	Superoxide
NaOH	$1.5 \cdot 10^{-4}$	$7.6 \cdot 10^{-2}$
KOH	$1.78 \cdot 10^{-5}$	$4.52 \cdot 10^{-4}$

At an oxygen partial pressure of ~1 atm and $pH_2O = 2$ in an LiOH melt at 750 K, concentrations of peroxide and superoxide equal to 6.3×10^{-7} M and 2.5×10^{-5} respectively are established. Thus under identical conditions, the concentration of active oxygen in a KOH melt is 160 times that in an NaOH melt. When an LiOH melt is in contact with oxygen, O_2^{2-} and O_2^- ions may also be present in this medium, but in extremely small quantities. These data are confirmed by the results of direct measurements of the concentrations of peroxide and superoxide in hydroxide melts[18,26].

Using electrochemical data, Ogryz'ko-Zhukovskaya[27] represented the reactions involved in the formation of higher oxgyen compounds in molten alkalis by the equations:

$$2OH^- + 1.5\,O_2 \rightleftarrows 2O_3^- + H_2O\,,$$

$$2OH^- + 0.5\,O_2 \rightleftarrows O_2^{2-} + H_2O\,.$$

The equilibrium constants for these equations

$$K_1 = [O_3^-]^2\,[H_2O]/[p_{O_2}]^{3/2},$$

$$K_2 = [O_2^{2-}]\,[H_2O]/[p_{O_2}]^{1/2}$$

in KOH at 200 °C are 6×10^{-4} and 2.5×10^{-6} respectively. In this melt at $c_{H_2O} = 10\%$, $p_{O_2} = 1$ atm, and $T = 200$ °C, the concentration of O_3^- is 7.75×10^{-3}M, and that of O_2^{2-}, 2.5×10^{-7} M. The concentration of KO_2, determined experimentally for these conditons, is 7.2×10^{-3} M.[27]

Table 2. Standard potentials of the redox systems.

No.	System	ΔG, kcal mole^{-1}	$E°$, V	ΔG, kcal mole^{-1}	$E°$, V	ΔG, kcal mole^{-1}	$E°$, V
		KOH, 700 K		NaOH, 700 K		LiOH, 750 K	
1	$O_2 + 2H_2O + 4e \rightleftarrows 4OH^-$	187	2.03	202	2.2	262	2.85
2	$O_3^- + 2H_2O + 3e \rightleftarrows 4OH^-$	144	2.09	164	2.37	225	3.26
3	$O_2^{2-} + 2H_2O + 2e \rightleftarrows 4OH^-$	104.5	2.27	116	2.52	160	3.47
4	$O_2 + e \rightleftarrows O_2^-$	42.7	1.85	39	1.69	36.8	1.60
5	$O_2 + 2e \rightleftarrows O_2^{2-}$	82.5	1.79	85.9	1.86	102.5	2.23
6	$O_2 + 4e \rightleftarrows 2O^{2-}$	122.8	1.33	152.2	1.65	218	2.37
7	$O_3^- + e \rightleftarrows O_2^{2-}$	—	1.73	—	2.03	65.8	2.86
8	$O_3^- + 3e \rightleftarrows 2O^{2-}$	—	1.16	—	1.63	183	2.63
9	$O_2^{2-} + 2e \rightleftarrows 2O^{2-}$	—	0.87	—	1.44	115.5	2.51

A number of papers have been published on the potentiometric study of redox systems involving oxygen-containing ions in hydroxide melts. Thus a study of the $Pt(O_2)$ electrode by measuring the e.m.f. of the following concentration cell at 500 °C and at 350–600 °C[15]

$$Pt(O_2/H_2O)\,|\,NaOH,\ O^{2-}\ \text{or}\ O_2^{2-}\,\|\,NaOH,\ O^{2-}\ \text{or}\ O_2^{2-}\,|\,Pt(O_2/H_2O)$$

showed that the dependence of its potential on the partial pressures of oxygen and water vapour is described by the following equation:

$$E = E^{\bullet} + \frac{RT}{4F}\ln p_{O_2} + \frac{RT}{2F}\ln p_{H_2O}. \qquad (9)$$

The concentration of the species taking part in reactions (1)–(5) are inter-related, so that the potential E in Eqn.(9) is a function of four different combinations of variables, ($a_{O^{2-}}$, p_{O_2}), ($a_{O_2^{2-}}$, p_{O_2}), ($a_{O_2^{2-}}$, p_{H_2O}), and ($a_{O_2^{2-}}$, a_{O_2}). Using Eqn.(9), Kureger and coworkers[6] took as reference potential the potential established at platinum in NaOH at $p_{O_2} = 0.98$ atm and $p_{H_2O} = 0.02$ atm. The results of the measurements show that the values of the prelogarithmic (Nernst) coefficients $\Delta E/\Delta \lg p_{O_2} = 38.3$ mV and $\Delta E/\Delta \lg p_{H_2O} = 76.5$ mV correspond to the theoretical values, that is $2.3RT/4F$ and $2.3RT/2F$ respectively.

Afanas'ev and Gamazov[28,29] were the first to measure the e.m.f. of gas concentration cells of the type

$$(p'_{O_2})\,M\,|\,NaOH\,|\,alundum\,|\,NaOH\,|\,(p''_{O_2})\,M$$
$$M = Pt, Ni, Au$$

and concluded that platinum, nickel, and gold behave as reversible oxygen electrodes, and that $\Delta E = 0.0383 \lg (p'_{O_2}/p''_{O_2})$ at 500 °C.

Using the dependence of the potential of the platinum–oxygen electrode on the concentration of oxygen ions in the sodium hydroxide melt, Krueger and coworkers[6] established that the addition of Na_2O and NaOH produces practically no change in the e.m.f. of the cell. From this it was concluded that the reaction

$$O_2 + 4\,e \rightleftarrows 2\,O^{2-}. \qquad (10)$$

is not potential-determining. Moreover, contrary to widespread opinion, Krueger and coworkers[6] concluded that the electrode reaction which corresponds to Eqn.(9) and as a result of the combination of Eqns.(6) and (10) gives the relationship

$$O_2 + 2H_2O + 4\,e = 4OH^- \qquad (11)$$

similarly cannot be potential-determining. Here it is assumed that reaction (6) takes place fairly rapidly, and that Na_2O is dissociated to Na^+ and O^{2-} ions.

At the same time it has been established[6,28] that the dependence of the potential of the platinum electrode on the concentration of sodium peroxide in NaOH is given by the equation

$$E = E^0 + \frac{RT}{2F} \ln c,$$

where c is the concentration of O_2^{2-} ions. It follows from these data that the electrode reaction

$$O_2 + 2e = O_2^{2-}, \qquad (12)$$

which is the reduction of oxygen to the peroxide ion, takes place rapidly and is potential-determining. The corresponding Nernst equation

$$E = E^0 - \frac{RT}{2F} \ln \frac{a_{O_2^{2-}}}{p_{O_2}}$$

shows good agreement with the experimental data.

On the other hand, according to the data of Krueger and coworkers[6], the electrode reaction

$$O_2^{2-} + 2e = 2O^{2-} \qquad (13)$$

cannot be potential-determining. From the experimental data given by Kruger and coworkers[6], it follows that the potential of an indifferent (platinum) electrode depends chiefly on the formation of peroxide and its decomposition according to Eqn.(2). This result agrees with the conclusion[18] that the establishment of equilibria (2) and (3) takes place more rapidly in a moist atmosphere than in an atmosphere of dry oxygen. In an atmosphere of O_2, the removal of the water produced is decisive. Thus with increase in the rate of flow of oxygen there is an increase in the intensity of peroxide formation, as confirmed[6] by the experimental data.

It follows from Eqns.(2), (3), and (11) that the redox potentials of the corresponding systems are influenced by the concentration of OH^- ions in the hydroxide melt. This has been demonstrated experimentally[19,28–30]. The studies reduced to the measurement of the e.m.f. of concentration cells of the type

$$M\,|\,NaOH\,|\,alundum\,|\,NaOH—NaNO_3\,(N)\,|\,M$$
$$(M = Pt, Ni, Au)$$

at 500 °C[28,29] and 340 °C.[30] The potential difference between the electrodes is a linear function of the logarithm of the mole fraction of sodium hydroxide in the melt. The slopes of the straight lines obtained by plotting E against $\lg [OH]$[28,29] are practically identical (0.156–0.160), and for a number of electrons n equal to 4 they correspond to the theoretical value in the equation

$$E = -\frac{2,3RT}{nF} \lg [OH^-]^4,$$

describing the change in the potential associates with the electrode process (11). With change in the concentration of LiOH from 2 mole % to 18 mole % in a eutectic melt of lithium, sodium, and potassium carbonates at 600 °C, the potential of a gold electrode is also described by the semi-empirical equation[19]

$$E = a - b \lg [OH^-].$$

In this expression, the value of the prelogarithmic coefficient is $b = 2.3RT/F = 0.194$. Thus the experimental data described above indicate that at 350–600 °C, platinum, nickel, and gold electrodes, like iron and silver electrodes[31,32], behave as reversible oxygen electrodes.

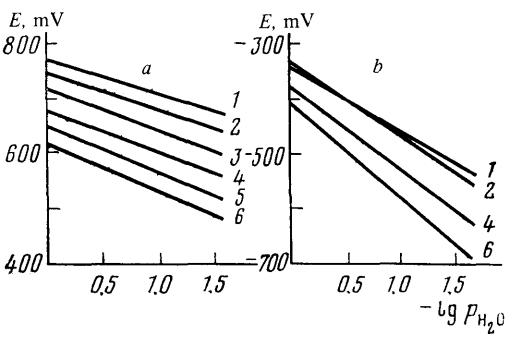


Figure 1. Isotherms giving the dependence of the potentials of oxygen (*a*) and hydrogen (*b*) electrodes in NaOH on the acidity of the electrolyte: *1*) 350, *2*) 400, *3*) 450, *4*) 500, *5*) 550, *6*) 600 °C.

The electrode processes described by Eqns.(2), (3), and (11) are not the only ones in which the hydroxide anion OH^- may take part. For example, Doisneau and Tremillon[15], who established an atmosphere of H_2 and H_2O above NaOH and used Pt and Ni electrodes at 350–600 °C, showed experimentally (Fig.1) that the electrode reaction taking place

$$4OH^- + 2H_2 \rightleftarrows 4H_2O + 4\,e$$

is described by the equation

$$E_{H_2} = E^*_{H_2} + \frac{2.3RT}{F} \lg p_{H_2O} - \frac{2.3RT}{2F} \lg p_{H_2}.$$

The calculated values of $E^*_{H_2}$ and $E^*_{O_2}$ show good agreement with the values obtained by extrapolating the straight lines (Fig.1) for $p_{H_2} = 1$ atm and $p_{O_2} = 1$ atm. The difference in

the standard potential $E^*_{O_2} - E^*_{H_2}$ corresponds to the e.m.f. of a cell of the form

$$Pt(H_2)\,|H_2O,\ NaOH|\,|NaOH,\ H_2O|\,(O_2)Pt,$$

in which the reaction

$$1/2O_2 + H_2 = H_2O \qquad (14)$$

takes place. The results of the calculation of this potential difference from the values of the Gibbs free energy show good agreement with experimental data[15].

IV. ELECTRODE PROCESSES

In recent years, original studies have been made of the electrode processes taking place at indifferent electrodes in alkali melts, involving alkali metal ions, water, and the anions OH^-, O^{2-}, and O_2^-. The concentrations of these ions and water can be varied by creating different atmospheres above the melt (p_{H_2O}, p_{O_2}) and by adding the oxides H_2O, Na_2O, and Na_2O_2 to the electrolyte. The products liberated at the electrodes may be the alkali metal, hydrogen, and hydride at the cathode, and water, oxygen, peroxide, and superoxide at the anode.

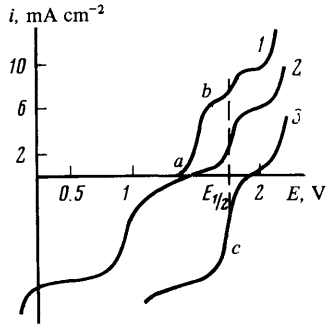


Figure 2. Polarisation curves characterising the electrochemical reaction $O_2^{2-} = 2O^{2-} - 2e$; *1*) Na_2O concentration in the melt 10^{-2} M, *2*) with oxygen bubbled through, *3*) the same after a long time interval; $2O^{2-} - 2e \rightarrow O_2^{2-}$ (*a*), $O_2^{2-} - e \rightarrow O_2^-$ (*b*), $O_2^{2-} + e + O_2^-$.

The behaviour of oxygen-containing anions in KOH–NaOH and NaOH melts has been studied in detail[5,7,15]. First of all, the behaviour of the O_2^{2-} and O_2^- ions at platinum and nickel electrodes was studied in a eutectic melt of sodium and potassium hydroxides at 220–270 °C and in sodium hydroxide at 350 °C. In particular, the electrode reaction (12) was studied at a rotating platinum electrode and at a nickel oxide electrode. A weighed specimen of sodium oxide was added to the melt, and the polarisation curves were recorded potentiodynamically. Two successive waves were observed (Fig.2), the height of the first being twice that of the second. The O^{2-} ion can be oxidised to peroxide and then to superoxide by the reactions

$$2O^{2-} - 2e \rightarrow O_2^{2-}, \qquad (15)$$

$$O_2^{2-} - e \rightarrow O_2^-. \qquad (16)$$

The O_2^{2-} ion is stable only in a basic medium; it exhibits amphoteric properties, and can be reduced to the oxide ion O^{2-} or oxidised to superoxide O_2^-. Oxidation according to the equation

$$O_2^- - e \rightarrow O_2$$

is not observed, since the hydroxide ions OH^- of the solvent are oxidised earlier: $E^0_{O_2-/O_2} = 2.33$ V.[10]

The half-wave potential of the first wave is not constant, and changes with change in the Na_2O concentration, but the potential $E_{1/2}$ of the second wave (Fig.2) remains unchanged. The limiting current of the first wave is proportional to the concentration of Na_2O in the melt[15]. The potentiodynamic studies[15] showed that the solubility of sodium oxide in NaOH at 350 °C is 2.3 mole kg^{-1} which is close to the value obtained (2.4 mole kg^{-1}) by measurements using a different method[21].

The existence of intermediate degrees of oxidation between O^{2-} and O_2 is confirmed by the disappearance of the wave for the oxidation of O^{2-} when dry oxygen is bubbled through the melt. When its passage is continued through a dilute solution of sodium oxide in an NaOH–KOH melt, a decrease in the height of the first wave and an increase in the height of the second is observed at first (Fig.2) as far as the appearance of curve *2*. When the bubbling is continued, the second oxidation wave also disappears[7] (curve *3* in Fig.2). Curve *3* shows only the wave corresponding to the reduction of O_2^- ions.

Under the conditions of this experiment, the oxide ion O^{2-} is oxidised by oxygen, first to peroxide according to Eqn.(1). Curve *2* (Fig.2) corresponds to the case where all the O^{2-} ions in the solution are converted into O_2^{2-} ions. This curve is characterised by a wave corresponding to the oxidation (16) and a wave corresponding to the reduction (13), the height of the latter being twice that of the former. The limiting current density for the cathodic reduction of Na_2O_2 in NaOH at 500 °C is also proportional to the concentration of peroxide in the melt[6]. The peroxide ions are then oxidised by oxygen according to Eqn.(4).

Curve *3* (Fig.2) corresponds to the case where the solution contains O_2^- ions, but O_2^{2-} ions are not present, since they have been oxidised by oxygen to superoxide. To some extent, these reactions "in solution" are analogous to the action of oxygen on solid K_2O, which forms K_2O_2 and then KO_2.

The experimental results indicate that the electrode reaction (16) is rapid, and its kinetics are determined by stationary diffusion[7]

$$E = E^0_{O_2^{2-}/O_2^-} + \frac{RT}{F} \ln \frac{[O_2^-]}{[O_2^{2-}]},$$

$$E = E_{1/2} + \frac{RT}{F} \ln \frac{i - i_1}{i_2 - i},$$

where i_1 and i_2 are the limiting currents of the reduction and oxidation respectively. They are proportional to the concentrations of O_2^- and O_2^{2-} in the solution:

$$i_1 = -k_1[O_2^-],$$

$$i_2 = k_2[O_2^{2-}].$$

$E_{1/2} = 1.75$ V relative to the sodium reference electrode.

It should be noted that at a platinum electrode, the wave corresponding to the oxidation (15) is observed from $E > 1.4$ V, but the wave corresponding to the reduction (13) appears only below 0.95 V ($\Delta E_{1/2} \cong 0.55$ V). This redox system is slow (like the H_2O_2/OH^- system in aqueous solution). These differences in the kinetics of the two systems (15) and (16)

being considered can be explained[7] from the structure of the species taking part in the reactions. Between peroxide and superoxide, only simple electron transfer involving two diatomic species takes place, whereas between peroxide and oxide the exchange of electrons is accompained by the rupture or formation of a covalent bond (oxide is monatomic, and peroxide diatomic). The authors cited[7] point out that the kinetics in the superoxide/oxide system, if they could be observed, would also be rapid, since they involve only two diatomic species.

It is possible to explain from this viewpoint the experimental fact[6] that at 500 °C in an NaOH melt, reaction (12) is rapid, whereas the electrode reaction (10) is slow.

A characteristic feature[7] is that the electrochemical reaction (15) ($E^0 = 1.4 \pm 0.05$ V) is rapid and reversible at a nickel oxide electrode, which catalyses the O^{2-}/O_2^{2-} system. This phenomenon is not new: in aqueous medium the decomposition of H_2O_2 is catalysed by nickel or cobalt oxides. It was also established[7] that when water is gradually added to an anhydrous dilute solution of O_2^{2-} ions, the height of the wave corresponding to the oxidation of these ions decreases, until it disappears completely. At the same time, O_2^- ions appear, and their reduction is reflected on the polarisation curves. This phenomenon is attributed[7] to the reaction taking place in the melt

$$3O_2^{2-} + 2H_2O \rightarrow 2O_2^- + 4OH^-$$

which corresponds to the dismutation equilibrium:

$$3O_2^{2-} \rightleftarrows 2O_2^- + 2O^{2-}. \qquad (17)$$

Like peroxide, superoxide may undergo dismutation, as follows:

$$4O_2^- \rightleftarrows 3O_2 + 2O^{2-}.$$

In the absence of water (strong O^{2-} acceptor), this reaction, like reaction (17), goes from right to left. It may be assumed that in the presence of H_2O, reaction (3) proceeds to the right, but the removal of the superoxide ion is difficult to achieve in practice. Prolonged bubbling of nitrogen leads to the gradual disappearance of superoxide (and also peroxide) as a result of dismutation, brought about by the removal of gaseous oxygen from the system. From an examination of the reactions of anionic oxidation in alkali melts, it was concluded[7] that the electrochemical oxidation of OH^- ions is probably accompanied by the formation of superoxide O_2^- by the reaction

$$4OH^- - 3e \rightarrow O_2^- + 2H_2O.$$

When a high current density is reached, however, the very high concentration of O_2^- ions and water may bring about partial dismutation of superoxide at the electrode according to Eqn.(3), and this is responsible for the familiar phenomenon of oxygen liberation in the electrolysis of molten NaOH. On the other hand, water does not react with superoxide, but facilitates its reduction.

These characteristic features of the course of reactions involving oxygen-containing species and the ranges of their existence can be represented graphically in the form of a E–pH_2O diagram (Fig.3): the method for constructing this diagram has been described in detail[7]. This diagram is similar to that for aqueous solutions on coordinates E–pH, which characterises the familiar redox equilibrium of water. The redox systems of oxygen differ (Fig.3), depending on whether water is present or absent, that is their ranges of existence are functions of pH_2O.

The above examination dealt chiefly with processes of oxidation at the anode. To obtain a complete picture of the electrochemical behaviour of molten alkalis, it is necessary to have information on the reactions of cathodic reduction. As already noted, the cathode products may be hydrogen, sodium, and sodium hydride. First of all, the values of the standard potentials of these electrode processes are of interest. Taking, as is usually done, as standard state the state of the electrochemical system in which all its components are in the state of pure substances, Doisneau and Tremillon[15] used thermochemical data to calculate E^* for the corresponding electrode reactions. These results, obtained with the condition $E^*_{M/M^+} = 0$, are given in Table 3.

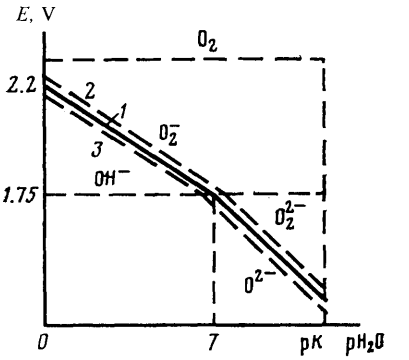


Figure 3. E–pH_2O diagram for oxygen redox systems at 227 °C; concentration of O_2^{2-} and O_2^- ions equal to: 10^{-2} M (*1*), 10^{-1} M (*2*), and 10^{-3} M (*3*).

Table 3. Standard potentials E^*, V of the electrochemical systems of molten alkali metal hydroxides.

t, °C	LiOH	NaOH	KOH	RbOH	CsOH
			H_2		
350	—	1.227	—	0.952	0.877
400	—	1.175	1.077	0.897	0.820
477	1.702	1.112	1.014	0.816	0.737
577	1.625	1.035	0.937	0.713	0.632
723	1.518	0.940	0.830	0.566	0.482
			MH		
350	—	0.655	—	—	—
400	—	0.612	0.545	—	—
477	1.031	0.547	0.478	—	—
577	0.952	0.465	0.394	—	—
723	0.837	0.218	0.272	—	—
			O_2		
350	—	2.330	—	2.055	1.979
400	—	2.264	2.166	1.987	1.940
477	2.771	2.181	2.083	1.885	1.806
577	2.667	2.077	1.979	1.755	1.674
723	2.517	1.940	1.829	1.566	1.482
			MO_2		
350	—	2.506	—	2.176	1.795
400	—	2.442	2.258	2.117	1.721
477	—	2.367	2.176	2.028	1.605
577	—	2.271	2.073	1.925	1.470
723	—	2.141	1.924	1.771	1.263
			M_2O_2		
350	—	2.701	—	2.710	2.601
400	—	2.628	2.566	2.639	2.499
477	3.033	2.552	2.457	2.528	2.369
577	2.934	2.461	2.386	2.405	2.221
723	2.799	2.364	2.234	2.170	1.995

The calculations were carried out with the assumption that the reactions taking place in the cell are

$$H_2O+M\rightarrow 1/2H_2+MOH,$$
$$H_2O+2M\rightarrow MH+MOH,$$

for which the standard e.m.f.'s are

$$E^*_{H_2}=\frac{\Delta G^*}{F}=\frac{1}{F}\left(\mu^*_{H_2O}-\frac{1}{2}\mu^*_{H_2}-\mu^*_{MOH}+\mu^*_M\right),$$
$$E^*_{MH}=\frac{\Delta G^*}{2F}=\frac{1}{2F}(\mu^*_{H_2O}-\mu^*_{MH}-\mu^*_{MOH}+2\mu^*_M).$$

Similar methods were used to calculate the standard potentials of the oxidation reactions accompanied by the formation of oxygen, peroxide, and superoxide:

$$4MOH\rightleftarrows O_2+2H_2O+4M\ ,$$
$$4MOH\rightleftarrows MO_2+2H_2O+3M\ ,$$
$$4MOH\rightleftarrows M_2O_2+2H_2O+2M\ .$$

The data obtained are given in Table 3.

It can be seen that the electrode potentials of the reactions (relative to the M/M^+ reference electrode) depend on the acidity of the melt, as follows

$$E_{H_2}=E^*_{H_2}+\frac{2.3RT}{F}\lg p_{H_2O}-\frac{2.3RT}{2F}\lg p_{H_2},$$
$$E_{MH}=E^*_{MH}+\frac{2.3RT}{2F}\lg p_{H_2O}-\frac{2.3RT}{2F}a_{MH},$$
$$E_{O_2}=E^*_{O_2}+\frac{2.3RT}{4F}\lg p_{O_2}+\frac{2.3RT}{2F}\lg p_{H_2O},$$
$$E_{MO_2}=E^*_{MO_2}+\frac{2.3RT}{3F}\lg a_{MO_2}+\frac{2\cdot 2.3RT}{3F}\lg p_{H_2O},$$
$$E_{M_2O_2}=E^*_{M_2O_2}+\frac{2.3RT}{2F}\lg a_{M_2O_2}+\frac{2.3RT}{F}\lg p_{H_2O}.$$

The electrode reactions are described by the equations:

$$H_2O+e\rightarrow 1/2H_2+OH^-\ ,$$
$$H_2O+M^++2e\rightarrow MH+OH^-\ ,$$
$$4MOH\rightarrow O_2+2H_2O+4M^++4e\ ,$$
$$4MOH\rightarrow MO_2+2H_2O+3M^++3e\ ,$$
$$4MOH\rightarrow M_2O_2+2H_2O+2M^++2e\ . \qquad (18)$$

The potentials of the cathode processes make it possible to characterise the conditions, for example the acidity of the medium, under which H_2, MH, and M are formed. An equilibrium is usually established between these products and MOH, but one of them predominates. Reduction leads to the formation of H_2 in an acidic medium, MH in a neutral medium, and M in a basic medium. Three cases can be distinguished, depending on the nature of the alkalis[15]. In LiOH, the acid–base dissociation, characterised by the quantity pK*, is not extensive, so that the reduction product is hydrogen, irrespective of the acidity. The second case corresponds to hydroxide having a high value of pK* (KOH, RbOH, CsOH). Since there are no data for Rb and Cs hydrides, it has been possible to carry out the calculations only for KOH. In this case, hydrogen is liberated in an acidic medium, and ptoassium in a basic medium. There is practically no range of acidity in which the solid hydride can exist. The third case corresponds to NaOH: close to the melting point, NaOH is reduced to hydrogen in an acidic medium and to the hydride in a basic medium, and at a higher temperature, the behaviour of NaOH is identical to that observed for KOH at the melting point. The conclusions reached agree with experimental data on reaction in the M–MOH system[33–43].

As in the case of the reduction reactions, different oxidation reactions are realised by creating a definite acidity of the medium: the coefficients of $\lg p_{H_2O}$ are also different. Oxidation takes place to oxygen in strongly acidic media, and to peroxide in the most basic media; in the intermediate acidity range, hydroxide is oxidised to superoxide. As far as the nature of the hydroxides themselves are concerned, examination of the oxidation reactions makes it possible to distinguish three cases. The first category corresponds to hydroxides having a low degree of dissociation (high value of pK*)—KOH, RbOH, and CsOH. In a neutral medium, the formation of superoxide takes place in an acidity range whose extent increases with the size of the cation of the solvent (Cs > Rb > K). Here, the CsOH represents an exceptional case, since it is oxidised to CsO_2 throughout the entire range of acidity at 350 °C, whereas KOH and RbOH are oxidised to O_2 in a strongly acidic medium and to peroxide in a strongly basic medium; LiOH is oxidised only to oxygen, irrespective of the acidity. As before, NaOH represents an intermediate case: there is no acidity range in which oxidation to superoxide could take place; oxidation leads to the liberation of oxygen in an acidic medium, and to peroxide formation in a basic medium. Thus oxygen acts on all molten hydroxides in a basic medium, with the exception of LiOH.

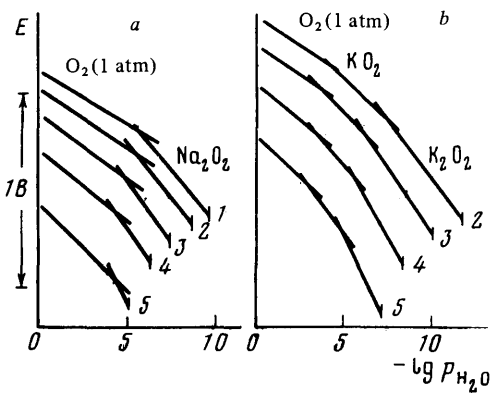


Figure 4. Isotherms giving the dependence of the equilibrium potentials in NaOH (*a*) and KOH (*b*) melts on the acidity of the medium in the presence of a strong oxidising agent at identical activities; *1*) 350, *2*) 400, *3*) 477, *4*) 577, *5*) 727 °C.

Fig. 4 shows the influence of the acidity of the medium on the electrode potential at different temperatures and equal activities (unity) of the oxidising agent. The results given for molten NaOH and KOH reveal the thermal instability of peroxides and superoxides, the range of formation of which decreases with increase in temperature. These data show good agreement with the results of thermochemical calculations[24] for the reactions involved in the oxidation of NaOH and KOH at 350 °C.

To some extent, the regular features described above can be represented by plotting the potential against the acidity of the medium, as shown in Fig.5. The difference in potentials between the upper and lower lines represents the "electro-activity region", that is the range of potentials lying between reduction and oxidation of the medium. In this case, for activities of the oxidising agent and reducing agent equal to unity, the extent and form of the "electro-activity range" (Fig.5) depends on temperature and, to a large extent, the nature of the cation. These ranges have been determined theoretically and confirmed experimentally[15]. At the same time it should be noted that the difference in the potentials $E^*_{O_2} - E^*_{H_2}$ is independent of the cation of the solvent, and is equal to the e.m.f. of the cell $Pt(H_2)\,|H_2O\,||\,H_2O\,|(O_2)Pt$. The current-producing process in the latter is reaction (14), which does not depend to a significant extent on the nature of the hydroxide. The potentials of the cathode and anode in this case are given by the following equations:

$$E_{H_2} = E^*_{H_2} - \frac{2,3RT}{2F}\lg p_{H_2} + \frac{2,3RT}{F}\lg p_{H_2O} - \frac{2,3RT}{F}\lg a_{NaOH},$$

$$E_{O_2} = E^*_{O_2} + \frac{2,3RT}{4F}\lg p_{H_2O} - \frac{2,3RT}{F}\lg a_{NaOH}.$$

Here, $E^*_{H_2}$ and $E^*_{O_2}$ are calculated from the data for the hypothetical cell in which the activities (partial pressures) of O_2, H_2, H_2O, and NaOH are equal to unity.

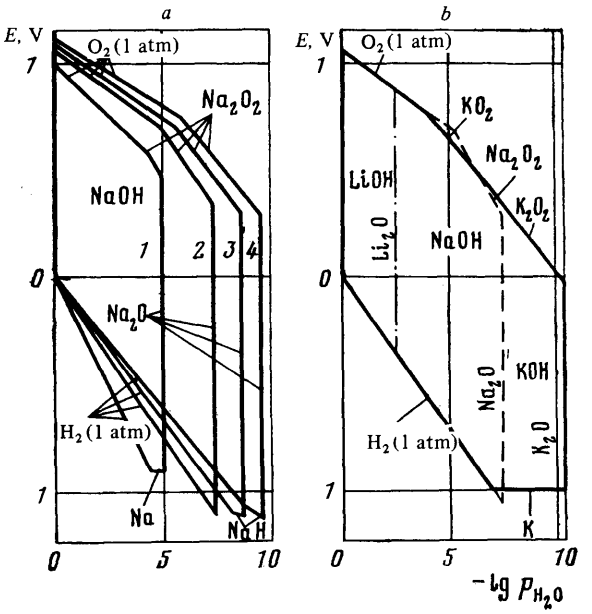


Figure 5. Dependence of the electro-activity ranges on the acidity of the medium; *a*) molten NaOH at different temperatures: *1*) 723, *2*) 477, *3*) 400, *4*) 350 °C; *b*) molten LiOH, NaOH, KOH at 477 °C.

As far as the stability of the products of the anodic oxidation are concerned, the following regular features may be noted[15]. In the solid state, the stability of peroxides increases with decrease in the radius of the alkali metal cation in the order $Cs_2O_2 < Rb_2O_2 < K_2O_2 < Na_2O_2 < Li_2O_2$, whereas the stability of the superoxides changes in the opposite order. In a molten alkali, a large radius for the cation facilitates the formation of superoxide and does not lead to the formation of peroxide.

The experimental study of the electrochemical behaviour of the ions O_2^{2-} and O_2^- in alkali melts was described above. It is of no less interest to examine the regular features of the liberation and consumption of the "visible" products of the electrode reactions, for example gaseous hydrogen and oxygen, and the alkali metals. This information is also important for the technical electrolysis of molten hydroxides.

The part played by the study of the electrolytic reduction of hydrogen ions from aqueous solutions is well known. A large number of studies have been devoted to this question. This problem is also of interest for the electrochemistry of ionic melts, since according to experimental data, hydrogen ions may be present in salt mixtures and molten slags at high temperatures. Water is also present in alkali melts, and in these electrolytes it is a product of an anode reaction[44-51]. Moreover, as noted above, the solution of H_2O in NaOH obeys Henry's law. In this connection, the processes involved in the discharge and ionisation of hydrogen in molten alkalis will be examined first.

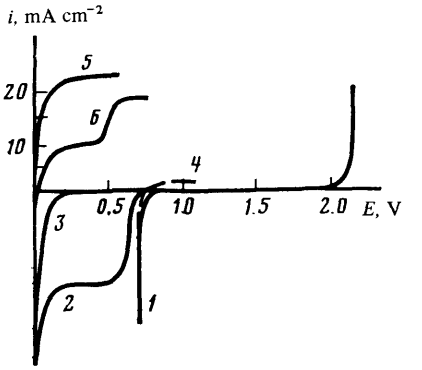


Figure 6. Polarisation curves obtained at a polished platinum electrode in an NaOH–KOH melt at 200 °C: *1* and *2*) reduction of H_2O from concentrated and dilute solutions respectively; *3*) decomposition of an anhydrous NaOH–KOH melt; *4*) oxidation of hydrogen, H_2O atmosphere; *5*) oxidation of sodium dissolved in an anhydrous melt; *6*) oxidation of sodium dissolved in an acidic melt.

The cathodic reduction of hydrogen ions in an NaOH–KOH eutectic melt at 220 °C was studied by Goret[5]. At a platinum electrode, when a potentiostatic method is used, the electroactivity range (decomposition voltage) of H_2O is 1.45 V. Reaction (18) takes place at the cathode.

In an NaOH–KOH melt not subjected to dehydration, and containing a high concentration of H_2O, the limiting current for the recduction of hydrogen is not observed (Fig.6). After drying (450 °C in a stream of dry nitrogen), a limiting current is observed on the *I–V* curve. The height of the corresponding wave (Fig.6) is proportional to the concentration of water in the melt. This wave is not observed in an anhydrous medium (curve *3* in Fig.6).

The oxidation of hydrogen in NaOH–KOH [5,52] and KOH (70–90 mass %)–H_2O (10–30 mass %) [52] melts has also been studied. A hydrated melt was used[5], and an atmosphere of hydrogen established ($p_{H_2} = 1$ atm). Since the solubility of hydrogen is low, the oxidation wave (curve *4* in Fig.6) shows a small limiting current. Its magnitude increases when a platinised platinum electrode is used[5].

Vasilistov and coworkers[52] used a palladium anode of the membrance type. With increase in temperature and the hydrogen pressure (from 0.2 atm to 1.5 atm), the activity of the process of H_2 ionisation increases sharply even in the initial polarisation range, and reaches 160 mA cm^{-2} at $E = 0.3$ V and $p_{H_2} = 1.5$ atm. In a hydrated KOH melt, this process takes place more effectively with increase in the H_2O concentration from 70% to 90%. At the same time, the exchange current increases from 1×10^{-4} A cm^{-2} to 5×10^{-4} A cm^{-2}. In the opinion of the authors cited[52], the anode reaction being considered takes place more intensively only through the formation and subsequent decomposition of a chemosorbed hydrate complex, which functions as an intermediate compound. According to their data[52], the anode current for the oxidation of hydrogen is controlled by its diffusion in metallic palladium. The activation energy of the last process is 3.5 kcal $mole^{-1}$.

According to Goret's results[5], reaction (18) is fast and reversible. The wave for the reduction of hydrogen is described by the equation

$$E = \text{const} + 0.050 \lg[(i - i_d)^2/i],$$

where i_d is the limiting current for the reduction of H_2O. The prelogarithmic coefficient calculated from the experimental data is close to 0.047.

It has also been shown[53,54] that reaction (18) at Pd [53] and Au [54] cathodes in an NaOH–KOH melt is a fast electrode reaction at 200–400 °C, and is described by the equation for diffusion kinetics. The height of the limiting current of the wave is proportional to the H_2O concentration, which decreases with time.

Since the concentration of water in the melt is proportional to the partial pressure of its vapour in the atmosphere, it is to be expected that increase in p_{H_2O} will lead to an increase in i_{d,H_2O}. This has been confirmed experimentally[6] by a potentiokinetic method at a platinum cathode at 500 °C using NaOH as background. The maxima formed, or more accurately the decrease in the current after the maxima, are attributed[6] to a decrease in the concentration of water in the catholyte. The current begins to increase at a potential of 1.3 ± 0.1 V, and, in the opinion of the authors cited, is due to reaction (18). The latter has been studied[55] by a chronopotentiometric method in an equimolar KOH–NaOH mixture at 460–530 K. An interesting feature is that the concentration of H_2O in the melt[55] was varied by adding SiO_2 to the cell. The silicon dioxide reacted quantitatively according to the scheme[56,57]:

$$SiO_2 + 4OH^- \rightarrow SiO_4^{4-} + 2H_2O \cdot$$

The chronopotentiometric curves for the reduction of hydrogen ions are described by the equation

$$E = E^0 + \frac{RT}{2F} \ln [H_2O] \left(\frac{D_{H_2}}{D_{H_2O}}\right)^{1/6} + \frac{RT}{2F} \ln \left\{2\left[1 - \left(\frac{t}{\tau}\right)^{1/2}\right]^2 / \left(\frac{t}{\tau}\right)^{1/2}\right\}.$$

Here, D_{H_2} and D_{H_2O} are the diffusion coefficients of hydrogen and water, t the time at a given point, and τ the transition time; the other symbols are generally adopted in electrochemistry.

According to the experimental data[55], the temperature dependence of the diffusion coefficient of water in the hydroxide melt is approximated by the relationship:

$$\lg D_{H_2O} = (1.143 \pm 0.18) - (2717 \pm 8.8)/T.$$

The activation energy of this process is 12.4 ± 0.4 kcal $mole^{-1}$. As noted above, polarography (volt–amperometry) can be used to determine the concentration of water in a hydroxide melt. It has been pointed out[55] that chronopotentiometry can also be used successfully for this purpose, although in the electrolyte the concentration of H_2O changes from 1 mmole kg^{-1} to 30 mmole kg^{-1}.

Most authors[3,45,58–60] consider that the subsequent increase in the cathodic current after the attainment of i_{d,H_2O} is due to the liberation of the alkali metal. This process, and also the reverse reaction, that is the ionisation of Na, have been studied[5,6]. At 220 °C in an NaOH–KOH melt, the Na^+ ion is reduced at a potential which is 0.65 V more negative than in the case of H_2O. [5] By dissolving metallic sodium in the anydrous NaOH–KOH eutectic, it was possible[5] to carry out the reaction

$$Na - e \rightarrow Na^+ .$$

The polarisation curve *5* (Fig.6) was obtained, and it was shown that this reaction, like the reverse reaction, is rapid. The result obtained makes it possible to recomment the Na/Na^+ electrode as a reference electrode in hydroxide melts. In this connection, somewhat unexpected results were obtained in a potentiokinetic study (rate of scanning 10 mV min^{-1}) [61] of the ionisation of sodium in an NaOH–KOH melt in the range 215–315 °C, where it was shown that the transfer coefficient $\beta = 0.35 \pm 0.05$, and the activation energy of this process is 6.8 ± 0.4 kcal $mole^{-1}$; the overvoltage reaches 300 mV at a current density of ~1 A cm^{-2}.

If H_2O is added to a solution of sodium in the anhydrous eutectic NaOH–KOH, the height of the wave for the oxidation of the alkali metal decreases (curve *6* in Fig.6). At the same time, a second oxidation wave is observed, the position of which is 0.5 V more electropositive than the sodium oxidation wave. Since this wave was also observed when sodium was added to the anhydrous melt in an atmosphere of hydrogen, Goret[5] tentatively attributed it to an electrode reaction involving the oxidation of the hydride:

$$2NaH - 2e \rightarrow 2Na^+ + H_2 .$$

This reaction should be slow, since the corresponding waves for the reduction of H_2O and H_2 to H^- are not observed.

Finally, published data on the characteristics of an anode reaction of the type

$$4OH^- - 4e \rightarrow 2H_2O + O_2 \qquad (19)$$

can be considered. As early as the start of the present century, LeBlanc[62], Sacher[63], and other workers, studying this reaction from the $I-V$ polarisation curves, reported that the liberation of oxygen is irreversible. Quantitative information on the discharge of OH^- ions was first obtained in a study[64] of the anodic polarisation of platinum and nickel electrodes in NaOH at 318–340 °C by automatic recording of the polarisation curves from very low current densities to 1 A cm^{-2}. It was established that reaction (19) takes place with overvoltage, which reached 0.2 V at the maximum current density used. Except for the data obtained at low current densities, the experimental results are described by the equation

$$\eta = b \lg(I/A),$$

where $A = 4–9$ mA cm^{-2}, $b = 0.121$ V.

In the liberation of oxygen into the atmosphere from alkali metal chloride melts at a zirconium anode[65] at 850–900 °C the data correspond to the semilogarithmic relationship

$$\Delta E = a + b \lg i, \qquad (20)$$

the coefficients of which are given below:

Melt		t, °C	a	b
NaCl — LiOH	(10 mole %)	850	1.348	0.785
NaCl — NaOH	(10 mole %)	850	1.117	0.655
NaCl — NaOH	(10 mole %)	900	0.925	0.310
KCl — KOH	(10 mole %)	850	1.456	0.560

Eqn.(20) indicates that the electrochemical process is irreversible. The data given were obtained on a "conditioned" (oxidised and passivated) anode. The $I-V$ curve was unstable at the start of the experiment, and became stable after several hours[65]. When "fresh" electrodes were used, the anodic polarisation curve[5,6,50,66] showed limiting currents due to the oxidation of the metals (Ni, Pt, Au) and the formation of sparingly soluble oxides on their surface. Lower oxides are formed first, followed by higher oxides. The oxides conduct electricity, and this is responsible for the subsequent increase in the current with increase in the potential. In this case, free oxygen is liberated. According to the results[5], the ability to undergo anodic oxidation, accompanied by solution of the metal in the electrolyte, decreases in the order Ag > Ni > Pt > Au.

The reaction of interest include not only the oxidation of the oxygen ions but also the reverse process, that is the electrolytic recduction of O_2 in alkali melts. The densities of the limiting current for the reduction of oxygen (mA cm^{-2}) at a smooth nickel electrode in alkali melts at 427 °C[67] are given below:

Melt	NaOH	KOH — NaOH (eutectic)	KOH	5 N KOH solution (25 °C)
$p_{O_2} = 0.2$ atm	0.66	13.3	69	—
$p_{O_2} = 1$ atm	1.08	18.6	110	0.02

These results show that the limiting currents for the reduction of oxygen in alkali melts[67] are appreciably greater than those in aqueous solutions. At the same time, i_d in KOH is two orders of magnitude greater than in NaOH, and in molten KOH–NaOH mixtures the limiting current increases with increase in the concentration of KOH in the electrolyte[22]. The value of i_d increases with increase in the concentration of water and in the temperature, and for a melt containing 78.6 mole % of KOH and 21.5 mole % NaOH the experimental data are described by the relationship

$$i_d = A \exp(-U/RT),$$

where U is the activation energy of the reduction, equal to 4.8 kcal mole^{-1}. This value is close to the activation energy for viscous flow of the melt.

From these data, it was concluded[68] that the rate of the reduction of oxygen in hydroxide melts is determined chiefly by the rate of diffusion of the reagents, and the measured limiting current is a diffusion current.

These regular features were attributed[67,69] to the formation in the electrolyte of higher oxygen compounds (Na_2O_2, KO_2), which act as carriers of oxygen from the oxygen–melt interface to the electrode surface. The general equations for the cathode processes associated with the electrolytic reduction of oxygen can be written[67,70] as follows:

$$O_2^{2-} + 2H_2O + 2e \rightarrow 4OH^-, \; E(\text{KOH}, 200\,^\circ\text{C}) = 1.45B, \qquad (21)$$

$$O_2^- + 2H_2O + 3e \rightarrow 4OH^-, \; E(\text{KOH}, 200\,^\circ\text{C}) = 1.27B. \qquad (22)$$

The limiting current for the cathodic reduction is determined chiefly by the rate of diffusion of the ions O_2^{2-} and O_2^-. Additional proof of this is provided by the observed[27,67] linear relationship between the density of the limiting current for the reduction of oxygen and the concentration of higher oxygen compounds in the hydroxide melt. The polarisation curves recorded at 200 °C at a platinum disc electrode in a KOH–H_2O (10%) melt containing KO_2 depolariser were used to calculate the valency of reaction (22), which was found to be equal to 3, and $D_{KO_2} = 8.25 \times 10^{-6}$ cm^2 s^{-1}.[24]

It follows from Eqns.(21) and (22) that for the reduction of oxygen to take place intensively, it is necessary to ensure a high rate of supply of H_2O to the electrode surface. It was established experimentally that for each specific set of conditions there is a minimum concentration of water below which the rate of the overall process is limited by its diffusion. The corresponding concentrations are marked by maxima on the $i_d = f(c_{H_2O})$ curves. The maxima divide the range of values into two sections; in one, the rate of reduction of oxygen is limited by the diffusion of peroxides and superoxides, and in the other by the diffusion of water.

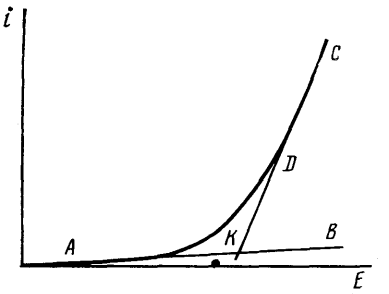


Figure 7. Determination of the decomposition voltage of an electrolyte.

In conclusion, the results of the measurement of the decomposition voltage of molten alkalis will be considered. It should first of all be noted that the concept of "decomposition voltage" has no strict scientific definition; for this reason, evidently, it is not encountered in handbooks and monographs of theoretical electrochemistry[71–73]. In textbooks on the electrochemistry of molten salts[2,3,74], the decomposition voltage is identified directly or indirectly with the e.m.f. of a reversible chemical cell, the magnitude of which can be calculated from thermodynamic data (this last assumption is rejected by Levin[75]), The concept of "decomposition voltage" has also been defined using such indefinite expressions as "visible products appear", "the e.m.f. reaches a certain definite value"[76], "minimum voltage", "for prolonged electrolysis to take place"[3].

The decomposition voltage E_d is usually determined from a graph (Fig.7) obtained by plotting current against voltage, at the point of intersection of the straight line CD with the abscissa. It should be noted that the concept of anodic decomposition voltage is encountered[77], but LeBlanc[62] does not consider it possible to record the residual current on the polarisation curve. In addition, completely different values of E_d for NaOH are obtained[62,78], depending on whether a micro-cathode or a micro-anode is used. Without going into a detailed analysis of this complex question here, it will probably be most correct to return to the source, that

is to the definition of decomposition voltage given by LeBlanc, who introduced this concept.

It is first of all necessary to take account of the fact that, in accordance with LeBlanc's theory, until the applied voltage becomes equal to or greater than the value E_d, no electrode processes are possible, and no current should pass through the cell[2]. It is obvious that this quantity E_d as a rule cannot be calculated from thermodynamic data; it depends on the nature and concentration of the electrolyte, the electrode materials, depolarisation and polarisation effects, and temperature. The experimentally determined value of E_d characterises a given specific electrolyte under fixed electrolysis conditions. In this connection, the section of the residual current A (Fig.7) distorts the determination of the decomposition voltage, which is apparently best obtained at the point K of intersection of the tangents AB and CD to the sections of the curves for the residual current and the electrolyte decomposition current.

It is generally accepted[3,45,78,85] that on the application of a direct current voltage (2.1–2.3 V) to indifferent electrodes immersed in a hydroxide melt, alkali metal is liberated at the cathode ($M^+ + e \rightarrow M$), and oxygen and water are liberated at the anode. In the case of a hydrated electrolyte, hydrogen is liberated at the cathode at a voltage of 1.1–1.3 V. The experimentally measured decomposition voltages of NaOH are given in Table 4. The decomposition voltage of molten potassium hydroxide at 390 °C is 2.1 V according to Ref.69, and 2.15 V according to Ref.79. In the latter case[79], an attempt was made to determine the decomposition voltage of molten LiOH. The value obtained at 460 °C was 1.3 V, which is clearly too low. Liberation of metal at the cathode was not observed.

Table 4. Measured values of the decomposition voltage of sodium hydroxide.

Method	Cathode	Anode	t, °C	E_d, V		Refs.
				I	II	
According to LeBlanc	Ni	Ni	350	1.3	2.2	62
According to LeBlanc	Fe	Fe	390	1.16	2.2	63
E.m.f. of the chemical cell	Fe	Ag	370	1.17	2.28	31
According to LeBlanc	Ag	Ag	393	—	2.32	80
According to LeBlanc	—	—	350	1.3	2.05	84
According to LeBlanc	Ni	Ni	450	1.28	1.96	58
According to LeBlanc	Fe	Fe	460	1.2	2.08	77
Potentiodynamic (KOH - NaOH melt)	Pt	Pt	200	1.45	2.10	5
Back e.m.f. in the electrolysis vessel	Cu	Ni	325	1.35	2.25	45
Back e.m.f. in the electrolysis vessel	Cu	Ni	300	—	2.3	45
According to LeBlanc	Ni	Ni	340	—	2.2	79
Polarisation curves	—	—	450	—	2.1	85

The temperature coefficient of the decomposition voltage of NaOH is 2.95×10^{-3} V K^{-1} according to Ref.79, and 1.3×10^{-3} V K^{-1} according to Ref.31. The temperature coefficient of the decomposition voltage of KOH is 2.15×10^{-3} V K^{-1}.[79]

A number of authors report that other electrode processes take place at the cathode and the anode. Thus an inflection was recorded on the $I-V$ curve at 1.87–2.00 V,[80] and its appearance was attributed to the reduction of the oxides Na_2O and Na_2O_2. In the opinion of the authors cited[80], these oxides are formed in well dried NaOH. As early as 1902, LeBlanc[62] noted the presence of an additional inflection on the polarisation curve for dried sodium hydroxide. Two inflections were also observed[81] on the $I-V$ for NaOH, at 1.73–2.04 V and 2.12–2.2 V, in the range 460–338 °C, but the first inflection was attributed[81] to the formation of sodium hydride at the cathode:

$$NaOH + e \rightarrow NaH + O^{2-} \qquad (23)$$

and to the following reaction at the anode:

$$O^{2-} - 2e \rightarrow 1/2O_2.$$

The second inflection was attributed to the overall reaction:

$$2NaOH + 2e \rightarrow 2Na + H_2O + 1/2O_2 . \qquad (24)$$

It was shown experimentally[81] that at current densities which are lower than those at which the liberation of sodium takes place but which ensure that the first reaction takes place, NaH is obtained with a current efficiency of up to 91%. This viewpoint[81] may be confirmed by the experimental fact that the first inflection on the $I-V$ disappears at 515 °C, since NaH does not exist under these conditions. Other workers[80] also did not observe the first inflection on the polarisation curve at 543 °C, and this was attributed[81] to the same factors.

Table 5. Comparison of the experimental values of the decomposition voltage and the values calculated for reactions (23) and (24) at different temperatures and the current density (i_c) at which liberation of sodium begins at these temperatures.

t, °C	E_1, V (first inflection)		E_2, V (second inflection)		i_c, A cm^{-2}
	experiment	calculation	experiment	calculation	
338	2.04	1.68	2.28	2.34	0.11
368	1.93	1.66	2.35	2.28	0.40
401	1.86	1.64	2.21	2.24	0.51
440	1.78	1.62	2.15	2.18	0.60
460	1.73	1.61	2.12	2.14	0.65
515	—	—	2.04	2.06	0.04

The experimental values of E for the formation of NaH (Table 5) are slightly higher than the values calculated by the same authors[81] from thermochemical data; this is due to the low activity of NaH in the melt in the experiment. The low values of E_d for NaOH are due to depolarisation phenomena resulting from the absence of separation between the electrode compartments and the fact that two parallel cathode processes are taking place at similar potentials.

An even more unusual conclusion was reached by Krueger[6], from whose results it would be expected that in pure NaOH at 500 °C the reaction taking place at the cathode would be

$$2OH^- + 2e \rightarrow 2O^{2-} + H_2,$$

and not the process

$$Na^+ + e \rightarrow Na;$$

that is sodium oxide and hydrogen, and not sodium, would be obtained as cathode products. According to Krueger's calculations[6], the decomposition voltage of NaOH in this case at 500 °C by the reaction

$$2NaOH = {}^1/_2O_2 + {}^1/_2H_2O + {}^1/_2H_2 + Na_2O$$

would be 2.1 V, which is close to that observed experimentally. No proof of the anodic formation of peroxide was obtained by Krueger[6].

At the same time, as early as 1895, Janeczek[82] suggested that the discharge of OH^- anions takes place with the formation of peroxide, and that the liberation of oxygen is brought about by a secondary reaction involving the decomposition of H_2O_2. This opinion was also held by Carrier[83]. Much later, Tremillon and coworkers[7,10] concluded that the OH^- ion is oxidised to superoxide O_2^-. When appreciable concentrations of this anion are reached (this is facilitated by high current densities), the dismutation process (3) takes place, accompanied by the liberation of oxygen into the atmosphere (as is usually the case in the electrolysis).

Thus in spite of the relatively large number of studies of the decomposition voltage of molten alkalis, this question requires further detailed study. It is necessary to obtain reliable experimental proof that the liberation of oxygen is a secondary reaction which is preceded by the electrochemical production of peroxide or superoxide. It is necessary to obtain unambiguous indications of additional inflections on the cathodic polarisation curves, and reliable experimental data on the decomposition voltage of pure molten potassium and lithium hydroxides.

REFERENCES

1. Yu.K.Delimarskii, O.G.Zarubitskii, and V.G.Budnik, "Diplom na Otkrytie SSSR" (USSR Diploma for Discovery), No.155; Byull.Izobr., No.24, 3 (1975).
2. Yu.K.Delimarskii and B.F.Markov, "Elektrokhimiya Rasplavlennykh Solei" (The Electrochemistry of Molten Salts), Metallurgizdat, Moscow, 1960.
3. Yu.V.Baimakov and M.M.Vetyukov, "Elektroliz Rasplavlennykh Solei" (The Electrolysis of Molten Salts), Izd.Metallurgiya, Moscow, 1966.
4. E.A.Ukshe (Editor), "Stroenie Rasplavlennykh Solei, Sbornik Statei" (Collected Papers on the Structure of Molten Salts), Izd.Mir, Moscow, 1966.
5. J.Goret, Bull.soc.chim.France, 1074 (1964).
6. H.J.Krueger, A.Rahmel, and W.Schwenk, Electrochim.Acta, **68**, 625 (1968).
7. J.Goret and B.Tremillon, Bull.soc.chim.France, 67 (1966).
8. J.Goret and B.Tremillon, Bull.Soc.chim.France, 2872 (1966).
9. J.Goret and B.Tremillon, Electrochim.Acta, 12, 1065 (1967).
10. A.Eluard and B.Tremillon, J.Electroanalyt.Chem., **18**, 277 (1968).
11. A.Eluard and B.Tremillon, Anal.Letters, 2, 221 (1968).
12. A.Eluard and B.Tremillon, J.Electroanalyt.Chem., **26**, 259 (1970).
13. A.Eluard and B.Tremillon, J.Electroanalyt.Chem., **27**, 117 (1970).
14. B.Tremillon and R.G.Doisneau, J.chim.phys., **71**, 1379 (1974).
15. R.G.Doisneau and B.Tremillon, J.chim.phys., **71**, 1445 (1974).
16. A.Eluard and B.Tremillon, J.Electroanalyt.Chem., **30**, 323 (1971).
17. A.Rahmel and H.J.Krueger, Z.phys.Chem., **55**, 25 (1967).
18. H.Lux, R.Kuhn, and T.Niedermaier, Z.anorg.allgem. Chem., **298**, 285 (1959).
19. A.B.Vandyshev, G.K.Stepanov, and G.G.Arkhipov, Trudy Inst.Elektrokhim.Ural.Nauch.Tsentr.Akad. Nauk SSSR, No.22, 93 (1975).
20. L.S.Itkina, "Gidroksidy Litiya, Rubidiya, Tseziya" (Lithium, Rubidium, and Caesium Hydroxides), Izd. Nauka, Moscow, 1973.
21. R.Bouaziz, G.Papin, and A.P.Rollet, Compt.rend., **262**, 1051 (1966).
22. E.B.Hout, J.Chem.Eng.Data, 12, 461 (1967).
23. I.S.Galinker and V.I.Korobkova, Dokl.Akad.Nauk SSSR, **81**, 407 (1951).
24. L.I.Antropov and D.A.Tkalenko, Elektrokhimiya, **6**, 1557 (1970).
25. L.I.Antropov, D.A.Tkalenko, and S.A.Kudrya, Ukrain.Khim.Zhur., **40**, 426 (1974).
26. I.I.Vol'nov, Zhur.Neorg.Khim., 12, 2253 (1967) [Russ.J.Inorg.Chem., No.8 (1967)].
27. S.G.Ogryz'ko-Zhukovskaya, V.O.Belokopytov, and N.A.Fedotov, Elektrokhimiya, **8**, 1602 (1972).
28. A.S.Afanas'ev and V.P.Gamazov, Zhur.Fiz.Khim., **38**, 2823 (1964) [Russ.J.Phys.Chem., No.12 (1964)].
29. V.P.Gamazov, Elektrokhimiya, **4**, 1353, 1355 (1968).
30. Yu.K.Delimarskii, O.G.Zarubitskii, V.G.Budnik, and O.A.Salabai, Zhur.Prikl.Khim., **41**, 741 (1968).
31. E.Baur, Z.Electrochem., **27**, 194 (1921).
32. B.A.Rose, G.J.Davis and H.J.T.Ellingham, Disc. Faraday Soc., **4**, 154 (1948).
33. I.E.Zhivolup and B.A.Shikhov, Zhur.Neorg.Khim., **23**, 1640 (1978) [Russ.J.Inorg.Chem., No.6 (1978)].
34. B.A.Shikhov, V.G.Karpenko, G.D.Chub, and N.M. Taran, Zhur.Prikl.Khim., **46**, 2331 (1973).
35. A.G.Morachevskii and A.I.Demidov, in "Itogi Nauki i Tekhniki.Rastvory.Rasplavy" (Progress in Science and Technology.Solutions.Melts), Vol.2, Izd.VINITI, Moscow, 1975, p.242.
36. N.I.Berdychevskii and A.G.Morachevskii, Zhur. Prikl.Khim., **41**, 1021 (1968).
37. S.Yoshizawa and N.Watanabe, Techn.Rep.Eng.Res. Inst.Kyoto, Univ., **10**, 201 (1960).
38. V.I.Mikheeva and M.M.Shkrabkina, Dokl.Akad.Nauk SSSR, **143**, 1362 (1962).
39. E.M.Mitkevich and B.A.Shikhov, Zhur.Neorg.Khim., 11, 633 (1966) [Russ.J.Inorg.Chem., No.3 (1966)].
40. B.A.Shikhov, Zhur.Neorg.Khim., 12, 1035 (1967). [Russ.J.Inorg.Chem., No.4 (1967)].
41. E.M.Mitkevich and L.S.Grot, Zhur.Neorg.Khim., 11, 902 (1966) [Russ.J.Inorg.Chem., No.4 (1966)].
42. P.Tonzain, Compt.rend., C276, 1583 (1973); C279, 41 (1974).
43. E.M.Mitkevich and B.A.Shikhov, Zhur.Neorg.Khim., 12, 1041 (1967) [Russ.J.Inorg.Chem., No.4 (1967)].
44. Yu.K.Delimarskii and O.G.Zarubitskii, "Elektrolitricheskoe Rafinirovanie Tyazhelykh Metallov v Ionnykh Rasplavakh" (The Electrolytic Refining of Heavy Metals in Ionic Melts), Izd.Metallurgiya, Moscow, 1975.
45. A.F.Alabyshev, K.Ya.Grachev, S.A.Zaretskii, and M.F.Lantratov, "Natrii i Kalii" (Sodium and Potassium), Khimizdat, Leningrad, 1959.
46. O.G.Zarubitskii and N.F.Zakharchenko, Ukrain. Khim.Zhur., **42**, 1126 (1976).
47. O.G.Zarubitskii, V.G.Budnik, and N.F.Zakharchenko, Khim.Tekhnol., No.6, 61 (1975).
48. Yu.K.Delimarskii, A.V.Gorodyskii, O.G.Zarubitskii, V.I.Shapoval, and E.V.Panov, "Elektrodnye Protsessy v Ionnykh Rasplavakh" (Electrode Processes in Ionic Melts), Izd.Naukova Dumka, Kiev, 1975.
49. Yu.K.Delimarskii, O.G.Zarubitskii, and V.G.Budnik, Ukrain.Khim.Zhur., **42**, 675 (1976).
50. Yu.K.Delimarskii, O.G.Zarubitskii, and I.G.Pavlenko, Ukrain.Khim.Zhur., **31**, 573 (1965).

51. Yu.K.Delimarskii, I.G.Pavlenko, O.G.Zarubitskii, and V.A.Oleinik, Zhur.Prikl.Khim., **38**, 816 (1965).
52. N.P.Vasilistov, G.S.Tyurikov, Yu.P.Shamagin, and A.V.Silakov, in collected papers, "Fizicheskaya Khimiya i Elektrokhimiya Rasplavlennykh Solei i Shlakov" (Collected Papers on the Physical Chemistry and Electrochemistry of Molten Salts and Slags), Izd. Naukova Dumka, Kiev, 1969, Part 2, p.278,
53. G.Kern, P.Degobert, and O.Bloch, Compt.rend., 256, 1500 (1963).
54. G.Kern and O.Bloch, Compt.rend., 258, 5431 (1964).
55. S.Zecchin, G.Schiavon, and G.G.Bombi, J.Electroanalyt.Chem., **50**, 261 (1974).
56. O.G.Zarubitskii, Yu.K.Delimarskii, B.F.Dmitruk, and I.R.Fishman, Khim.Tekhnol., No.5, 30 (1973).
57. Yu.K.Delimarskii, B.F.Dmitruk, and O.G.Zarubitskii, in collected papers "Ionnye Rasplavy" (Collected Papers on Ionic Melts), No.4, Izd.Naukova Dumka, Kiev, 1976, p.56.
58. Yu.K.Delimarskii, P.P.Turov, and E.B.Gitman, Zhur.Prikl.Khim., 28, 1170 (1955).
59. G.Eger, Handbuch der technischen Elektrochemie, Akademische Verlagsgesellschaft, Bd.3, Leipzig, 1955.
60. Yu.K.Delimarskii, O.G.Zarubitskii, and V.G.Budnik, Elektrokhimiya, 6, 1635 (1970).
61. M.Bonnemay, L.Lacourcelle, and J.Royon, Compt. rend., C271, 246 (1970).
62. M.LeBlanc and J.Brode, Z.Electrochem., 8, 697, 717 (1902).
63. F.Sacher, Z.anorg.Chem., 28, 385 (1901).
64. J.N.Agar and F.P.Bowden, Proc.Roy.Soc., A169, 206 (1938).
65. I.N.Ozeryanaya and I.V.Zauzolkov, Trudy Inst. Elektrokhim.Ural.Nauch.Tsentr.Akad.Nauk SSSR, No.22, 80 (1975).
66. Yu.K.Delimarskii and O.G.Zarubitskii, Dokl.Akad. Nauk SSSR, No.5, 619 (1965).
67. L.I.Antropov and D.A.Tkalenko, Elektrokhimiya, 6, 595 (1970).
68. D.A.Tkalenko, S.A.Kudrya, and L.I.Antropov, Ukrain.Khim.Zhur., **38**, 435 (1972).
69. L.I.Antropov, D.A.Tkalenko, and V.E.Sheremet, in collected papers "Fizicheskaya Khimiya i Elektrokhimiya Rasplavlennykh Solei i Shlakov" (Collected Papers on the Physical Chemistry and Electrochemistry of Molten Salts and Slags), Vol.2, Izd.Naukova Dumka, Kiev, 1969, p.268.
70. S.G.Ogryz'ko-Zhukovskaya, N.A.Fedotov, and V.P. Belokopytov, Elektrokhimiya, 7, 1541 (1971).
71. L.I.Antropov, "Teoreticheskaya Elektrokhimiya" (Theoretical Electrochemistry), Izd.Vysshaya Shkola, Moscow, 1969.
72. B.B.Damaskin and O.A.Petrii, "Vvedenie v Elektrokhimiyu" (Introduction to Electrochemistry), Izd. Vysshaya Shkola, Moscow, 1975.
73. K.J.Vetter, "Electrochemical Kinetics" (Translated into Russian), Izd.Khimiya, Moscow, 1967.
74. A.I.Belyaev, E.A.Zhemchuzhina, and L.A.Firsanova, "Fizicheskaya Khimiya Rasplavlennykh Solei" (The Physical Chemistry of Molten Salts), Metallurgizdat, Moscow, 1957.
75. L.I.Levin, "Teoreticheskie Osnovy Elektrokhimii" (Theoretical Principles of Electrochemistry), Izd. Metallurgiya, Moscow, 1972, p.254.
76. V.V.Skorchelletti, "Teoreticheskaya Elektrokhimiya" (Theoretical Electrochemistry), Goskhimizdat, Leningrad, 1959.
77. L.Rolla and R.Salani, Gazz.chim.ital., 52, 286 (1922).
78. C.Liebenow and D.Strasser, Z.Electrochem., 3, 16 (1896/1897).
79. B.Neumann and E.Bergve, Z.Electrochem., 21, 143 (1915).
80. I.P.Tverdovskii and V.S.Molchanov, Zhur.Fiz.Khim., 9, 239 (1937).
81. G.A.Vorob'ev and V.L.Kubasov, Elektrokhimiya, 17, 1048 (1975).
82. G.Janeczek, Ber., 8, 1018 (1895).
83. C.F.Carrier, Trans.Amer.Electrochem.Soc., 9, 363 (1906).
84. D.P.Zosimovich and V.A.Tsimmergakl. Ukrain.Khim. Zhur., 15, 351 (1949).
85. V.P.Kochergin, Uch.Zap.Ural.Gos.Univ., No.92, Part 2, 62 (1969).

Institute of General and
Inorganic Chemistry, Academy
of Sciences of the Ukrainian SSR,
Kiev

Translated from *Uspekhi Khimii*, 49, 1039-1056 (1980) U.D.C. 547.512

Nucleophilic Substitution Reactions of Cyclopropane Derivatives

V.S.Aksenov, G.A.Terent'eva, and Yu.V.Savinykh

The review is devoted to the solvolysis of cyclopropane compounds. The influence of structural and external factors on the rate and direction of the reaction are considered.
The bibliography includes 63 references.

CONTENTS

I. Introduction 549
II. The mechanism of the solvolysis of cyclopropane derivatives 549
III. The role of structural factors in the solvolysis of cyclopropyl halides and cyclopropyl tosylates (toluene-*p*-sulphonates) 550
IV. The influence of external factors on the rate and direction of solvolysis of cyclopropane derivatives 554

I. INTRODUCTION

Owing to advances in the chemistry of carbenes, particularly the development of new methods for the generation of carbenes, many cyclopropane derivatives have become available, which stimulated the study of their further reactions. The increased interest in these compounds is due to the fact that, by virtue of the unusual nature of the bonds in the strained three-membered ring, they possess a whole series of properties which distinguish them sharply from other carbocylic compounds. The solvolysis of cyclopropane derivatives is particularly characteristic in this respect—in this reaction treatment with a nucleophile as a rule entails the cyclopropyl–allyl rearrangement and not substitution.

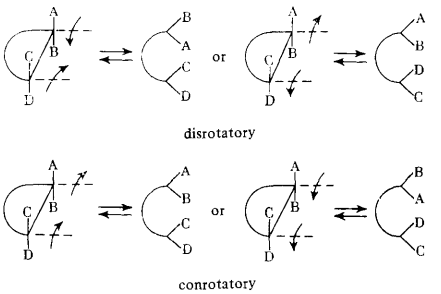
The aim of the present review is to specify the general and specific features of the solvolysis of cyclopropane derivatives.

II. THE MECHANISM OF THE SOLVOLYSIS OF CYCLOPROPANE DERIVATIVES

The specific feature of the behaviour of cyclopropane compounds in nucleophilic substitution consists in the fact that the reaction results in the formation of allyl derivatives and not substitution products. At the early stages in the relevant investigations a two-stage mechanism of the nucleophilic substitution reaction involving cyclopropane derivatives was proposed[1]: slow ionisation with formation of the cyclopropyl cation and subsequent rapid opening of the ring of the latter to give the allyl cation:

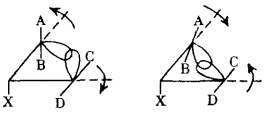


The error of this approach was demonstrated in numerous later studies. Kinetic[2,3] and quantum-chemical[4] investigations showed that the solvolysis of cyclopropane derivatives is a synchronous process involving the abstraction of an anion and the opening of the cyclopropane ring. According to the classification of Woodward and Hoffmann[5], the cyclopropyl–allyl rearrangement (opening of the three-membered ring to give the allyl cation) is an electrocyclic reaction. The authors define electrocyclic reactions as processes involving the formation of a single bond between the ends of the linear system containing k π-electrons (or the reverse process). The conversion of the cyclic form into an acyclic form and conversely can be disrotatory or conrotatory:



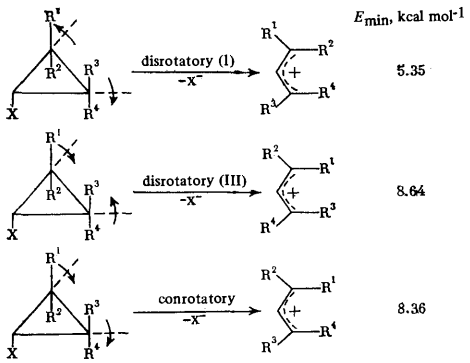
According to orbital symmetry conservation rules[5,6], thermal electrocyclic reactions are disrotatory for $k = 4n + 2$ and conrotatory for $k = 4n$. The cyclopropyl-allyl rearrangement constitutes a 2π-electrocyclic ring opening ($n = 0$). The disrotatory opening of the three-membered ring has been confirmed by quantum-chemical calculations using the MO-LCAO SCF method[7]. It has been shown[8] that the ring opening and the rotation of the methylene groups take place simultaneously; the central angle in the ring then increases from 60° to 120° and the σ-orbitals of the terminal groups are gradually converted into p-orbitals. Among all the possible structures of the $C_3H_5^+$ cation, the planar allyl cation is the most stable[4]. The energy of the cyclopropyl cation is greater by 39 kcal mol^{-1} than the energy of the allyl cation, so that there is no energy barrier to the isomerisation of the former to the latter.

In the disrotatory opening of the three-membered ring, there is a possibility of two stereochemically non-equivalent pathways—external (I) and internal (II):



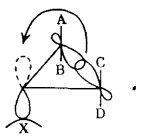
Calculations based on the principle of minimum movement[9-11] for the synchronous process involving the removal of the anion and the opening of the three-membered ring show that the two disrotatory ring opening pathways [(I) and (II)] are energetically non-equivalent: in pathway (I) there is virtually no energy barrier, while in pathway (II) there is a

considerable barrier.



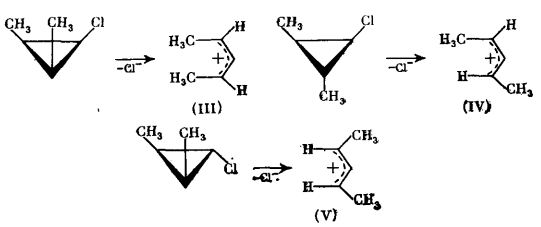
Here E_{min} is the minimum energy required for the rearrangement of the atoms in the molecular skeleton.

Calculation of the energies of the two pathways in the cyclopropyl–allyl isomerisation by the extended Hückel method[12,13] showed that substituents in the *cis*-position in the leading group rotate towards one another, while trans-substituents rotate away from one another, i.e. the disrotatory pathway (I) is followed regardless of the configuration. This result is a consequence of a secondary orbital effect in the transition state, which is due to the additional interaction of the molecular orbitals. This interaction does not lead to the formation of new bonds but lowers the activation energy for the reaction[14]:



Woodward and Hoffmann[5] note that in practice pathway (I) entails the S_N2 substitution of the leaving group X^- by the electrons of the ruptured C–C bond on the side opposite to that of the direction in which the X^- ion is eliminated.

A direct experimental confirmation of the validity of the disrotatory pathway (I) has been provided by the study of the allyl cations formed from isomeric 2,3-dimethylcyclopropyl chlorides by ^{1}H NMR.[15] The stereochemistry of the allyl cations confirms the stereospecificity of the opening of the three-membered ring. The formation of three individual 1,3-dimethylallyl cations (III), (IV), and (V) from the isomeric 2,3-dimethylcyclopropyl chlorides rules out the existence of the cyclopropyl cation as an intermediate. The disrotatory pathway (I) and the synchronous nature of the ionisation with ring opening have also been confirmed by the kinetics of the acetolysis of the isomeric 2,3-dimethylcyclopropyl chlorides [$k_{trans,trans}(17800) > k_{cis,trans}(210) > k_{cis,cis}$ (1)] [15] and 2,3-dimethylcyclopropyl toluene-*p*-sulphonates [$k_{trans,trans}$ (38000) > $k_{cis,trans}$ (460) > $k_{cis,cis}$ (2.2)].[16]



III. THE ROLE OF STRUCTURAL FACTORS IN THE SOLVOLYSIS OF CYCLOPROPYL HALIDES AND CYCLOPROPYL TOSYLATES (TOLUENE-*p*-SULPHONATES)

1. The Relative Positions of the Leaving Group and the Substituent in the Cyclopropane Ring

The fact that one of the two possible pathways in the disrotatory opening of the three-membered ring is preferred leads to different reactivities of the *cis*- and *trans*-substituted cyclopropyl halides and tosylates. According to the data in Table 1, the reactivity of cyclopropane derivatives containing substituents and the leaving group on one side of the ring is appreciably lower than the reactivity of the corresponding compounds in which the substituents and the leaving group are located on opposite sides of the ring. In the case of the *cis*-isomers ring opening is hindered by the steric interactions between the substituents in the cyclopropane ring, while in the opening of the *trans*-isomers weaker steric interactions are observed between two hydrogen atoms.

Table 1. The rates of solvolysis of isomeric 1-chloro-2,3-dipropylcyclopropanes[17] and 1-chloro-2,3-diphenylcyclopropanes[18].

2,3-Disubstituted cyclopropyl halide	Reaction conditions	k, s^{-1}
cis, cis-1-Chloro-2,3-dipropylcyclopropane	C_2H_5OH; 80°	$2.17\cdot10^{-8}$
trans, trans-1-Chloro-2,3-dipropylcyclopropane	ditto	$8.2\cdot10^{-5}$
cis, trans-1-Chloro-2,3-dipropylcyclopropane	»	$1.26\cdot10^{-6}$
cis, cis-1-Chloro-2,3-diphenylcyclopropane	CH_3COONa/CH_3COOH; 95.2°	$3.59\cdot10^{-6}$
trans, trans-1-Chloro-2,3-diphenylcyclopropane	ditto	$1.15\cdot10^{-3}$
cis, trans-1-Chloro-2,3-diphenylcyclopropane	»	$2.46\cdot10^{-4}$

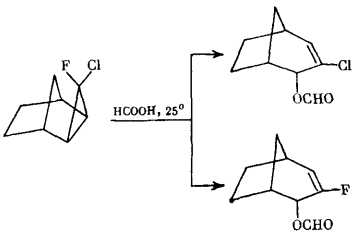
The steric repulsions of substituents in the cyclopropyl–allyl rearrangement can be so significant that *cis*-cyclopropyl halides sometimes virtually do not undergo this reaction. Thus, when a mixture of isomers of 1-chloro-2,3-dimethyl-1-phenylcyclopropane[19] or 2-aryl-1-bromo-1-fluorocyclopropanes[20] is treated with a methanol solution of silver nitrate at moderate temperatures, the *cis*-isomers remain unaltered. Under the same conditions, the *trans*-isomers undergo the cyclopropyl–allyl rearrangement. The study of the behaviour of the isomeric 2-phenylcyclopropyl halides[18,21] and cyclopropyl tosylates[12] in solvolysis showed that the *trans*-isomers react faster than the *cis*-isomers. A similar ratio of the rates has been observed also for trisubstituted cyclopropane derivatives[22,23].

Thus, in solvolysis the disrotatory ring opening of monocyclic cyclopropane systems leads to a greater ease of the elimination of the halogen in the *trans*-position with respect to the substituents in the ring.

The operation of the disrotatory pathway (I) as the only possible process involving the opening of the ring in cyclopropane derivatives has also been confirmed by the study of the solvolysis of bicyclic cyclopropane systems. The opening of a three-membered ring incorporated in a bicyclic system takes place smoothly when the leaving group is in the *endo*-position. Thus the solvolysis of *endo*-bicyclo[4,1,0]-heptyl chloride is 180 times faster than the solvolysis of the

exo-isomer[24]; *exo*-7-tosylbicyclo[4,1,0]heptane is inert under acetolysis conditions at 100 °C.[12]

The solvolysis of polycyclic asymmetric dihalogenocyclopropanes involves the hydrolytic dissociation of the *endo*-bond also in those cases where the latter is stronger than the *exo*-bond[25]:



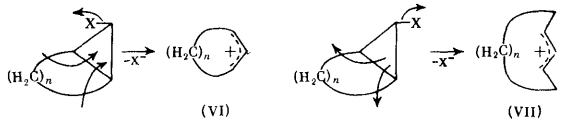
However, the elimination of the *endo*-halogen (or tosylate) is difficult in bicyclic systems with large rings. Thus in the series of bicyclo[5,1,0]octane and bicyclo[6,1,0]nonane derivatives the *exo*-isomers are found to be more reactive[26–28].

Table 2. Relative rate constants (k_{rel}) for the acetolysis of *endo*- and *exo*-bicyclo[*n*,1,0]alkyl tosylates[27].

n	0	3	4	5	6
endo	1	2500	62	3.1	3.5
exo	1	0.01	1.7	2500	10 000

Table 2 shows that the ease of the opening of the three-membered ring at the $C_{(1)}$–$C_{(n+2)}$ bond in derivatives of bicyclo[*n*,1,0]alkanes depends on the length of the bridge. The cause of this behaviour has been formulated as follows[27]: for low values of *n*, there is a possibility only of disrotatory movement in which the *cis*-allyl cation (VI) is formed, which favours the abstraction of the *endo*-halogen. With increase of *n* from 3 to 5, the stability of the cyclic *cis*-allyl cation (VI) is reduced and the reactivity of the *endo*-isomers diminishes.

The ionisation of the *exo*-isomers is sterically hindered owing to the considerable strain in the allyl cation (VII) having two *trans*-bonds. This strain is particularly large for low values of *n*; it diminishes with increase of *n*, which leads to an increase of the reactivity of the *exo*-isomers;



Thus the disrotatory opening of the cyclopropane ring incorporated in a bicyclic system takes place with elimination of the *endo*-halogen atom for small values of *n*, in contrast to the solvolysis of monocyclic cyclopropane systems. With increase of *n*, this specific feature disappears.

2. The Influence of the Nature of the Leaving Group

The ease of elimination of halogens in nycleophilic substitution at a saturated carbon atom increases from fluorine to iodine: F < Cl < Br < I.[29] The reactivity of cyclopropyl halides varies in the same series[30]. If the leaving group is a sulphonate anion (for example the tosylate anion), then cyclopropyl derivatives exhibit certain characteristic features. Acyclic alkyl tosylates are solvolysed appreciably faster than the corresponding alkyl bromides[31]. Table 3 shows that the higher reactivity of cyclopropyl tosylates compared with the corresponding halides is manifested clearly only for the *trans*-isomers. In the case of the *cis*-isomers the bromide becomes more reactive in the presence of certain β-substituents.

The greater reactivity of β-phenyl-substituted *cis*-cyclopropyl bromides has been explained[18] by the greater energy of the ground state of the bromides compared with that of the tosylates. Sliwinski et al.[3] share this view in relation to norcarane and 2,3-dimethylcyclopropane derivatives: in these compounds the steric repulsions between the *cis*-β-substituents are the leaving group are much more pronounced in the presence of the bulky bromine atom compared with the oxygen of the tosylate group, since the sulphonate residue is oriented in such a way that it is not involved in steric interaction with the β-substituent.

Table 3. The rate constants for the acetolysis (at 100 °C) of β-substituted cyclopropyl halides[3,21,32] and cyclopropyl tosylates[3,16].

Compound	k_1, s^{-1}	
	trans	*cis*
2-Methyl-1-tosylcyclopropane	$57.5\cdot10^{-7}$	$2.40\cdot10^{-7}$
1-Bromo-2-methylcyclopropane	$9.78\cdot10^{-7}$	$7.17\cdot10^{-8}$
2-t-Butyl-1-tosylcyclopropane	$13.7\cdot10^{-6}$	$2.11\cdot10^{-7}$
1-Bromo-2-t-butylcyclopropane	$16.1\cdot10^{-7}$	$14.3\cdot10^{-8}$
2-t-Butyl-1-chlorocyclopropane	$10.5\cdot10^{-8}$	$4.04\cdot10^{-9}$
2-Phenyl-1-tosylcyclopropane	$12.5\cdot10^{-6}$	$6.20\cdot10^{-7}$
1-Bromo-2-phenylcyclopropane	$82.2\cdot10^{-7}$	$20.6\cdot10^{-7}$
1-Chloro-2-phenylcyclopropane	$1.68\cdot10^{-7}$	$4.10\cdot10^{-8}$
	exo	*endo*
7-Tosylnorcarane*	$2.67\cdot10^{-4}$	$2.52\cdot10^{-2}$
7-Bromonorcarane*	$0.70\cdot10^{-6}$	$3.20\cdot10^{-2}$
7-Chlorononorcarane*	$0.40\cdot10^{-6}$	$0.15\cdot10^{-2}$
	trans, trans	*цис cis*
2,3-Dimethyl-1-tosylcyclopropane	$1.59\cdot10^{-3}$	$9.0\cdot10^{-8}$
1-Bromo-2,3-dimethylcyclopropane	$0.78\cdot10^{-3}$	$13.6\cdot10^{-8}$
1-Chloro-2,3-dimethylcyclopropane	$0.02\cdot10^{-3}$	$0.30\cdot10^{-8}$

*The values of k_1 at 200 °C are quoted.

Hausser's model[18] suffers from a number of disadvantages. Firstly, despite the high energy of the ground state of the *cis*-β-t-butyl-substituted bromide compared with the corresponding tosylate[3], the latter is more reactive (Table 3). Secondly, according to Sliwinski et al.[3], the steric strain in the ground state varies in parallel with the van der Waals radii of the leaving groups: Br (1.95 Å) >Cl (1.8 Å) >O (1.4 Å); on this basis, it was to be expected that the *cis*-chlorides would be more reactive than the *cis*-tosylates. However, kinetic results (Table 3) indicate a lower reactivity of the chlorides.

The energy of the ground state of *cis*-β-substituted derivatives of cyclopropane is probably not the only factor which determines the relative reactivities in the solvolysis of the halides and tosylates.

The next distinctive feature of β-substituted cyclopropyl halides and tosylates relative to the acyclic derivatives and unsubstituted cyclopropane derivatives is the lower sensitivity of the rate of their solvolysis to the nature of the leaving group (Table 4). In the cyclopropane series the

rates of solvolysis of the halides and tosylates differ comparatively little. One of the attempts to explain this finding was undertaken by Hausser and Uchic[18], who postulated a relation between the capacity of the leaving group for elimination and the degree of opening of the three-membered ring in the transition state. This idea was rejected by Schleyer and coworkers[3], who postulated that the degree of opening of the cyclopropane ring is independent of the nature of the leaving group. The latter workers assume[3] that the weak sensitivity to the nature of the leaving group can be explained by the fact that the same β-substituent accelerates solvolysis in different ways depending on the reactivity of the leaving group (Table 5). Comparison of the relative rate constants for the solvolysis of β-substituted cyclopropane derivatives shows that β-substituents have the greatest accelerating effect on cyclopropyl chlorides and smaller on the tosylates, which abolishes the difference between the rates of reaction of the halides and tosylates.

Table 4. Influence of the leaving group on the rate of solvolysis of acyclic aliphatic derivatives[29,31] and unsubstituted and β-substituted derivatives of cyclopropane[3,18,32,33].

Compound	k_{rel}	Reaction conditions
t-C_4H_9Br	1	C_2H_5OH; 50°
t-C_4H_9OTs	3000	»
H_5C_6, H_3C CHBr	1	C_2H_5OH; 50°
H_5C_6, H_3C CHOTs	845	»
H_3C, H_3C CHCl	1	CH_3COOH; 100°
H_3C, H_3C CHBr	25	»
H_3C, H_3C CHOTs	13 000	»
Cl	1	CH_3COOH, 100°
Br	86	»
OTs	231	»
	trans / *cis*	
$(CH_3)_3C$—Cl	1 / 1	CH_3COOH, 100°
$(CH_3)_3C$—Br	16 / 35	»
$(CH_3)_3C$—OTs	130 / 53	»
H_5C_6—Cl	1 / 1	CH_3COOH, 100°
H_5C_6—Br	5 / 50	»
H_5C_6—OTs	80 / 15	»

Table 5. The effect of β-substitution for different leaving groups in the compounds R—X.[3,21,24]

R	X	k_{rel}* *trans*	k_{rel}* *cis*	R	X	k_{rel}* *trans*	k_{rel}* *cis*
$C(CH_3)_3$	OTs	330	5	C_6H_5	OTs	300	15
$C(CH_3)_3$	Br	1040	92	C_6H_5	Br	5310	11 330
$C(CH_3)_3$	Cl	5830	220	C_6H_5	Cl	9340	2 300

*In relation to the corresponding non-substituted cyclopropyl derivatives.

3. The Influence of the Nature of the β-Substituent on the Rate of Solvolysis of Cyclopropane Derivatives

As in reactions involving nucleophilic substitution at a saturated carbon atom, alkyl substituents in the β-position accelerate the solvolysis of cyclopropane derivatives. When alkyl groups are introduced in the *trans*-β-position in the cyclopropane ring, the rate of solvolysis of the halides and tosylates increases (Table 6), the acceleration becoming more pronounced with increase in the length and degree of branching of the alkyl substituent[3,30], which is consistent with the inductive effects of the alkyl groups.

Table 6. The relative rates of solvolysis of β-substituted cyclopropyl derivatives R—X.[3,16,35]

R	X	k_{rel} *trans*	k_{rel} *cis*	Reaction conditions
H	OTs	1*	1*	CH_3COOH, 100°
CH_3	OTs	138	5.7	»
CH_2CH_3	OTs	180	7.4	»
$CH(CH_3)_2$	OTs	230	8	»
$C(CH_3)_3$	OTs	330	5	»
H	Br	1**	1**	»
CH_3	Br	630	46	»
$C(CH_3)_3$	Br	1040	92	»
H	Br	1***	1***	50% C_2H_5OH, 100°
CH_2CH_3	Br	460	20	»
$CH=CH_2$	Br	1770	160	»
	Br	7350	290	»

*$k = 4.16 \times 10^{-8}$ s^{-1}.
**$k = 1.55 \times 10^{-9}$ s^{-1}.
***$k = 2.18 \times 10^{-7}$ s^{-1}.

Table 7. The rates of acetolysis of β-phenylcyclopropane derivatives[12,21,32].

Compound	t, °C	k, s^{-1}
Chlorocyclopropane	150.1	$5.5 \cdot 10^{-10}$
cis-1-Chloro-2-phenylcyclopropane	150.1	$5.91 \cdot 10^{-4}$
trans-1-Chloro-2-phenylcyclopropane	150.1	$3.01 \cdot 10^{-3}$
Bromocyclopropane	160.3	$6.92 \cdot 10^{-7}$
cis-1-Bromo-2-phenylcyclopropane	119.4	$1.46 \cdot 10^{-5}$
trans-1-Bromo-2-phenylcyclopropane	119.4	$6.31 \cdot 10^{-5}$
Tosylcyclopropane	100	$4.16 \cdot 10^{-8}$
cis-2-Phenyl-1-tosylcyclopropane	108	$2.1 \cdot 10^{-6}$
trans-2-Phenyl-1-tosylcyclopropane	108	$3.2 \cdot 10^{-5}$

The accelerating effect of a *trans*-β-substituent is appreciably greater than that of a *cis*-β-substituent, which confirms the synchronous nature and the disrotatory pathway leading to the opening of the cyclopropane ring with rotation of the substituents on the outside in the case of the *trans*-isomers and on the inside for the *cis*-isomers. The steric repulsions arising in the opening of *cis*-β-substituted cyclopropyl halides and tosylates weakens the accelerating effect of the alkyl groups. The introduction of the second and subsequent *trans*-alkyl substituents is accompanied by a weaker acceleration[16].

The reactivity of cyclopropane derivatives increases also after the introduction of a phenyl substituent in the β-position (Table 7).

Under the influence of the inductive effect of the phenyl group, the rate of solvolysis of β-phenylcyclopropane derivatives should fall. The reaction is then accelerated by the +*M* effect of the phenyl group, which results in the stabilisation of the partial positive charge on the β-carbon atom in the transition state.

The change in the rate of solvolysis of cyclopropane derivatives induced by the phenyl group is greater than in the analogous substitution by the methyl group (Table 8), which can be explained by the fact that the phenyl group ensures a more effective delocalisation of the partial positive charge in the transition state. Recent studies have shown[36] that the ability of substituents to stabilise the aryl cation decreases in the sequence phenyl > cyclopropyl ≫ methyl.

Table 8. The relative reactivities of derivatives of β-methyl-[3] and β-phenyl-cyclopropanes[32,34] in the acetolysis reaction at 100 °C.

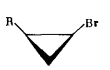
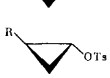
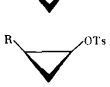
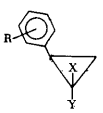
Compound	k_{CH_3}/H	$k_{C_6H_5}/H$
	630	5310
	46	1330
	138	300
	5.7	15

Table 9. The rates of solvolysis of β-arylcyclopropane derivatives



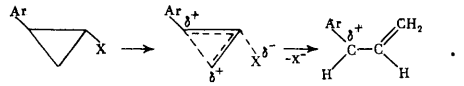
R	10^4k, s^{-1}	
	X=H, Y=OTs *, (Ref.34)	X=F, Y=Br ** (Ref.20)
H	0.305	0.89
p-CH_3	0.747	2.91
m-CH_3	0.656	1.19
m-Cl	0.0538	—
p-Br	—	0.38
m-Br	—	0.11

*Reaction conditions: CH_3COOH/CH_3COONa, 108 °C.
**Reaction conditions: CH_3OH, Ag^+, 50 °C.

The degree of acceleration of the solvolysis of cyclopropane derivatives by β-phenyl and β-methyl groups approaches that for the α- and γ-substituted allyl halides[37], which supports the existence of a proto-allyl transition state in the solvolysis of cyclopropane systems.

The study of the solvolysis of β-arylcyclopropyl derivatives showed that electron-donating substituents in the aromatic ring accelerate and the electron-accepting substituents retard the reaction (Table 9).

The correlation between the reactivity of *trans*-2-arylcyclopropyl tosylates ($\rho = -1.75$) [34] and *trans*-2-aryl-1-bromo-1-fluorocyclopropanes ($\rho = -2.0$),[20] on the one hand, and the σ^+ constants of the substituents, on the other, permitted the conclusion that the opening of the three-membered ring and ionisation take place synchronously and that the partial positive charge in the transition state is localised at the benzyl carbon atom. The value of ρ indicates an electrophilic mechanism of the rate-limiting stage and a nearly ionic transition state:



An appreciable acceleration of solvolysis is attained when an alkoxy-substituent is introduced in the β-position in cyclopropane derivatives[17,38,39] (Table 10) by virtue of the effective stabilisation of the carbonium ion by the electrons of the oxygen in the alkoxy-group.

Table 10. The relative rates of solvolysis of β-substituted dichlorocyclopropanes  (n-C_4H_9OH; Ag^+; 80 °C) [39].

R	C_6H_5	OC_6H_5	C_6H_9	OC_6H_9
k_{rel}	0.2	0.8	1.0	20.0

4. The Influence of the Nature of the α-Substituent on the Rate of Solvolysis of Cyclopropyl Derivatives

The solvolysis of α-substituted cyclopropanes has been studied to a much lesser extent. The available literature data show that the reactivity of α-substituted cyclopropyl bromides[16,34] and cyclopropyl tosylates[32] is appreciably higher than that of the unsubstituted derivatives. Table 11 shows that the α-phenyl group stabilises more effectively the developing positive charge than the α-methyl group. The constant ρ for the series of α-arylcyclopropanes exceeds the reaction constant for the β-derivatives. According to Schleyer and coworkers[3], the high sensitivity of α-arylcyclopropyl tosylates in the solvolysis reaction to the introduction of the substituents into the aromatic ring is due to the fact that the transition state has a structure close to that of the cyclopropyl cation stabilised by the aryl group, although the solvolysis product is 2-arylallyl acetate.

The idea that the α-phenyl substituent can stabilise the cyclopropyl cation has been recently confirmed[40]: the 1-phenylcyclopropyl cation has been "captured" with the aid of the hydroborate anion before it could isomerise to the allyl cation.

Yet another argument has been adduced[34] against the existence of a transition state of the allyl type in the solvolysis reactions of α-arylcyclopropyl tosylates, namely the weak sensitivity of the solvolysis of 2-arylallyl tosylates to the introduction of substituents into the aromatic ring ($\rho = -0.4$).

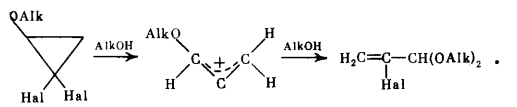
IV. THE INFLUENCE OF EXTERNAL FACTORS ON THE RATE AND DIRECTION OF SOLVOLYSIS OF CYCLOPROPANE DERIVATIVES

As shown in Section II, the solvolysis of cyclopropyl halides and tosylates leads to the formation of allyl derivatives. The charge distribution in the substituted allyl cation must be regarded as one of the factors which determine the site of addition of the anion to the allyl cation.

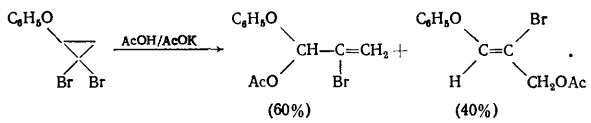
Table 11. The effect of α-methyl-[16,32] and α-phenyl-substitution[34] in the solvolysis of cyclopropane derivatives.

Compound	k_{CH_3}/H	$k_{C_6H_5}/H$	ρ (R=Ar)	Reaction conditions
	1100	390 000	—4.31(σ⁺),(108°)	CH_3COOH; 25°
	40	—	—	50% C_2H_5OH; 130°

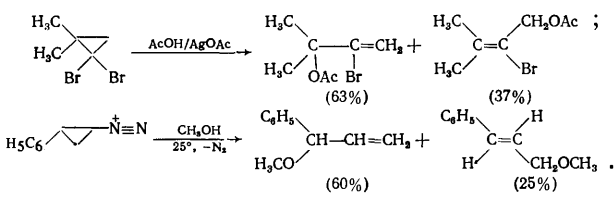
The localisation of the positive charge in the α-position relative to the substituent results in the formation of the acetals of α-halogenoacroleins in the solvolysis of alkoxydihalogenocyclopropanes[38,40,41]:



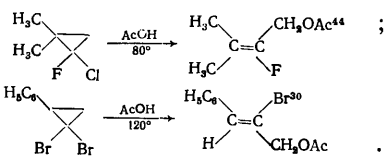
The stabilisation of the charge by the phenoxy-group is less effective owing to the conjugation of the lone electron pair of oxygen with the aromatic ring[42]:



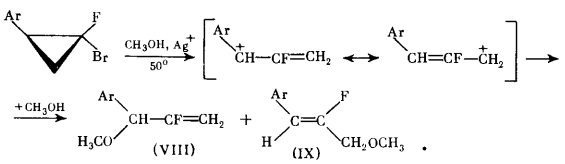
Charge control obtains also in the solvolysis reactions of derivatives of alkylcyclopropanes[30] and phenylcyclopropanes[43]:



However, in many cases the structure of the products of the solvolysis of alkyl- and phenyl-substituted dihalogenocyclopropanes is inconsistent with the charge distribution in the intermediate allyl cation:



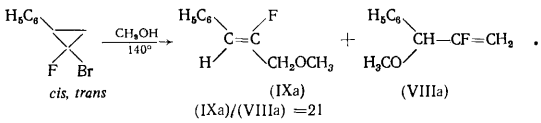
Evidently the second factor which determines the structure of the products of the solvolysis of cyclopropane derivatives is the stability of the olefins formed. It has been shown recently[20] that, under kinetically controlled reaction conditions, an allyl product with a terminal methylene group is formed preferentially:



Ar:	C_6H_5	*p*-$CH_3C_6H_4$	*m*-$CH_3C_6H_4$	*p*-BrC_6H_4	*m*-BrC_6H_4
(VIII)/(IX):	2.5	4.0	3.5	2.0	1.5

The arylallyl cation, formed as a result of the opening of the three-membered ring, reacts with methanol via both the α- and γ-carbon atoms with formation of products (VIII) and (IX) respectively. The degree of localisation of the charge on the α- and γ-carbon atoms of the allyl system, which depends on the nature of the substituent, determines the composition of the solvolysis products. The experimentally observed predominance of the yield of compound (VIII) over that of compound (IX) suggests that the charge is concentrated at the benzyl carbon atom of the arylallyl cation. The disproportion in the charge distribution increases following the introduction of electron-donating substituents into the aromatic ring and diminishes when electron acceptors are introduced.

On the other hand, under thermodynamically controlled conditions, the most stable olefins, in which the double bond is conjugated with the phenyl group (or olefins having the maximum number of substituents at the double bond), predominate:

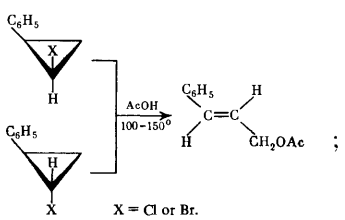


cis, trans (IXa) (VIIIa)

(IXa)/(VIIIa) =21

In the majority of studies on the solvolysis of arylcyclopropane derivatives[12,18,29,30,34] the formation of allyl products of the styrene type only has been observed, which must be attributed to the fairly severe reaction conditions (≥100–120 °C, 20–40 h).

It is remarkable that the acetolysis of *cis*- and *trans*-isomeric phenylhalogenocyclopropanes results in the formation of the *trans*-olefin only[21,22]:

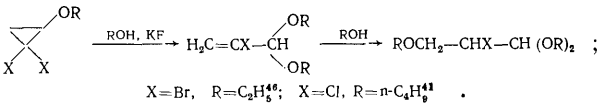


Some investigators[21] believe that the opening of the ring in *cis*-substituted halogenocyclopropanes is not subject to secondary orbital control. In other studies[45] the idea of *cis–trans* isomerisation in the allyl cation stage or of the reaction products is invoked. Bearing in mind the experimentally observed isomerisation of the *cis*-allyl cation to the *trans*-isomer[15,36], one must recognise that this view is more valid.

1. The Role of Accelerating Agents in Nucleophilic Substitution Reactions of Cyclopropane Derivatives

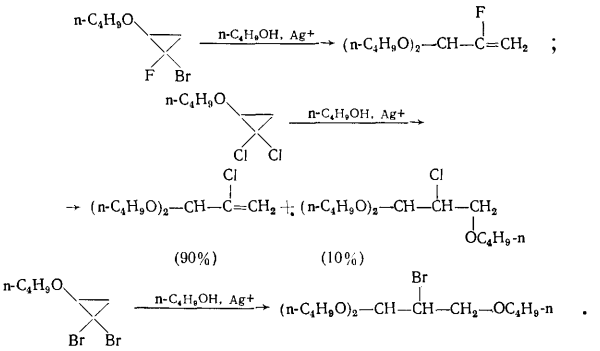
Electrophilic and nucleophilic accelerating additives are widely used in reactions involving nucleophilic substitution at a saturated carbon atom. The role of accelerating agents becomes still more marked in the solvolysis of cyclopropane derivatives, which are much less reactive than acyclic alkyl halides. Apart from the acceleration, electrophilic and nucleophilic additives can promote a further transformation of the allyl products formed.

Thus alcoholysis of alkoxy-*gem*-dihalogenocyclopropanes, accelerated by additives which generate an acid medium during the reaction (silver or alkali metal salts), is accompanied by secondary processes involving the addition of solvent molecules to the double bonds of the aryl derivatives:



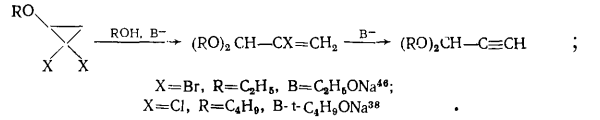
X=Br, R=C_2H_5[46]; X=Cl, R=n-C_4H_9[41].

The ability of the dialkyl acetal of α-halogenoacrolein to combine with the alcohol is determined by the nature of the α-halogeno-group[39]:



Thus the stability of the primary products of the solvolysis of alkoxy-*gem*-dihalogenocyclopropanes in an acid medium is consistent with the +*M* effect of the halogen in the molecule of the dialkyl acetal of α-halogenoacrolein.

When an organic or inorganic base is used as the reactive nucleophile, dehydrohalogenation of the primary solvolysis product is observed:



X=Br, R=C_2H_5, B=C_2H_5ONa[46];
X=Cl, R=C_4H_9, B-t-C_4H_9ONa[38].

The yield of the dialkoxypropyne increases both with increase of the basicity of the reactive agent (NaOH < KOH < n-C_4H_9.ONa < n-C_4H_9OK) and with increase of its concentration[39].

The stability of the dialkyl acetal of α-halogenoacrolein in an alkaline medium varies in the same sequence as in an acid medium: the fluoro-compounds are more stable than the chloro- and bromo-derivatives (F > Cl > Br).[39]

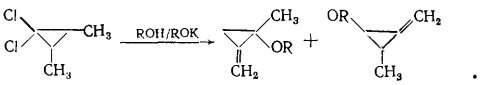
One must note that the solvolysis in the presence of strong bases proceeds with higher degrees of conversion of the primary products than in the presence of electrophilic additives. The formation of unsaturated aldehydes, enynes, and other unidentified products in solvolysis under the influence of t-C_4H_9OK has been described[47].

The cyclopropyl–allyl rearrangement, accompanied by secondary process, does not constitute the only pathway in the reactions of cyclopropane derivatives under solvolysis conditions subject to the influence of nucleophilic additives. If a strong base is used as the nucleophile then, as in the series of acyclic halogeno-derivatives, the elimination reaction competes with the substitution process.

The formation of cyclopropene from cyclopropane derivatives via β-elimination was observed for the first time by Kohler and Darling[48]. However, the isolation of the cyclopropene derivatives was not achieved for a long time owing to the instability of the three-membered ring with an *endo*-double bond. The low stability of cyclopropene and its derivatives is caused by the high strain energy of the ring[49,50]. The stability of cyclopropene compounds increases with increase of the degree of substitution, electron-donating substituents stabilising the molecule less effectively than electron-accepting substituents[51]. The high stability of polyhalogenocyclopropenes made it possible to obtain these compounds in a pure state[52].

The cyclopropenes formed under the conditions of the nucleophilic substitution reaction using highly basic additives can undergo further transformations: (a) isomerisation accompanied by the migration of the double bond outside the limits of the three-membered ring[53–55]; (b) the addition of a molecule of the nucleophile (solvent)[55] to the double bond of cyclopropene; (c) the opening of the three-membered ring with rupture of a C–C single bond in cyclopropene[39,41]. The operation of one of the above reaction pathways is determined by the structure of the initial cyclopropane or, more precisely, by the nature of its substituents.

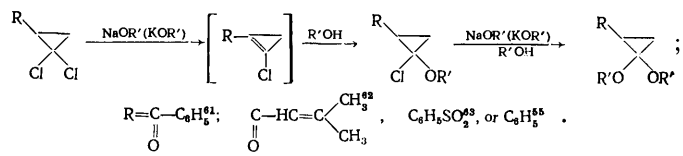
According to the data of Ampilogova et al.[56], compounds with a double bond in the three-membered ring are thermodynamically less stable than the isomeric methylenecyclopropanes. This has been confirmed experimentally by the irreversible isomerisation of alkylcyclopropenes to methylenecyclopropanes[54]. In the solvolysis of alkylhalogenocyclopropanes in the presence of strong bases the migration of the double bond outside the limits of the ring and the addition of a solvent molecule occur simultaneously in some cases[55]:



The ability of cyclopropene derivatives to undergo nucleophilic addition reactions indicates an unusual nature of the double bond in cyclopropenes, because such reactions are not characteristic of ethylenic double bonds. According to Kosai and Meyer[57], the C–H bonds in cyclopropene have an increased amount of *S*-character, while the C–C bonds have an increased amount of *p*-character. The study of the ^{13}C NMR spectra of cyclopropene derivatives led to the conclusion that the carbon–carbon double bonds in cyclopropene resemble acetylenic bonds[58]. Data for the geometry of cyclopropene (the C=C bond length is 1.3 Å [57] or 1.28 ± 0.04 Å [59]) and spectroscopic studies on substituted cyclopropenes (stretching vibrations of the C=C bond in the range 1800–1900 cm^{-1})[60] confirm the "acetylenic" properties of the cyclopropene double bond.

The elimination of the hydrogen halide with subsequent nucleophilic addition to the cyclopropene double bond under the conditions of the solvolysis of β-substituted halogenocyclopropanes under the influence of nucleophilic additives is determined by the basicity of the latter and the mobility of the hydrogen atom in the α-position relative to the substituent. Such reactions occur when strong bases (metal alkoxides) are used as nucleophiles and the cyclopropane ring has a substituent which increases the proton mobility

at the α-atom:



The dialkyl ketals of cyclopropanone formed are either stable under the reaction conditions or undergo further transformations.

In a study of the solvolysis of 2-aryl-1-bromo-1-fluorocyclopropane in deuterated methanol (CD_3OD) under the influence of potassium t-butoxide it was established[20] that the formal substitution products are not formed as a result of direct substitution of the halogen by the alcoholic residue but arise in the subsequent elimination–addition reaction.

Table 12. Degrees of conversion of 2-aryl-1-bromo-1-fluorocyclopropanes in methanolysis under the influence of t-C_4H_9OK (at 50 °C).

Reaction time, min	Conversion, %					
						
	cis	*trans*	*cis*	*trans*	*cis*	*trans*
10	35	17	—	—	100	100
20	60	28	—	—	—	—
30	—	—	7	4	—	—
60	80	40	17	8	—	—
90	—	—	21	12	—	—
120	92	56	29	15	—	—

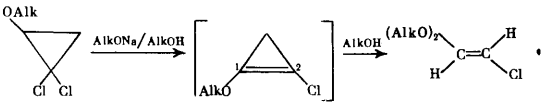
The solvolysis of aryl-*gem*-dihalogenocyclopropanes[20] in the presence of a strong base is accelerated by electron-accepting substituents and retarded by electron-donating substituents in the aromatic ring, as a result of the activation or deactivation of the benzyl proton (Table 12).

The higher reactivity of the *cis*-isomers is probably associated with the preferential *trans*-dehydrohalogenation. Similar relations between the rates of reaction of the *cis*- and *trans*-isomers have been observed in the solvolysis of 2-benzoyl-1-chlorocyclopropanes[61].

Consequently, the type of accelerating additive plays a decisive role in determining the direction of the process as a whole, the relative reactivities of the *cis*- and *trans*-isomers, and also the type of influence of the substituents in the aromatic ring on the rate of solvolysis of arylhalogenocyclopropanes. As shown above, in the presence of an electrophile (Ag^+) only the opening of the three-membered ring, accelerated by electron-donating substituents in the aromatic ring, takes place, the *trans*-isomers being more reactive than the *cis*-isomers. A strong base induces preferential reactions involving the retention of the cyclopropane ring, which are accelerated by electron-donating groups in the aromatic ring; under these conditions, the *cis*-isomer is more reactive. The cause of this sharp difference consists in the reaction mechanism; the electrophile attacks the halogen atom with formation of a carbonium ion, while the strong base attacks the mobile benzyl proton.

As already mentioned, the possibility of the solvolysis of halogenocyclopropanes with retention of the three-membered ring depends on the presence of a β-substituent activating the geminal proton. If the β-substituents are groups such as C_6H_5S [47] and OAlk,[39,41] then, under solvolysis conditions in the presence of both an electrophile and a strong base, the cyclopropyl–allyl rearrangement takes place. In the solvolysis of asymmetric alkoxy-*gem*-dihalogenocyclopropanes[39] the *trans*-isomer is more reactive in both cases.

Together with the products of the cyclopropyl–allyl rearrangement, the dialkyl acetals of *trans*-β-chloroacrolein are formed in the solvolysis of 2-alkoxy-1,1-dichlorocyclopropanes[39,41]:



The first stage probably involves the formation of 1-alkoxy-2-chlorocyclopropene, in which the $C_{(1)}$–$C_{(2)}$ bond is ruptured under the reaction conditions with addition of an alcohol molecule.

---o0o---

The above analysis of the influence of various factors on nucleophilic substitution reactions in the series of cyclopropanes showed that, in contrast to the usual S_N processes, the opening of the three-membered ring, controlled by orbital symmetry, takes place, while the elimination reaction under the influence of strong bases is undergone by both the initial compounds and the primary reaction products.

REFERENCES

1. J.D.Roberts and V.S.Chambers, J.Amer.Chem.Soc., 73, 5034 (1951).
2. P.R.Schleyer and R.D.Nicholas, J.Amer.Chem.Soc., 83, 182 (1961).
3. W.F.Sliwinski, T.M.Su, and P.R.Schleyer, J.Amer. Chem.Soc., 94, 133 (1972).
4. L.Radom, P.C.Hariharan, J.Pople, and P.R.Schleyer, J.Amer.Chem.Soc., 95, 6531 (1973).
5. R.B.Woodward and R.Hoffmann, "The Conservation of Orbital Symmetry" (Translated into Russian), Izd.Mir, Moscow, 1971, p.47.
6. T.L.Gilchrist and R.C.Storr, "Organic Reactions and Orbital Symmetry" (Translated into Russian), Izd.Mir, Moscow, 1976, p.69.
7. P.Coffey and K.Jug, Theor.Chim.Acta, 34, 213 (1974).
8. P.Merlet, S.D.Peyerimhoff, R.I.Buenker, and S.Shih, J.Amer.Chem.Soc., 96, 959 (1974).
9. M.J.S.Dewar and S.Kirschner, J.Amer.Chem.Soc., 96, 5244 (1974).
10. O.S.Tee and K.Yates, J.Amer.Chem.Soc., 94, 3074 (1972).
11. A.F.Khlebnikov, Symposium, "Sovremennye Problemy Organicheskoi Khimii" (Current Problems in Organic Chemistry), Izd.Leningrad.Gos.Univ., Leningrad, 1976, No.5, p.5.
12. C.H.De Puy, L.G.Schnack, J.K.Hausser, and W.Wiedermann, J.Amer.Chem.Soc., 87, 4006 (1965).
13. D.T.Clark and G.Smale, Tetrahedron, 25, 13 (1969).
14. A.P.Molchanov, Symposium, "Sovremennye Problemy Organicheskoi Khimii" (Current Problems in Organic Chemistry), Izd.Leningrad.Gos.Univ., Leningrad, 1975, No.4, p.53.
15. P.R.Schleyer, T.M.Su, M.Saunders, and J.C.Rosenfeld, J.Amer.Chem.Soc., 91, 5177 (1969).

16. P.R.Schleyer, W.F.Sliwinski, G.W.Van Dine, U.Schollkopf, J.Paust, and K.Fallenberger, J.Amer. Chem.Soc., **94**, 125 (1972).
17. W.E.Parham and K.S.Yong, J.Org.Chem., **35**, 683 (1970).
18. J.W.Hausser and J.T.Uchic, J.Org.Chem., **37**, 4087 (1972).
19. D.B.Ledlie and S.Maclean, J.Org.Chem., **34**, 1123 (1969).
20. V.S.Aksenov and G.A.Terent'eva, Izv.Akad.Nauk SSSR, Ser.Khim., 1344 (1978).
21. J.W.Hausser and N.J.Pinkowski, J.Amer.Chem.Soc., 89, 6981 (1967).
22. K.A.Holbrook and A.W.Parry, J.Chem.Soc.B, 1019 (1976).
23. C.B.Reese and A.Shaw, Chem.Comm., 1365 (1970).
24. S.J.Cristol, R.M.Swequeira, and C.H.De Puy, J.Amer.Chem.Soc., **87**, 4008 (1965).
25. C.W.Jefford, A.N.Kabengele, and U.Burger, Tetrahedron Lett., 4799 (1972).
26. C.B.Reese and A.Swan, J.Amer.Chem.Soc., 92, 2566 (1970).
27. U.Schollkopf, K.Fellenberger, and M.Patsch, Tetrahedron Lett., 3639 (1967).
28. C.B.Reese and A.Shaw, J.Chem.Soc., Perkin Trans.I, 2422 (1975).
29. C.K.Ingold, "Theoretical Principles of Organic Chemistry" ["Structure and Mechanism in Organic Chemistry"] (Translated into Russian), Izd.Mir, Moscow, 1973, p.376.
30. S.R.Sanders, J.Org.Chem., 32, 3876 (1967).
31. M.H.R.Hoffman, J.Chem.Soc., 6253, 6762 (1965).
32. J.W.Hausser and M.J.Grubber, J.Org.Chem., **37**, 2648 (1972).
33. P.R.Schleyer, G.W.Van Dine, U.Schollkopf, and J.Paust, J.Amer.Chem.Soc., **88**, 2868 (1966).
34. C.H.De Puy, L.G.Schnack, and J.W.Hausser, J.Amer.Chem.Soc., **88**, 3343 (1960).
35. J.A.Landgrebe and L.W.Becker, J.Org.Chem., **33**, 1173 (1968).
36. G.A.Olah and R.J.Spear, J.Amer.Chem.Soc., **97**, 1539 (1975).
37. C.A.Vernon, J.Chem.Soc., 423 (1954).
38. L.Skattebol, J.Org.Chem., **81**, 1554 (1966).
39. Yu.V.Savinykh and V.S.Aksenov, Izv.Sibir.Otd. Akad.Nauk SSSR, Ser.Khim., 125 (1978).
40. X.Creary, J.Org.Chem., **41**, 3734 (1976).
41. V.S.Aksenov and R.S.Min, Izv.Sibir.Otd.Akad.Nauk SSSR, Ser.Khim., No.5, 139 (1974).
42. G.Paradisi and G.Zechi, Gazzette, **104**, 881 (1974).
43. W.Kirmse and H.Schutte, J.Amer.Chem.Soc., **89**, 1284 (1967).
44. Le Van Chau and M.Schlosser, Synthesis, 115 (1976).
45. W.E.Parham and K.S.Yong, J.Org.Chem., **33**, 3947 (1968).
46. V.S.Aksenov and V.A.Filimoshkina, Izv.Sibir.Otd. Akad.Nauk SSSR, Ser.Khim., No.3, 147 (1975).
47. W.E.Parham, S.Kajigaeschi, and S.Groening, Bull. Chem.Soc.Japan, **45**, 509 (1972).
48. E.P.Kohler and S.F.Darling, J.Amer.Chem.Soc., **52**, 1174 (1930).
49. N.C.Baird and M.J.S.Dewar, J.Amer.Chem.Soc., **89**, 3966 (1967).
50. I.A.D'yakonov and R.R.Kostikov, Uspekhi Khim., **36**, 1305 (1967)[Russ.Chem.Rev., No.8 (1967)].
51. T.N.Grigorova, Symposium, "Sovremennye Problemy Organicheskoi Khimii" (Current Problems in Organic Chemistry), Izd.Leningrad.Gos.Univ., Leningrad, 1974, No.3, p.100.
52. M.A.Battiste and R.G.Posey, J.Org.Chem., 41, 333 (1976).
53. W.E.Billups, T.S.Schields, W.Y.Chow, and N.C.Deno, J.Org.Chem., **37**, 3676 (1972).
54. N.A.Ampilogova, I.A.D'yakonov, and R.R.Kostikov, Zhur.Org.Khim., 2, 1898 (1966).
55. T.C.Schields and P.D.Gardner, J.Amer.Chem.Soc., **89**, 5425 (1967).
56. N.A.Ampilogova, I.A.D'yakonov, and R.R.Kostikov, "Tezisy Dokladov Simpoziuma po Stroeniyu, Reaktsionnoi Sposobnosti, Mekhanizmam Prevrashchenii Soedinenii s Kratnymi Svyazyami i Malymi Tsiklami, Leningrad 1967" (Abstracts of Reports at the Symposium on the Structures, Reactivities, and Mechanisms of the Reactions of Compounds with Multiple Bonds and Small Rings, Leningrad, 1967), p.103.
57. P.H.Kosai and R.J.Meyer, J.Chem.Phys., **30**, 512 (1959).
58. G.L.Closs, Proc.Chem.Soc., 152 (1962).
59. J.D.Dunitz, H.G.Feldman, and V.Schomacker, J.Chem.Phys., **20**, 1708 (1952).
60. N.I.Komendantov and R.R.Kostikov, Zhur.Org.Khim., **4**, 1128 (1968).
61. I.G.Tishchenko, O.G.Kulinkovich, and Yu.V.Glazkov, Zhur.Org.Khim., 11, 581 (1975).
62. I.G.Tishchenko, O.G.Kulinkovich, Yu.V.Glazkov, and N.K.Pershtuk, Zhur.Org.Khim., 11, 576 (1975).
63. W.E.Parham, W.D.McKown, V.Nelson, S.Kajigaeshi, and N.Ishikava, J.Org.Chem., **38**, 1361 (1973).

Institute of Petroleum Chemistry
Tomsk

Translated from *Uspekhi Khimii*, 49, 1057-1078 (1980) U.D.C. 547.57

Aromatic Monocarbonylpolyfluoro-compounds

T.N.Gerasimova and E.P.Fokin

The literature data on the methods of synthesis and chemical and photochemical reactions of aromatic polyfluoro-substituted aldehydes and ketones are surveyed and arranged systematically. Attention is concentrated on the most characteristic reactions of these compounds with nucleophiles. The characteristics of the structure and reactivity of monocarbonylpolyfluoro-compounds due to the presence of electron-accepting fluorine atoms in their molecules are considered. Methods are described for the preparation of aromatic *o*-hydroxy- and *o*-amino-substituted polyfluoroketones and certain aspects of their employment in the synthesis of polyfluoro-substituted benzoheterocycles are examined.
The bibliography includes 148 references.

CONTENTS

I. Introduction 558
II. Methods of synthesis of aromatic polyfluoro-substituted aldehydes and ketones 558
III. Chemical properties 559
IV. Aromatic *o*-hydroxy- and *o*-amino-substituted polyfluoroketones 565

I. INTRODUCTION

During the last two decades, there has been an intense development of the chemistry of aromatic polyfluoro-compounds. In recent years a number of reviews devoted to the methods of synthesis[1,2] and individual types of their reactions[3-6] as well as problems of the influence of polyfluorobenzene ring and the reactivity of the functional groups linked to it[7,8] have been published. However, the volume of experimental data has increased so much that its detailed consideration and survey in terms of individual classes of compounds has become necessary. In the present review an attempt is made to do this in relation to aromatic carbonyl polyfluoro-compounds. The review includes data on the methods of synthesis and chemical properties of aromatic polyfluoro-substituted aldehydes and ketones of the type Ar_FCHO and Ar_FCOR containing the C=O group linked directly to the aromatic polyfluoro-ring. Polyfluorobenzoic acids and their derivatives are not considered in this review.

II. METHODS OF SYNTHESIS OF AROMATIC POLYFLUORO-SUBSTITUTED ALDEHYDES AND KETONES

The classical method of synthesis of aromatic ketones—the Friedel–Crafts acylation[9]—has not been used widely in the chemistry of aromatic polyfluoro-compounds. Only isolated instances of the application of this reaction in the preparation of aromatic polyfluoroketones are known. Thus the possibility of synthesising pentafluorobenzophenones by the reaction of pentafluorobenzoyl chloride with benzene and alkylbenzenes has been demonstrated[10-12]:

$$C_6H_6 + C_6F_5COCl \xrightarrow[90-100^\circ]{AlCl_3} \underset{(55\%)}{C_6H_5COC_6F_5} \ ;$$

$$C_6Alk_6 + C_6F_5COCl \xrightarrow[20^\circ]{AlCl_3} \underset{(26-50\%)}{C_6Alk_5COC_6F_5} \ ;$$

Alk=Me, or Et .

The acylation reactions of pentafluorobenzene in the presence of aluminiumchloride take place under severe conditions and are complicated by side processes[10], but the synthesis of decafluorobenzophenone and a number of aliphatic aromatic polyfluoroketones by the reaction of pentafluorobenzene with carboxylic acid anhydrides and halides in antimony pentafluoride has been described[13]:

$$C_6F_5H \xrightarrow[SbF_5]{R_FCOX \text{ или } (R_FCO)_2O} \underset{(20-80\%)}{C_6F_5COR_F} \qquad R_F=Alk_F, \text{ or } C_6F_5 \ .$$

Polyfluorobenzophenones have also been obtained by the hydrolysis of the salts of α-fluorodiarylmethyl cations synthesis from partly fluorinated aromatic hydrocarbons and trifluoromethylbenzenes in antimony pentafluoride[14,15]:

$$R^1C_6F_4CF_3 + R^2C_6F_4H \xrightarrow{SbF_5} R^1C_6F_4\overset{+}{C}FC_6F_4R^2 \xrightarrow{H_2O} \underset{(75-93\%)}{R^1C_6F_4COC_6F_4R^2} \ ;$$

R^1=H, or F; R^2=H, F, or Me .

The most widely used method of synthesis of aromatic polyfluoro-substituted aldehydes and ketones is based on organoelemental compounds. Penta- and tetra-fluorobenzaldehydes have been obtained from the corresponding polyfluorophenylmagnesium halides and *N*-methylformanilide in 50–80% yield[16-19]. The attempts to carry out the reaction with ethyl formate or orthoformate resulted in appreciable reduction of the yield of products[16,20]. Pentafluorophenyl-lithium has been used successfully instead of a Grignard reagent[21-23].

Aromatic and aliphatic-aromatic polyfluoroketones are usually obtained by the interaction of polyfluorophenyl derivatives of metal—magnesium, copper, cadmium, and aluminium—with carboxylic acid derivatives[16,17,24-33]. There are extremely few examples of the use of aromatic polyfluoro-substituted carbonyl compounds or their analogues in such reactions[34-36]:

$$C_6F_5MgX \xrightarrow{(MeCO)_2O} C_6F_5COMe \quad (48\%)$$

$$C_6F_5MgX \xrightarrow{CF_3CO_2Li} C_6F_5COCF_3 \quad (71\%)$$

$$C_6F_5MgX \xrightarrow{PhCOCl} C_6F_5COPh \quad (62\%)$$

$$C_6F_5MgX \xrightarrow{ClCO_2Me} C_6F_5COC_6F_5 \quad [(33\%) \ ;$$

$$C_6F_5CN \xrightarrow{RMgX} \underset{(40-60\%)}{C_6F_5COR}; \quad R=Me, \text{ or } Ph \ ;$$

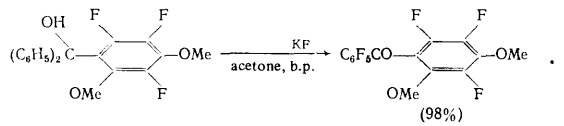
$$C_6F_5COCl \xrightarrow{Me_2Cd} \underset{(56\%)}{C_6F_5COMe} \ .$$

A preparatively important version of this method is based on the interaction of benzaldehyde or its substituted derivatives with Grignard reagents in combination with the classical reaction involving the oxidation of the secondary alcohols thus produced. The oxidant is usually chromium trioxide in glacial acetic acid[16,37–43]. Polyfluoro-substituted benzo- and aceto-phenones containing various functional groups have been prepared by this method[43–45].

Aliphatic-aromatic polyfluoroketones with ester and other functional groups have been synthesised successfully with the aid of the disodium salt of iron hydrocarbonyl[46]:

$$Na_2Fe(CO)_4 + n\text{-}C_5H_{11}OCO(CH_2)_4CH_2Br + C_6F_5COCl \rightarrow C_6F_5CO(CH_2)_5CO_2C_5H_{11}\text{-}n \ .$$

A specific reaction for the synthesis of aromatic polyfluoroketones involves the cleavage of polyarylfluorocarbinols in an alkaline medium[47–49]. The use of anhydrous potassium fluoride as the base ensures that the process proceeds unambiguously and is preparatively valuable[36,50]:



(98%)

A number of other methods normally employed in the chemistry of non-fluorinated analogues have also been applied successfully in the synthesis of aromatic polyfluoro-substituted carbonyl compounds. Pentafluorobenzaldehyde has been obtained from pentafluorobenzonitrile by reduction with stannous chloride[34] or Raney nickel[35]. The formation of polyfluorobenzophenones by the oxidation of olefins[51] and by the thermolysis of salts of polyfluorobenzoic acids[52–55] or pentafluorobenzoyl chloride in the presence of alkali metal salts[56] has been described.

III. CHEMICAL PROPERTIES

The substitution of hydrogen atoms in the aromatic ring of the carbonyl compound by fluorine atoms, which are highly electronegative, alters the electronic character of the aromatic ring and the properties of the carbonyl group linked to it. In aromatic polyfluoro-substituted carbonyl compounds the $-I$ effect of the pentafluorophenyl group[57,58] is enhanced by the breakdown of the coplanarity of the molecules, which hinders the conjugation of the carbonyl group with the aromatic ring. The difficulty of the rotation of the C_6F_5 groups about the $C_{arom}-C_{C=O}$ bond has been noted for decafluorobenzophenone[59]. The determination of the dipole moments of pentafluorobenzaldehyde and pentafluoroacetophenones in solution and their comparison with the calculated values showed that the formyl and acetyl groups deviate from the plane of the ring (the dihedral angles are 28° and 58° respectively) largly due to the Coulombic repulsion between the oxygen atoms or between the methyl group and fluorine atoms[60]. It is noteworthy that the molecules of the non-fluorinated analogues of these compounds are planar. Direct evidence for the greater electron-accepting influence of the pentafluorophenyl group compared with the phenyl group is provided by the hypsochromic shift (by 20–30 cm^{-1}) of the stretching vibration band of the carbonyl group in the infrared spectra of aromatic polyfluoro-substituted aldehydes and ketones[61].

The $-I$ effect of the pentafluorophenyl residue should lead, on the one hand, to an enhancement of the electrophilic properties of the carbon atom of the carbonyl group linked to it and to a facilitation of nucleophilic attack via this carbon atom and, on the other hand, to a decrease of the basicity of the C=O group and a greater difficulty of acid catalysts, which plays an important role in many reactions of carbonyl compounds. Unfortunately there are no quantitative literature data for the relative basicities of aromatic polyfluoro-substituted aldehydes and ketones. It has only been shown that perfluorobenzophenone is appreciably protonated on dissolution in sulphuric or fluorosulphonic acids[62] and forms the corresponding oxycarbonium in in the SbF_5–HF–SO_2ClF system[63].

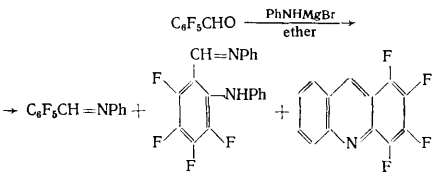
The presence of the polyfluoroaryl residue in the molecule of the aromatic polyfluoro-substituted carbonyl compound not only transforms the properties of the carbonyl group but is also responsible for the possibility of nucleophilic substitution in the fluorine atoms. The carbonyl group has an activating influence on this process. Overall, aromatic polyfluoro-substituted aldehydes and ketones are polyfunctional compounds, the characteristics and chemical properties of which are determined by the mutual influence of the carbonyl and polyfluorophenyl groups linked directly.

1. Reactions with *N*-Nucleophiles

The interaction of aromatic aldehydes and ketones with nitrogen bases, which is the most important and most thoroughly investigated type of their reactions, usually leads to the formation of derivatives of the carbonyl group. The reactions of aromatic polyfluoro-substituted carbonyl compounds with *N*-nucleophiles are less unambiguous. Depending on the structure of the reactants under the reaction conditions, they can involve both the carbonyl group, with formation of the corresponding nitrogen-derivatives, or the haloform decomposition of the initial compound, or the substitution of fluorine atoms.

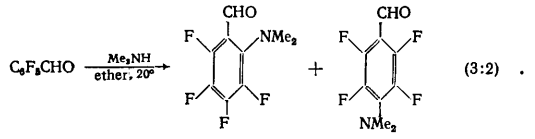
Aromatic polyfluoroaldehydes react with hydrazine, semicarbazide, thiosemicarbazide, and 2,4-dinitrophenylhydrazine, forming the corresponding derivatives of the carbonyl group under the usual conditions[18–20,34,64,65]. When pentafluorobenzaldehyde was allowed to react with *O*,*N*-bis(trifluoroacetyl)-hydroxylamine—a new reagent for the carbonyl group—pentafluorobenzonitrile was obtained in 76% yield[66].

Pentafluorobenzaldehyde exhibits a high reactivity in relation to primary aliphatic and aromatic amines via its carbonyl group. It reacts with ethylamine in water without the elimination of fluoride ions, forming *N*-(pentafluorobenzylidene)-ethylamine[64]. Its react with aniline and the very weakly basic pentafluoroaniline ($pK_a = -0.28$) [67] leads to the formation of the corresponding Schiff bases[16,17,68]. The interaction with the more nucleophilic bromomagnesylaniline results in the formation not only of the anil of pentafluorobenzaldehyde but also of products of its further reactions[68]:

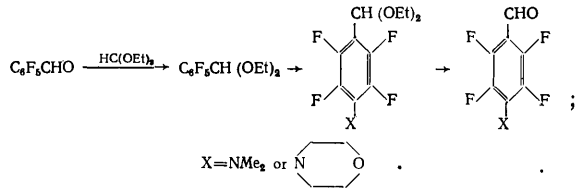


Pentafluorobenzaldehyde reacts with dimethylamine in ethereal solution at room temperature, the process involving the substitution of a fluorine atom by the dimethylamino-group[64]. The preferential *ortho*-directing effect observed in

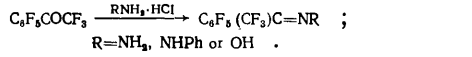
this reaction is in all probability caused by the specific interaction of the reagent with the formyl group:



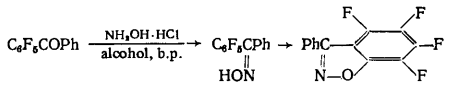
p-Aminotetrafluorobenzaldehydes can be obtained by an indirect method via the diethyl acetal of pentafluorobenzaldehyde[69]:



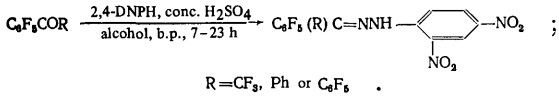
2,3,4,5,6-Pentafluoroacetophenone† exhibits a reactivity towards substituted hydrazines which resemble that of the non-fluorinated analogue[34,70]. Octafluoroacetophenone, containing the highly electronegative trifluoromethyl group, reacts vigorously with free hydrazine[71]. However, in contrast to aliphatic polyfluoroketones[72,73], it does not then form a stable geminal addition product, but undergoes the haloform decomposition with elimination of the relatively stable pentafluorophenyl anion[8]. Reactions with the less nucleophilic phenylhydrazine and hydroxylamine take place on heating and lead to appreciable elimination of fluoride ions and formation of complex mixtures. Derivatives of the carbonyl group have been obtained on refluxing octafluoroacetophenone with the hydrochlorides of the corresponding bases in an aqueous alcoholic medium[71,74]:



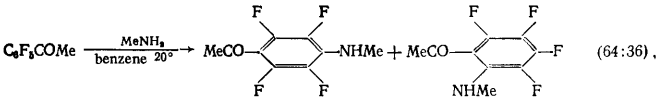
The oximes of 2,3,4,5,6-pentafluoro- and decafluoro-deoxybenzoins[75] as well as the oxime of pentafluorobenzophenone have been obtained similarly. The latter is unstable and undergoes spontaneous cyclisation to an oxazole derivative[16,74]:



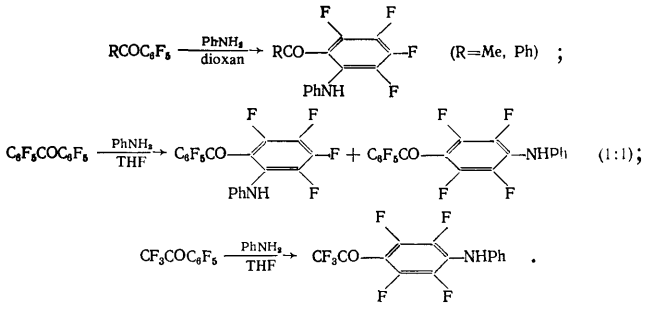
Polyfluorobenzophenones react with hydrazine and phenylhydrazine with substitution of a fluorine atom by the RNHNH group and do not change on prolonged refluxing with their hydrochlorides in an aqueous alcoholic solution[39,71]. The lack of interaction with free bases via the carbonyl group can be accounted for by the influence of a number of factors, the most important of which is apparently the steric effect of the *ortho*-fluorine atoms, which hinder the approach of the nucleophile to the central carbon atom[16,71,76]. The reduced reactivity of aromatic polyfluoroketones under the conditions of acid catalysis, caused by their low basicity, is also manifested under very severe conditions, compared with the non-fluorinated analogues, in the synthesis of 2,4-dinitrophenylhydrazones[39,71]:



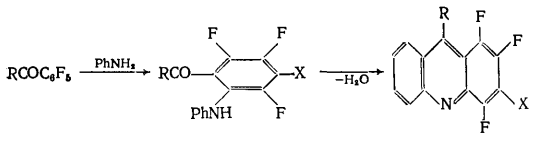
Aromatic polyfluoroketones react with ammonia and aliphatic amines with substitution of one or several fluorine atoms by the corresponding amino-groups, exhibiting at the same time a higher reactivity than hexafluorobenzene[48,77-79]. A preferential *para*-directing effect is shown in a polar medium, while the reaction is a non-polar solvent can lead to an increased content of the *ortho*-isomer in the product[77]:



The interaction of polyfluoro-substituted aceto- and benzophenones with aromatic amines in aromatic solvents proceeds only via the substitution of fluorine by the arylamino-group. The isomeric composition of the reaction product depends on the structure of the initial ketones and on the polarity of the medium[80-82]:



When the reaction of aromatic polyfluoroketones with aniline is carried out without a solvent in the presence of an excess of aniline, somewhat different results are obtained. The main reaction products are in this case polyfluoroacridines, the formation of which can be represented schematically in the following manner[80]:



The unusual conditions of the intramolecular cyclisation of *o*-anilinoketones, which usually occurs in acid media, are striking[83]. Presumably in this instance the $PhNH_3^+$ ions, formed as a result of the nucleophilic substitution of fluorine, play the role of the acid catalyst. Accordingly, the addition of potassium carbonate to the reaction mixture prevents the formation of acridines[80,81].

† Henceforth the positions of the fluorine atoms in 2,3,4,5,6-pentafluoroacetophenone and 2,3,4,5,6-pentafluorobenzophenone will not be indicated in this review.

2,4-DNPH = 2,4-dinitrophenylhydrazine [2,4-$(NO_2)_2C_6H_3$.$NHNH_2$].

The study of the interaction of aromatic polyfluoroketones with aniline showed that nucleophilic addition to the carbonyl group, leading to the formation of anils, takes place to an appreciable extent only for octafluoroacetophenone[80]. A method of synthesising anils from other ketones of this series has been recently discovered[84]. It consists in the interaction of the ketone with aniline in benzene or chlorobenzene in the presence of anhydrous aluminium chloride. The role of the latter evidently reduces to the activation of the carbonyl group with respect to nucleophilic attack as a result of complex formation via the oxygen atom:

$$C_6F_5COR \xrightarrow[C_6H_6 \text{ or } C_6H_5Cl]{PhNH_2,\ AlCl_3} C_6F_5C(R)=NPh\ ;$$
$$R=Me,\ Ph,\ \text{or}\ C_6F_5\ .$$

2. Reactions with *O*-Nucleophiles

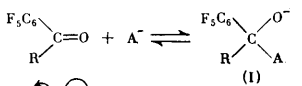
Aliphatic perfluoro-substituted aldehydes and ketones, in which the electrophilic properties of the carbonyl group are greatly enhanced as a result of the strong electron-accepting influence of the perfluoroalkyl groups, react extremely readily with compounds of the type ROH (R = H or alkyl), forming geminal addition products[72,73,85].

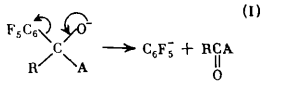
Decafluorobenzophenone, which is an aromatic perfluoroketone, does not form a hydrate[16]. In contrast to its non-fluorinated analogue, pentafluorobenzaldehyde reacts with methanol in the absence of acid to form a hemiacetal. Its acetals have been obtained only after prolonged refluxing with alcohols in the presence of concentrated hydrochloric acids[64]. The use of orthoformic ester instead of alcohol made it possible to obtain a high yield of the diethyl acetal of pentafluorobenzaldehyde[69].

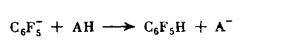
In contrast to its non-fluorinated analogue, pentafluorobenzaldehyde exhibits a very high tendency towards the haloform decomposition; under the conditions of the Cannizzaro reaction, it is cleaved with formation of pentafluorobenzene and formic acid[16,86]. 4-X-tetrafluorobenzaldehydes[64] as well as aromatic polyfluoroketones[16,38,45,71] undergo a similar reaction in an alkaline medium. Among the latter, the highest reactivity is shown by decafluorobenzophenone, which decomposes at room temperature under the influence of 10% KOH:[71]

$$C_6F_5COC_6F_5 \xrightarrow[H_2O,\ 20^\circ]{KOH} C_6F_5H + C_6F_5CO_2H\ .$$

The mechanism of the cleavage of aromatic polyfluoro-substituted carbonyl compounds is in all probability analogous to that proposed earlier for the decomposition of non-enolising ketones in an alkaline medium[87]:


(1)


(2)


(3)

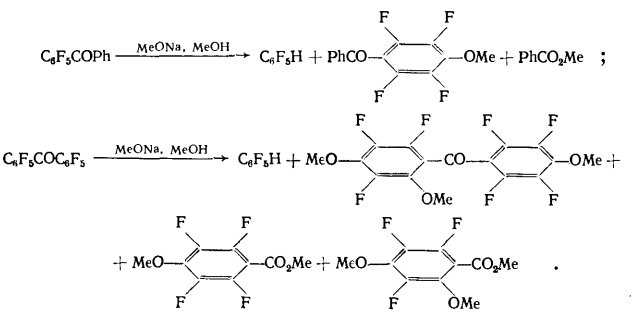
The increased tendency of aromatic polyfluoroketones to undergo cleavage compared with their non-fluorinated analogues can be explained by the more marked electrophilic properties of the carbon atom of the carbonyl group and also by the possibility of the elimination of the stable pentafluorophenyl anion. The relative ease of decomposition of decafluorobenzophenone is evidently caused by the favourable energy change in stage (2) in consequence of the steric strain in the intermediate anion (I) and also the electron shift, indicated in the above scheme by arrows, under the influence of the two electron-accepting pentafluorophenyl groups.

The mode of the cleavage reaction is determined by the relative stability of the carbanions, which are potential leaving groups. A detailed analysis of the products of the cleavage of aliphatic-aromatic polyfluoroketones, carried out by Coe et al.[38] (see Table), confirmed this view. The relative stability of the anions corresponding to the hydrocarbons formed decreases in the sequence [8,88] $CCl_3^- > C_6F_5^- > CF_3^- > C_6H_5^-$.

The haloform decomposition of aliphatic-aromatic fluoroketones (4 *N* KOH, refluxing for 4 h).[38]

Initial ketone	Reaction product	
	hydrocarbon	acid
C_6F_5COMe	C_6F_5H	$MeCO_2H$
$C_6F_5COCH_2Br$	C_6F_5H	$BrCH_2CO_2H$
$C_6F_5COCHCl_2$	C_6F_5H	Cl_2CHCO_2H
$C_6F_5COCF_3$	C_6F_5H	CF_3CO_2H
$C_6F_5COCCl_3$	$CHCl_3$	$C_6F_5CO_2H$
$C_6H_5COCF_3$	CHF_3	$C_6H_5CO_2H$

The haloform decomposition reaction is extremely characteristic of aromatic polyfluoro-substituted carbonyl compounds and proceeds in the presence of not only aqueous alkali but also of other charged nucleophiles. It is possible that this process is in fact the cause of the low yield of 4-methoxytetrafluorobenzaldehyde, obtained by the reaction of pentafluorobenzaldehyde with sodium methoxide in methanol[64]. In contrast to their non-fluorinated analogue, which is stable under the conditions of prolonged refluxing with sodium methoxide in methanol, penta- and deca-fluorobenzophenones undergoe reactions of two kinds in this medium at room temperature; nucleophilic substitution of fluorine atoms by methoxy-groups and cleavage with elimination of the pentafluorophenyl residue and the formation of methyl esters of benzoic and pentafluorobenzoic acids[38,89]:



In order to reduce the extent of the second process and to increase the yield of methoxy-ketones, one must prevent the presence of an excess of sodium methoxide in the reaction mixture[62].

3. Reactions with Sulphur Compounds

Pentafluorobenzaldehyde forms a bisulphite compound on being shaken with a saturated solution of sodium bisulphite[16]. Its equimolar mixture with thiophenol in acetone gives rise to a crystalline hemithioacetal partly dissociated into the initial components on dissolution in carbon tetrachloride or acetone[64].

On the other hand, according to other data[90], pentafluorobenzaldehyde does not react appreciably, like its non-fluorinated analogue, with propane-1-thiol in methylene chloride solution in the absence of acid; the addition of the latter leads to the formation of the thioacetal. The diethyl thioacetal has been obtained from pentafluorobenzaldehyde by reaction with ethanethiol in the presence of concentrated hydrochloric acid[64] or with phenyldi(ethylthio)borane[91].

$$C_6F_5CHO + PhB(SEt)_2 \rightarrow 1/3\,(PhBO)_3 + \underset{(45\%)}{C_6F_5CH(SEt)_2}\quad .$$

Several examples of the nucleophilic substitution of fluorine in pentafluorobenzaldehyde by sulphur-containing residues are known[64]. 4-Mercaptotetrafluorobenzaldehyde has been obtained in 61% yield by the reaction of pentafluorobenzaldehyde with sodium hydrogen sulphide in dimethylformamide (DMF) at 0 °C. The reaction with sodium thiophenoxide in DMF proceeds with evolution of heat and the substitution of all five fluorine atoms by PhS groups; in methanol the main reaction product is 4-phenylthiotetrafluorobenzaldehyde (yield 68%).[64]

The interaction of aromatic polyfluoro-sbustituted aldehydes and ketones with sulphur tetrafluoride leads to the substitution of the carbonyl oxygen atom by two fluorine atoms. The reaction conditions depend on the structure of the initial carbonyl compound and the introduction into its molecule of electron-accepting groups leads to a decrease of reactivity. The reaction with perfluoroketones requires either a high temperature or the presence of acid catalysts. This reaction can serve as a method for the preparation of polyfluorinated hydrocarbons containing fluorine atoms in both the aromatic ring and in the side chain, which are otherwise difficult to obtained:

$$C_6F_5COR \xrightarrow{SF_4} C_6F_5CF_2R\quad ;$$

R=H, 140—170°, yield 51%[92] or 100°, HF, 80%[93]; R=Me, 115°, 79%[93];

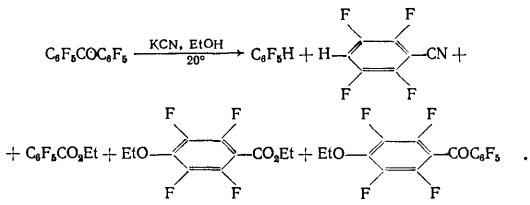
R=CF_3, 170°, HF, 85%[93]; R=Alk_F, 180°, AlF_3, 90%[91,94];

R=Ph, 180°, 40%[95]; R=C_6F_5, 235°, 88%[95].

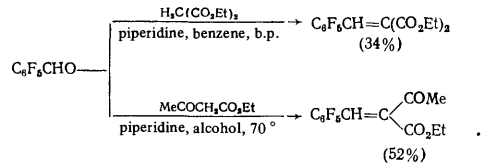
4. Reactions with *C*-Nucleophiles

(a) *Reactions with pseudoacids.* In contrast to its non-fluorinated analogue, pentafluorobenzaldehyde does not undergo the benzoin condensation with potassium cyanide in aqueous alcoholic solution[86]. Its cyanohydrin has been obtained in a low yield by the reaction of the bisulphite derivative with NaCN in aqueous solution[20].

In contrast to hexafluoroacetone, which forms stable cyanohydrin salts on interaction with sodium or potassium cyanides in tetrahydrofuran[96], aromatic polyfluoroketones remain unchanged on being refluxed with KCN in this solvent. In alcohol the reaction proceeds in several ways, the main one involving the haloform decomposition of the initial ketone and also of the product of the substitution of the *p*-fluorine atom of the carbonyl group can be in this instance either the cyanide ion or the EtO^- ion. The presence of the latter in the reaction mixture is indicated by the formation of the corresponding nucleophilic substitution products. Among aromatic polyfluoroketones, the most reactive is decafluorobenzophenone, which forms a complex mixture of products on reaction with KCN in alcohol at room temperature[44]:



Polyfluorobenzaldehydes undergo aldol condensation with compounds containing active methyl or ethylene groups, exhibiting the usual reactivity or a reactivity which is somewhat reduced compared with its non-fluorinated analogues. Pentafluorobenzaldehyde reacts with malonic and acetoacetic esters in the pesence of piperidine under more severe conditions than does benzaldehyde, forming the corresponding α,β-unsaturated carbonyl compounds[97]:



2,3,4,5-Tetrafluorocinnamic acid has been obtained by the reaction of 2,3,4,5-tetrafluorobenzaldehyde with malonic acid (in pyridine, in the presence of piperidine)[19]. On the other hand, the initial condensation product (the hydroxy-acid) was obtained under similar conditions from pentafluorobenzaldehyde and then converted into 2,3,4,5,6-pentafluorocinnamic acid by heating with concentrated H_2SO_4.[16]

Pentafluorobenzaldehyde could not be made to undergo the Claisen–Schmidt reaction with acetone and acetaldehyde in the presence of aqueous alkali[97]. In alcoholic solutions of alkalis the reaction with acetone leads to a low yield of 2,3,4,5,6-pentafluorobenzylideneacetone and its *p*-alkoxy-derivative[98]:

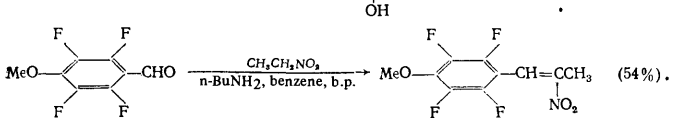
$$C_6F_5CHO \xrightarrow[HO^-,\,ROH]{(CH_3)_2CO} \underset{(6—13\%)}{C_6F_5CH{=}CHCOCH_3} + \underset{(26\%)}{n\text{-}ROC_6F_4CH{=}CHCOCH_3}\quad .$$

The condensation of pentafluorobenzaldehyde with acetaldehyde was achieved only in an anhydrous medium in the presence of piperidine and the formation of the aldol (II) was detected[97]:

$$C_6F_5CHO \xrightarrow[\text{piperidine, }35°]{CH_3CHO} \underset{OH\ (II)}{C_6F_5CHCH_2CHO} \xrightarrow{I_2} C_6F_5CH{=}CHCHO\quad (47\%).$$

The increased stability of the aldol addition products, obtained from pentafluorobenzaldehyde, is in all probability due to the electron-accepting influence of the pentafluorophenyl group, which hinders dehydration by increasing the amount of double bond character of the C=O linkage and strengthening it[16,97]. The formation of nitroalcohols instead of nitro-olefins from pentafluorobenzaldehyde and nitroalkanes when the reaction is carried out in aqueous alcoholic alkali at 0 °C can be explained similarly[34,99,100]. More severe reaction conditions are essential for the synthesis of nitro-olefins[23]:

$$C_6F_5CHO \xrightarrow[MeOH—H_2O,\ 0°]{CH_3NO_2,\ NaOH} \underset{OH}{C_6F_5CHCH_2NO_2}\quad (78\%)\quad ;$$

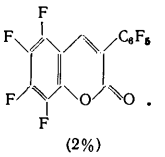


Pentafluorobenzaldehyde has been successfully made to undergo the Perkin reaction[16]:

$$C_6F_5CHO \xrightarrow[130^\circ]{(CH_3CO)_2O,\ CH_3CO_2K} C_6F_5CH{=}CHCO_2H \quad (36\%) \ .$$

The interaction with 2,3,4,5,6-pentafluorophenylacetic acid gives rise to decafluoro-α-phenylcinnamic acid with an admixture of 3-pentafluorophenyl-5,6,7,8-tetrafluorocoumarin, which is apparently a product of the subsequent reaction of the latter[101]:

$$C_6F_5CHO + C_6F_5CH_2CO_2H \xrightarrow[Et_3N,\ b.p.]{(CH_3CO)_2O} C_6F_5CH{=}C(C_6F_5)CO_2H + \underset{(64\%)}{}$$



(2%)

The condensation of polyfluorobenzaldehydes with thiocyanogen[18] and hippuric acid[102–104] has been described. A complex mixture of products has been obtained from pentafluorobenzaldehyde and 2,3,4,5,6-pentafluorophenylacetonitrile in dimethoxyethane in the presence of KF.[105]

The reaction of pentafluorobenzaldehyde with acetophenone in aqueous alcoholic alkali leads to the formation of 2,3,4,5,6-pentafluorobenzylideneacetophenone[27,97]. Pentafluoroacetophenone can serve as the methylene component; the concentration of alkali should not exceed 1.5% to avoid the subsequent haloform decomposition of decafluorobenzylideneacetophenone into pentafluorobenzene and pentafluorocinnamic acid:

$$C_6F_5CHO + CH_3COAr \xrightarrow[\text{aq. alcohol}]{NaOH} C_6F_5CH{=}CHCOAr \ ;$$
$$Ar = Ph \text{ or } C_6F_5 \ .$$

The condensation of pentafluoroacetophenone with aromatic aldehydes can proceed in the presence of a strong protic acid, but in this case it is accompanied by the interaction of the resulting benzylideneacetophenones with the initial ketone, which leads to the formation of pentafluorophenylpyrylium salts[106].

The use of pentafluoroacetophenone as the methylene component in condensation reactions with aromatic and aliphatic acid esters has been described[28,107,108].

On the basis of general ideas concerning the mechanisms of the reactions of carbonyl compounds with C–H acids[109], presumably the enolic form of pentafluoroacetophenone, which can be formed under the influence of both a base and an acid§, can serve as an intermediate in the reactions of this compound described above regardless of the medium. The ambident behaviour of the aromatic fluorine atom of the enolate pentafluoroacetophenone anion, obtained by the reaction of sodium hydride in polar aprotic solvents, has been demonstrated[111] in a nucleophilic substitution reaction:

$$C_6F_5COCH_3 + C_6F_5CF_3 \xrightarrow[\text{diglyme}]{NaH} \underset{(26\%)}{p\text{-}CF_3C_6F_4CH_2COC_6F_5} + \underset{(25\%)}{p\text{-}CF_3C_6F_4OC(C_6F_5){=}CH_2} \ .$$

The enol of pentafluoroacetophenone is evidently an intermediate in its bromination to α-bromopentafluoroacetophenone[34,38,112]. By virtue of the strong electron-accepting influence of the pentafluorobenzoyl group, the bromine atom in the latter assumes to a large extent the character of a positively charged halogen atom and is readily substituted by hydrogen on treatment with dilute aqueous alkali or sodium iodide in alcohol[112]. This is also the cause of the different behaviour, compared with its non-fluorinated analogue, of α-bromopentafluoroacetophenone in reactions with sodioacetoacetic ester in an ethereal medium[112] and also with solutions of sodium methoxide or potassium fluoride in methanol[113].

(b) *Reactions with organometallic compounds.* Organomagnesium synthesis using carbonyl compounds plays an extremely important role in the chemistry of aromatic polyfluoro-compounds. The reactions of polyfluorophenylmagnesium halides with non-fluorinated carbonyl compounds are very widely used[1,114]. On the other hand, very little is known about the interaction of aromatic polyfluoro-substituted carbonyl compounds with Grignard reagents.

Pentafluorobenzaldehyde reacts with organomagnesium compounds in the usual way with formation of secondary alcohols. Both alkyl- and arylmagnesium halides, including derivatives of halogenopolyfluorobenzenes, can be introduced into the reaction. The reaction of 4-methoxytetrafluorobenzaldehyde with 2,3,4,5-tetrafluorophenylmagnesium bromide has also been described[45]:

$$C_6F_5CHO \xrightarrow[\text{ether}]{RMgHal} C_6F_5CH(OH)R \qquad R{=}CH_2Ph^{64},\ Ph^{68},\ C_6F_5^{16},$$
$$p\text{-}XC_6F_4^{39,44},\ \text{or } 2,3,4,5\text{-}F_4C_6H^{41} \ .$$

The interaction of aromatic polyfluoroketones with organomagnesium compounds is more complex and more ambiguous. The type of reaction depends on the structure of the ketone and the Grignard reagent. Thus tris(pentafluorophenyl)-methanol has been obtained from decafluorobenzophenone and pentafluorophenylmagnesium bromide in tetrahydrofuran (THF).[115] On the other hand, phenylmagnesium bromide reacts with polyfluorobenzophenone in two ways: via the carbonyl group with formation of a tertiary alcohol (and predominantly), via substitution of the *o*-fluorine atom by the phenyl group[116,117]. Pentafluorophenyl(diphenyl)methanol and 3,4,5,6-tetrafluoro-2-phenylbenzophenone have been obtained from pentafluorobenzophenone under these conditions. In the case of decafluorobenzophenone more than 70% of F^- is split off and a complex mixture of products is formed whose infrared spectrum contains C=O and OH absorption bands and from which 2,2-diphenyloctafluorobenzophenones was isolated[117]:

$$C_6F_5COPh \xrightarrow[\text{ether, } 20^\circ]{PhMgBr} \underset{(27\%)}{Ph_2(C_6F_5)COH} + PhCO\text{–}C_6F_3Ph\text{–}F \ ;$$

(52%)

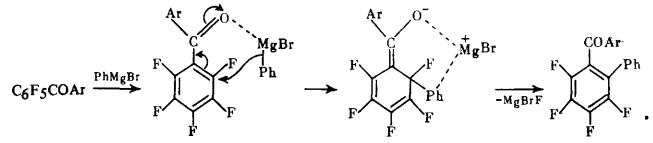
$$C_6F_5COC_6F_5 \xrightarrow[\text{ether, } 20^\circ]{PhMgBr} F\text{–}C_6F_2Ph\text{–}CO\text{–}C_6F_2Ph\text{–}F \quad (25\%) \ .$$

Pentafluoroacetophenone reacts with phenylmagnesium bromide without elimination of F^- and with formation of 1-pentafluorophenyl-1-phenylethanol, while octafluoroacetophenone gives rise to a complex mixture of products[117].

The reaction involving the substitution of a *o*-fluorine atom in polyfluorobenzophenones by the phenyl residue is caused, in all probability, by two factors: the reduced reactivity of their carbonyl group with respect to phenylmagnesium bromide owing to the presence of two (or four) o-fluorine atoms and also by the extremely high nucleophilic mobility of the latter. The specific *o*-directing effect in the process indicates the formation in the transition state of a type (III) cyclic complex with participation of the C=O group of the

§ The anomalous course of the reaction of pentafluoroacetophenone with the Vilsmeier reagent is apparently due to the influence of the *o*-fluorine atoms[110].

ketone and a PhMgBr molecule[116], which is promoted when weakly polar ethyl ether is used as the solvent:



(III)

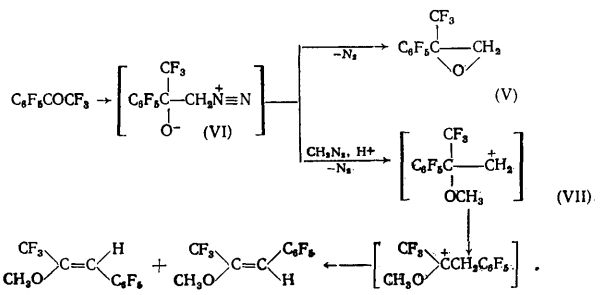
Methylmagnesium iodide, whose reactions via the carbonyl group are less sensitive to steric hindrance[118], reacts with polyfluorobenzophenones and also with octafluoroacetophenone mainly via the carbonyl group with formation of tertiary alcohols[117,119]. On the other hand, the reaction of pentafluoroacetophenone with methylmagnesium iodide is complicated by the aldol condensation. The diol (IV) isolated is a product of the interaction of the intermediate aldol with the reagent:

$$C_6F_5COMe \xrightarrow[\text{ether, } 20^\circ]{MeMgI} \underset{\substack{|\\OH}}{C_6F_5CMe_2} + \underset{\substack{|\\OH}}{C_6F_5(Me)CCH_2}\underset{\substack{|\\OH}}{C}(Me)C_6F_5$$

(32%) (IV)

The interaction of aromatic polyfluoro-substituted carbonyl compounds with organolithium compounds has been little investigated. It has only been shown that aromatic polyfluoroketones react with pentafluorophenyl-lithium via the carbonyl group with formation of tertiary alcohols[120,122]. Presumably their interaction with other organolithium compounds is complicated by the reaction involving the substitution of fluorine atoms.

(c) *Reactions with diazomethane.* Acetophenone reacts with diazomethane at an appreciable rate only in the presence of an acid catalyst[123]. Pentafluoroacetophenone also remains unchanged when the reaction is carried out in ether at room temperature without added catalyst[124]. Like aliphatic polyfluoroketones[125], octafluoroacetophenone reacts readily with diazomethane in an ethereal solution at 0 °C, being wholly converted into a mixture of substances whose main component is 1-pentafluorophenyl-1-trifluoromethylepoxyethane (V).[124] Furthermore, the geometrical isomers of 1-methoxy-2-pentafluorophenyl-1-trifluoromethylethylene have been isolated from the mixture. They are not products of the conversion of the epoxide (V), since it has been established that the latter is resistant to the action of diazomethane at room temperature. Their formation can be represented by the following scheme, which includes stages where the intermediate species (VI) is methylated with subsequent rearrangement of the carbonium ion (VII) via the migration of the C_6F_5 group to a neighbouring electron-unsaturated carbon atom:



(V) (VI) (VII)

The possibility of such migration has been confirmed in relation to the acid-catalysed conversion of decafluorodiphenylacetaldehyde into decafluorodeoxybenzoin[33].

5. Reactions with Phosphorus Compounds

Like other aromatic aldehydes containing electron-accepting substituents[126], pentafluorobenzaldehyde readily reacts with tris(dimethylamino)phosphine to give a mixture of diastereoisomeric oxides of decafluorostilbene[33]:

$$2C_6F_5CHO + (Me_2N)_3P \rightarrow C_6F_5CH{-}CHC_6F_5 + (Me_2N)_3P{=}O$$

Triphenylphosphine imine causes the haloform decomposition of octafluoroacetophenone in ether at room temperature[71]:

$$C_6F_5(CF_3)C{=}O \xrightarrow[\text{ether, } 20^\circ]{Ph_3P{=}NH} C_6F_5H + CF_3CON{=}PPh_3$$

A similar reaction has been observed[127] in an attempt to explain the imine of nitroperfluoroacetone. The interaction of octafluoroacetophenone and also 4-anilineheptafluoroacetophenone with triphenylphosphine *N*-phenylimine, which is less nucleophilic than $Ph_3{=}NH$, led to the formation of their anils[71]:

$$Ar_F(CF_3)C{=}O \xrightarrow[\text{ether}]{Ph_3P{=}NPh} Ar_F(CF_3)C{=}NPh \quad (58\text{—}83\%)$$

$Ar_F = C_6F_5$ or *p*-$PhNHC_6F_4$.

Pentafluoroacetophenone and pentafluorobenzophenone do not react with triphenylphosphine *N*-phenylimine on refluxing in ether. Decafluorobenzophenone reacts with the latter compound to form a very complex mixture of products from which *p*-anilinononafluorobenzophenone was isolated[71] in a low yield. The ability of triphenylphosphine *N*-phenylimine to substitute fluorine via a nucleophilic mechanism had been pointed out earlier[128].

Pentafluorobenzaldehyde reacts with pentafluorophenyl- and pentafluorobenzoylmethylenetriphenylphosphoranes, the corresponding products of the reaction via the carbonyl group being formed[129,130]:

$$C_6F_5CHO \xrightarrow{RCH{=}PPh_3} C_6F_5CH{=}CHR \quad (32\text{—}50\%)$$

$R = C_6F_5$ or C_6F_5CO.

The attempt to carry out the Wittig reaction between aromatic polyfluoroketones and methylenetriphenylphosphorane led to their haloform decomposition[71]. Phosphorus pentachloride reacts with pentafluorobenzaldehyde and octafluoroacetophenone to form the corresponding dichloro-derivatives:

$$C_6F_5(R)C{=}O \xrightarrow[100^\circ]{PCl_5} C_6F_5(R)CCl_2$$

R=H, yield 100%[16];

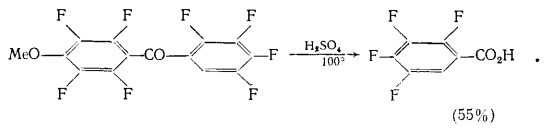
$R = CF_3$, yield 87%[38].

The resistance of decafluorobenzophenone to the action of PCl_5 under severe conditions has been noted[131].

6. Oxidation Reactions

Only a few examples of the oxidation of polyfluorobenzaldehydes to the corresponding acids are known. Pentafluorobenzaldehyde is oxidised smoothly to pentafluorobenzoic acid in oxygen at 110 °C.[16] The oxidation can be carried out under the influence of potassium or sodium dichromate in sulphuric acid at 100 °C. This method is convenient and can be used in the preparative synthesis of polyfluorobenzoic acid[132] and also for the oxidation of other polyfluorobenzaldehydes[19,69] or their diacetals[69]. It has been shown[45] that *p*-methoxy-2,2',3,3',4,5,5',6-octafluorobenzophenone undergoes oxidative cleavage with formation of 2,3,4,5-tetrafluorobenzoic

acid on heating with concentrated sulphuric acid at 100 °C:



(55%)

7. Reduction Reactions

The reduction reactions of aromatic polyfluoro-substituted carbonyl compounds take place under the usual conditions, but are in many instances complicated by the side processes.

Polyfluorobenzaldehydes are reduced to the corresponding alcohols by refluxing with Raney nickel in alcohol[64] and with lithium tetrahydroaluminate in ether at 20 °C.[16,22] Decafluorodiphenylmethanol has been obtained in a low yield by the reaction of decafluorobenzophenone with $LiAlH_4$.[131] When this method of reduction is used for aromatic polyfluoro-substituted carbonyl compounds, one should bear in mind that the reaction may be accompanied by the substitution of the *o*-fluorine atom by hydrogen[42].

The reduction of decafluorobenzophenone with hydriodic acid in the presence of red phosphorus at 170–200 °C yielded bis(pentafluorophenyl)methane[131]. At the instant of evolution (Zn + acetic acid) hydrogen reduces this ketone to decafluorodiphenylmethanol, while pentafluorobenzophenone is reduced to the corresponding pinacol[40]. The reduction of pentafluorobenzaldehyde by metallic zinc in the presence of hydrochloric acid in alcohol did not lead to the formation of the expected decafluorohydrobenzoin, the corresponding acetal of the initial aldehyde being produced instead[86]:

$$3C_6F_5CHO \xrightarrow[\text{alcohol}]{Zn+HCl} C_6F_5CH\begin{matrix}OCHC_6H_5\\ |\\ OCHC_6F_5\end{matrix} \quad (78\%)$$

The photochemical reduction of aromatic ketones is a convenient preparative method for the synthesis of pinacols. The ability of carbonyl compounds to undergo photochemical reduction depends mainly on the nature of the lowest triplet state and its energy. A high efficiency of the intercombination transition is characteristic of decafluorobenzophenone as well as its non-fluorinated analogue and the n,π^*-triplet state has the lowest energy[133]. Its energy in polar and non-polar media is close to that of the corresponding excited state of benzophenone.

The initial stages of the photochemical reduction of decafluorobenzophenone, involving the abstraction of a hydrogen atom from the medium and the formation of a ketyl radical, are analogous to the reactions of benzophenone, but they are much faster owing to the higher polarisation of the charge in the triplet state caused by the inductive effect of the fluorine atoms. The EPR spectrum of the radical obtained by the ultraviolet irradiation of decafluorobenzophenone in alcohol at 80 °C in the cuvette of the EPR spectrometer has been described[134] and agrees fully with the calculated spectrum. The addition of sodium methoxide to the irradiated solution enabled the authors[135] to observe the EPR spectrum of the corresponding radical-anion. Unsuccessful attempts to obtain the latter had been reported earlier[136,137].

The ketyl radicals generated by irradiating decafluorobenzophenone in cyclohexane undergo recombination and radical–radical aromatic substitution reactions to give a tertiary alcohol and cyclohexylnonafluorobenzophenones[133]:

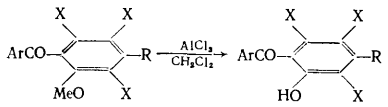
$$(C_6F_5)_2C{=}O \xrightarrow{h\nu} (C_6F_5)_2\dot{C}{-}\dot{O} \xrightarrow{RH} (C_6F_5)_2\dot{C}{-}OH \rightarrow C_6H_{11}\overset{OH}{\overset{|}{C}}(C_6H_5)_2 +$$
$$+ C_6F_5COC_6F_4C_6H_{11}\text{-}n + C_6F_5COC_6F_4C_6H_{11}\text{-}o \quad .$$

In contrast to its non-fluorinated analogue, decafluorobenzophenone does not give rise to perfluoropinacol (VIII) on irradiation in a hydrocarbon medium or in isopropyl alcohol even in the presence of reducing agents[40,133,138–140]. Evidently the dimerisation of ketyl radicals is difficult owing to the repulsion of the C_{ortho}–F bond dipoles and also owing to the shift of the unpaired electron density to the ring as a result of the electron-accepting influence of the fluorine atoms.

The pinacol (VIII) has been obtained by the photolysis of a solution of decafluorobenzophenone in perfluoromethylcyclohexane containing isopropyl alcohol[141]. It is unstable and decomposes in alcohols with formation of decafluorobenzophenone and decafluorodiphenylmethanol; in ether and hydrocarbons this process is much slower. The pinacols (IX) and (X), obtained by the photochemical reduction of octafluoroacetophenone[142] and pentafluorobenzophenone[40], are stable compounds:

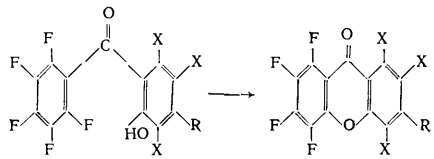
$$C_6F_5COR \xrightarrow{h\nu} C_6H_5(R)\,C\text{—}C(R)\,C_6F_5 \quad ;$$
$$\quad\quad\quad

chloride[36]:



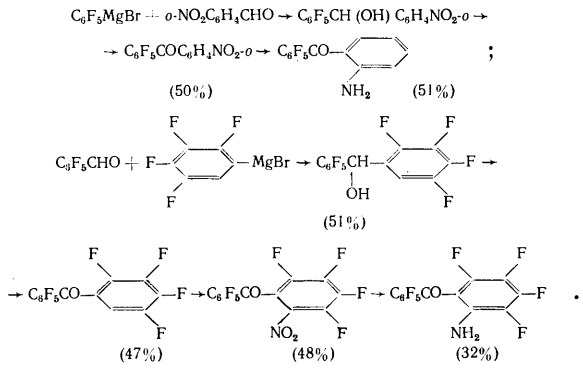
Ar=Ph or C_6F_5, X=H or F; R=H, MeO, or OH.

The presence of an intramolecular hydrogen bond, whose strength is comparable to that in non-fluorinated analogues, has been established in 2-hydroxypolyfluorobenzophenones by infrared and ultraviolet spectroscopy and ^1H NMR.[49] They readily undergo the intramolecular nucleophilic substitution of fluorine, giving rise to polyfluoroxanthones. The much milder, compared with 2-halogeno-2-hydroxybenzophenones[146], conditions in the cyclisation reaction, which partly occurs on simple dissolution in aqueous alkali or in polar solvents such as DMF, are due to the high nucleophilic mobility of the fluorine atoms in aromatic polyfluoroketones. Polyfluoroxanthones have been obtained in high yields on refluxing 2-hydroxypolyfluorobenzophenones with anhydrous KF in acetone or under the influence of ignited potassium carbonate in DMF at room temperature[36]:

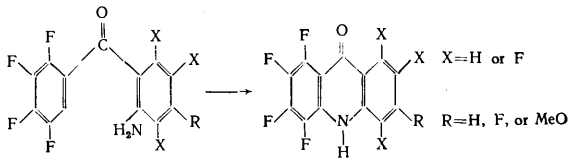


X=H or F; R=H, OH, or MeO.

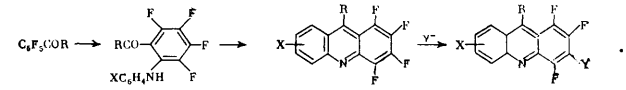
The reactions of aromatic polyfluoroketones with aqueous ammonia and aliphatic amines in organic solvents leads to the preferential substitution of the *p*-fluorine atom[48,77] and cannot therefore be used as a method for the synthesis of *o*-aminoketones. They were synthesised by the reduction of the corresponding nitro-compounds, which were obtained in their turn from aromatic carbonyl compounds and polyfluorophenylmagnesium bromides in accordance with the schemes presented below[41,43,45]:



2-Aminopolyfluorobenzophenones have been converted into polyfluoroacridones by electrolytic oxidation or by heating with KF in anhydrous DMF:[41,45]:



The above methods for the synthesis of polyfluoroacridine derivatives can be of no preparative value in view of the large number of their stages and their limited applicability. A more promising approach has been demonstrated in other studies[80,81,147,148]. It includes as the first stage the nucleophilic substitution of the *o*-fluorine atom in aromatic polyfluoro-substituted carbonyl compounds by an arylamino-group and makes it possible to obtain a large set of polyfluoroacridines from readily available aromatic polyfluoro-compounds:



Thus the chemical properties of aromatic polyfluoro-substituted aldehydes and ketones are to a large extent different from those of their non-fluorinated analogues. The presence in their molecules of several electron-accepting fluorine atoms not only alters their reactivity in relation to nucleophiles but also greatly complicates the reactions owing to the ease of the haloform decomposition with ejection of the relatively stable polyfluorophenyl anion, and also because of the possibility of the nucleophilic substitution of one or several fluorine atoms. This wide variety of chemical reactions of aromatic polyfluoro-substituted carbonyl compounds and their relative availability are responsible for the continued interest in these compounds by investigators and lead to wide possibilities for synthesis.

REFERENCES

1. N.N.Vorzhtsov, Jr., Zhur.Vses.Khim.Obshch.im. Mendeleeva, **15**, 52 (1970).
2. G.G.Yakobson and V.M.Vlasov, Synthesis, 652 (1976).
3. L.S.Kobrina, Fluorine Chem.Rev., **7**, 1 (1974).
4. V.E.Platonov and G.G.Yakobson, Synthesis, 374 (1976).
5. R.Bolton and G.H.Williams, "Advances in Free-Radical Chemistry" (Edited by G.H.Williams), Elek Science, London, 1975, Vol.5, p.1.
6. L.S.Kobrina, Uspekhi Khim., **46**, 660 (1977) [Russ. Chem.Rev., No.4 (1977)].
7. V.M.Vlasov and G.G.Yakobson, Uspekhi Khim., **43**, 1642 (1974) [Russ.Chem.Rev., No.9 (1974)].
8. R.Filler, Fluorine Chem.Rev., **8**, 1 (1978).
9. P.H.Gore, "Friedel-Crafts and Related Reactions", (Edited by G.A.Olah), Interscience Publ., New York–London–Sydney, 1964, Vol.3, Part 1, p.1.
10. S.A.Anichkina, V.A.Barkhash, and N.N.Vorozhtsov, Jr., Zhur.Obshch.Khim., **38**, 2493 (1968).
11. V.A.Koptyug, B.I.Mokrousov, and A.N.Rezvukhin, Zhur.Org.Khim., **4**, 662 (1968).
12. G.A.Olah and S.Kobayashi, J.Amer.Chem.Soc., **93**, 6964 (1971).
13. G.G.Furin and G.G.Yakobson, Izv.Sibir.Otd.Akad. Nauk SSSR, Ser.Khim.Nauk, No.2, Issue 1, 78 (1974).
14. Yu.Pozdnyakovich and V.D.Steingarts, J.Fluorine Chem., **4**, 317 (1974).
15. G.G.Furin, L.N.Shchegoleva, and G.G.Yakobson, Zhur.Org.Khim., **11**, 1290 (1975).
16. A.K.Barbour, M.W.Buxton, P.L.Coe, R.Stephens, and J.C.Tatlow, J.Chem.Soc., 808 (1961).
17. N.N.Vorozhtsov, Jr., V.A.Barkhash, N.G.Ivanova, S.A.Anichkina, and O.I.Andreevskaya, Dokl.Akad. Nauk SSSR, **159**, 125 (1964).
18. M.D.Castle, R.G.Plevey, and J.C.Tatlow, J.Chem.Soc. (C), 1225 (1968).
19. L.J.Belf, M.W.Buxton, and J.F.Tilney-Basset, Tetrahedron, **23**, 4719 (1967).

20. E.Nield, R.Stephens, and J.C.Tatlow, J.Chem.Soc., 166 (1959).
21. P.L.Coe, R.Stephens, and J.C.Tatlow, J.Chem.Soc., 3227 (1962).
22. R.Filler and E.W.Choe, J.Amer.Chem.Soc., **91**, 1862 (1969).
23. W.L.White and R.Filler, J.Chem.Soc.(C), 2062 (1971).
24. A.E.Jukes and H.Gilman, J.Organomet.Chem., **17**, 145 (1969).
25. A.F.Webb and H.Gilman, J.Organomet.Chem., 20, 281 (1969).
26. A.E.Jukes, S.S.Dua, and H.Gilman, J.Organomet. Chem., **21**, 241 (1970).
27. R.Filler, V.D.Beaucaire, and H.H.Kang, J.Org.Chem., **40**, 935 (1975).
28. R.Filler, J.S.Rao, A.Biezais, F.N.Miller, and V.D.Beaucaire, J.Org.Chem., **35**, 930 (1970).
29. M.Schmeisser and M.Weidenbruch, Chem.Ber., **100**, 2306 (1967).
30. R.D.Chambers and J.A.Cunningham, J.Chem.Soc.(C), 2185 (1967).
31. P.L.Coe and A.Whittingham, J.Chem.Soc., Perkins Trans.I, 917 (1974).
32. R.D.Chambers and D.J.Spring, J.Chem.Soc.(C), 2394 (1968).
33. R.Filler and Y.S.Rao, J.Org.Chem., **39**, 3421 (1974).
34. N.B.Chapman, K.Clarke, R.M.Pinder, and S.N.Sawhney, J.Chem.Soc.(C), 293 (1967).
35. J.M.Birchall, R.N.Haszeldine, and M.E.Jones, J.Chem. Soc.(C), 1343 (1971).
36. E.G.Lubenets, T.N.Gerasimova, and E.P.Fokin, Zhur. Org.Khim., **7**, 805 (1971).
37. G.E.Ditchfield and A.E.Pedler, J.Fluorine Chem., **10**, 447 (1977).
38. P.L.Coe, R.G.Plevey, and J.C.Tatlow, J.Chem.Soc. (C), 597 (1966).
39. T.N.Gerasimova, T.N.Vasilevskaya, V.A.Barkhash, and N.N.Vorozhtsov, Jr., Izv.Akad.Nauk SSSR, Ser Khim., 450 (1967).
40. R.Filler and H.H.Kang, J.Org.Chem., **40**, 1173 (1975).
41. C.M.Jenkins, A.E.Pedler, and J.C.Tatlow, Tetrahedron, **27**, 2557 (1971).
42. T.N.Gerasimova, N.V.Semikolenova, and E.P.Fokin, Zhur.Org.Khim., **14**, 100 (1978).
43. P.L.Coe, A.E.Jukes, and J.C.Tatlow, J.Chem.Soc.(C), 2020 (1966).
44. T.N.Vasilevskaya, A.G.Badashkeeva, T.N.Gerasimova, V.A.Barkhash, and N.N.Vorozhtsov, Jr., Zhur.Org. Khim., **6**, 126 (1970).
45. D.M.Owen, A.E.Pedler, and J.C.Tatlow, J.Chem.Soc., Perkin Trans.I, 1380 (1975).
46. J.P.Collman and N.W.Hoffman, J.Amer.Chem.Soc., **95**, 2689 (1973).
47. S.A.Anichkina, G.S.Khramtsova, V.A.Barkhash, and N.N.Vorozhtsov, Jr., Zhur.Obshch.Khim., **39**, 1766 (1969).
48. T.N.Gerasimova, E.G.Lokshina, V.A.Barkhash, and N.N.Vorozhtsov, Jr., Zhur.Obshch.Khim., **37**, 1300 (1967).
49. E.G.Lubenets, Candidate's Thesis, Institute of General Chemistry, Siberian Division of the USSR Academy of Sciences, Novosibirsk, 1971.
50. T.N.Gerasimova, E.G.Lubenets, and V.A.Barkhash, Zhur.Org.Khim., **8**, 430 (1972).
51. V.V.Brovko, V.M.Vlasov, L.I.Kann, T.D.Petrova, V.A.Sokolenko, and G.G.Yakobson, Zhur.Org.Khim., **11**, 1042 (1975).
52. P.Sartori and M.Weidenbruch, Angew.Chem., **77**, 1076 (1965).
53. P.Sartori and M.Weidenbruch, Chem.Ber., **100**, 3016 (1967).
54. M.Schmeisser, P.Sartori, and M.Weidenbruch, German P.1 242 208 (1965); Chem.Abs., **67**, 73 364 (1967).
55. V.N.Odinokov, G.G.Yakobson, and N.N.Vorozhtsov, Jr., Zhur.Obshch.Khim., **37**, 176 (1967).
56. G.G.Yakobson, V.E.Platonov, and L.I.Kann, USSR P.413 772 (1972); Byul.Izobret., No.52, 167 (1975).
57. W.A.Sheppard, J.Amer.Chem.Soc., **92**, 5419 (1970).
58. W.A.Sheppard and C.M.Sharts, "Organic Fluorine Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1972, p.381.
59. D.B.Farmer and S.Walker, Trans.Faraday Soc., **63**, 966 (1967).
60. M.J.Aroney, G.Cleaver, R.K.Pierens, and R.J.W.Le Fèvre, J.Chem.Soc., Perkin Trans.II, 1854 (1976).
61. I.K.Korobeinicheva, A.K.Petrov, and V.A.Koptyug, "Atlas Spektrov Aromaticheskikh i Geterotsiklicheskikh Soedinenii" (Atlas of the Spectra of Aromatic and Heterocyclic Compounds), Izd.Nauka, Novosibirsk, 1967, No.1.
62. R.D.Chambers and D.J.Spring, Tetrahedron, **25**, 565 (1969).
63. G.A.Olah and J.K.Mo, J.Org.Chem., **38**, 2682 (1973).
64. E.V.Aroskar, P.J.N.Brown, R.G.Plevey, and R.Stephens, J.Chem.Soc.(C), 1569 (1968).
65. N.P.Buu-Hoi and G.Saint-Ruf, Bull.Soc.chim.France, 661 (1968).
66. L.J.Belf, M.W.Buxton, and G.Fuller, J.Chem.Soc., 3373 (1965).
67. V.P.Petrov and V.A.Koptyug, Reakts.Sposobn.Org. Soed., **3**, No.1 (7), 135 (1966).
68. T.N.Gerasimova, N.V.Semikolenova, and E.P.Fokin, Izv.Sibir.Otd.Akad.Nauk SSSR, Ser.Khim.Nauk, No.4, Issue 2, 142 (1977).
69. V.I.Vysochin, V.A.Barkhash, and N.N.Vorozhtsov, Jr., Zhur.Obshch.Khim., **39**, 1607 (1969).
70. A.T.Prudchenko and V.A.Barkhash, Zhur.Org.Khim., **6**, 727 (1970).
71. T.N.Vasilevskaya, Candidate's Thesis, Institute of General Chemistry, Siberian Division of the USSR Academy of Sciences, Novosibirsk, 1971.
72. N.P.Gambaryan, E.M.Rokhlin, Yu.V.Zeifman, Chen Cheng-Yun, and I.L.Knunyants, Angew.Chem., **78**, 1008 (1966).
73. C.G.Krespan and W.J.Middleton, Fluorine Chem.Revs., **1**, 145 (1967).
74. G.S.Shchegoleva, Candidate's Thesis, Institute of General Chemistry, Siberian Division of the USSR Academy of Sciences, Novosibirsk, 1971.
75. G.S.Shchegoleva and V.A.Barkhash, Izv.Sibir.Otd. Akad.Nauk SSSR, Ser.Khim.Nauk, No.14, Issue 6, 123 (1971).
76. R.Filler and A.E.Fiebig, Chem.Comm., 606 (1968).
77. L.S.Kobrina, G.G.Furin, and G.G.Yakobson, Zhur. Org.Khim., **6**, 512 (1970).
78. P.P.Rodionov and S.M.Shein, Izv.Sibir.Otd.Akad.Nauk SSSR, Ser.Khim.Nauk, No.7, Issue 3, 86 (1971).
79. S.M.Shein and P.P.Rodionov, Kinetika i Kataliz, **14**, 1128 (1973).
80. T.N.Vasilevskaya, I.I.Baturina, M.I.Kollegova, T.N.Gerasimova, and V.A.Barkhash, Zhur.Org.Khim., **7**, 1230 (1971).
81. T.N.Gerasimova, L.L.Gelumbovskaya, I.I.Baturina, and E.P.Fokin, Izv.Sibir.Otd.Akad.Nauk SSSR, Ser.Khim. Nauk, No.4, Issue 2, 88 (1973).
82. O.P.Sheremet, P.P.Rodionov, and S.M.Shein, Izv. Sibir.Otd.Akad.Nauk SSSR, Ser.Khim., No.14, Issue 6, 71 (1975).

83. R.M.Acheson, "Acridines", Interscience Publ., New York, 1956, p.39.
84. T.V.Fomenko, T.N.Gerasimova, and E.P.Fokin, Zhur. Vses.Khim.Obshch.im.Mendeleeva, **24**, 92 (1979).
85. H.P.Braendlin and E.T.McBee, "Advances in Fluorine Chemistry" (Translated into Russian), Izd.Khimiya, Leningrad, 1970, Vols.3–4, p.231.
86. N.N.Vorozhtsov, Jr., V.A.Barkhash, and L.M.Bova, Izv.Akad.Nauk SSSR, Ser.Khim., 362 (1966).
87. D.G.Davies, M.Derenberg, and P.Hodge, J.Chem.Soc. (C), 455 (1971).
88. K.J.Klabunde and D.J.Burton, J.Amer.Chem.Soc., **94**, 5985 (1973).
89. E.G.Lubenets, T.N.Gerasimova, V.V.Furov, and V.A.Barkhash, Zhur.Org.Khim., **6**, 365 (1970).
90. L.Field and B.J.Sweetman, J.Org.Chem., **34**, 1799 (1969).
91. R.H.Cragg and J.P.N.Husband, Inorg.Nuclear Chem. Letters, **6**, 773 (1970).
92. R.H.Mobbs, J.Fluorine Chem., **1**, 361 (1972).
93. B.G.Oksenenko, V.A.Sokolenko, V.M.Vlasov, and G.G.Yakobson, Izv.Sibir.Otd.Akad.Nauk SSSR, Ser. Khim.Nauk, No.2, Issue 1, 102 (1970).
94. J.C.Tatlow and P.L.Coe, B.P.1 102 693 (1964); Chem. Abs., **69**, 43 602 (1968).
95. E.P.Fokin, T.N.Gerasimova, T.N.Vasilevskaya, I.I.Baturina, and K.I.Matoshina, Izv.Sibir.Otd.Akad. Nauk SSSR, Ser.Khim.Nauk, No.9, Issue 4, 135 (1971).
96. T.Mill, J.O.Rodin, R.M.Silverstein, and C.Woolf, J. Org.Chem., **29**, 3715 (1964).
97. N.G.Ivanova, V.A.Barkhash, and N.N.Vorozhtsov, Zhur.Obshch.Khim., **39**, 1347 (1969).
98. B.Unterhalt and U.Pindur, Arch.Pharm., **306**, 589 (1973); Chem.Abs., **79**, 136 717 (1973).
99. V.P.Petrov, V.A.Barkhash, G.S.Shchegoleva, T.D.Petrova, T.P.Savchenko, and G.G.Yakobson, Dokl.Akad.Nauk SSSR, **178**, 864 (1968).
100. V.V.Petrov and V.A.Barkhash, Zhur.Obshch.Khim., **39**, 1615 (1969).
101. V.P.Molosnova, V.A.Barkhash, and N.N.Vorozhtsov, Jr., Zhur.Obshch.Khim., **39**, 1774 (1969).
102. G.V.Shishkin and V.P.Mamaev, Zhur.Obshch.Khim., **36**, 660 (1966).
103. A.T.Prudchenko, Izv.Sibir.Otd.Akad.Nauk SSSR, Ser. Khim.Nauk, No.14, Issue 6, 95 (1970).
104. R.Filler, N.R.Ayyagar, W.Gustowski, and H.H.Kang, J.Org.Chem., **34**, 534 (1969).
105. V.M.Vlasov and G.G.Yakobson, Zhur.Obshch.Khim., **39**, 2071 (1969).
106. V.M.Vlasov, Izv.Sibir.Otd.Nauk SSSR, Ser.Khim.Nauk, No.4, Issue 2, 96 (1971).
107. J.F.Engel and C.C.Chappelow, J.Chem.Eng.Data, **16**, 381 (1971).
108. C.C.Chappelow and J.F.Engel, US.P.3 742 062 (1970); Chem.Abs., **79**, 78 395 (1973).
109. J.W.Baker, "Electronic Theories of Organic Chemistry: An Introductory Treatment" (Translated into Russian), Izd.Mir, Moscow, 1977, p.327.
110. V.M.Vlasov and G.G.Yakobson, Izv.Akad.Nauk SSSR, Ser.Khim., 893 (1969).
111. O.V.Zakharova, V.M.Vlasov, and G.G.Yakobson, Izv. Akad.Nauk SSSR, Ser.Khim., 1670 (1974).
112. V.A.Barkhash, O.I.Andreevskaya, and N.N.Vorozhtsov, Jr., Dokl.Akad.Nauk SSSR, **166**, 1343 (1966).
113. O.I.Andreevskaya, V.A.Barkhash, I.K.Korobeinicheva, E.D.Krivousova, V.A.Sokolenko, G.G.Yakobson, and L.M.Yan'kova, Zhur.Org.Khim., **6**, 711 (1970).
114. S.C.Cohen and A.G.Massey, "Advances in Fluorine Chemistry" (Edited by J.C.Tatlow, R.D.Peacock, and H.H.Hyman), London, 1970, Vol.6, p.83.
115. W.F.Beckert, "The IIIrd International Symposium on Fluorine Chemistry, Abstracts of Papers, Munich, 1965", p.200.
116. T.N.Gerasimova, I.I.Baturina, T.V.Fomenko, V.S.Chertok, V.F.Kollegov, and E.P.Fokin, Zhur.Org. Khim., **10**, 2166 (1974).
117. G.N.Gerasimova, T.V.Fomenko, and E.P.Fokin, Zhur. Org.Khim., **13**, 1562 (1977).
118. G.N.Gerasimova, T.V.Fomenko, and E.P.Fokin, Izv. Sibir.Otd.Akad.Nauk SSSR, Ser.Khim.Nauk, No.12, Issue 5, 100 (1975).
119. S.A.Pozdnyakovich, Candidate's Thesis, Institute of General Chemistry, Siberian Division of the USSR Academy of Sciences, Novosibirsk, 1971.
120. N.N.Vorozhtsov, Jr., V.A.Barkhash, T.N.Gerasimova, E.G.Lokshina, and N.G.Ivanova, Zhur.Obshch.Khim., **37**, 1293 (1967).
121. T.N.Gerasimova, A.G.Badashkeeva, E.G.Lubenets, V.A.Barkhash, and N.N.Vorozhtsov, Jr., Zhur.Org. Khim., **5**, 2199 (1969).
122. R.Filler, Chen-Shen Wang, M.A.McKinney, and F.N.Miller, J.Amer.Chem.Soc., **89**, 1026 (1967).
123. H.O.House, E.J.Grubbs, and W.F.Gannon, J.Amer. Chem.Soc., **82**, 4099 (1960).
124. T.N.Vasilevskaya, T.N.Gerasimova, L.A.Kazbaeva, and V.A.Barkhash, Zhur.Org.Khim., **6**, 1645 (1970).
125. H.E.Simmons and D.W.Wiley, J.Amer.Chem.Soc., **82**, 2288 (1960).
126. V.Mark, J.Amer.Chem.Soc., **85**, 1884 (1963).
127. Yu.V.Zeifman, N.P.Gambaryan, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 450 (1965).
128. N.P.Gambaryan, E.M.Rokhlin, Yu.V.Zeifman, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 749 (1965).
129. V.P.Molosnova, V.I.Vysochin, V.A.Barkhash, and N.N.Vorozhtsov, Jr., Izv.Akad.Nauk SSSR, Ser.Khim., 146 (1969).
130. V.M.Vlasov, Zhur.Vses.Khim.Obshch.im.Mendeleeva, **15**, 476 (1970).
131. N.N.Vorozhtsov, Jr., V.A.Barkhash, and S.A.Anichkina, Dokl.Akad.Nauk SSSR, **166**, 598 (1966).
132. V.M.Vlasov, G.F.Grebenshchikova, A.Ya.L'vova, and G.G.Yakobson, "Sintesy Ftororganicheskikh Soeninenii" (Syntheses of Organofluorine Compounds), Izd.Khimiya, Moscow, 1973, p.168.
133. J.Dedinas and T.H.Regan, J.Phys.Chem., **76**, 3926 (1972).
134. F.P.Sargent and M.G.Bailey, Canad.J.Chem., **76**, 3926 (1972).
135. F.P.Sargent and M.G.Bailey, Canad.J.Chem., **49**, 2350 (1971).
136. J.F.Brown and W.G.Williams, Trans.Faraday Soc., **64**, 298 (1968).
137. S.V.Kulkarni and C.Trapp, J.Amer.Chem.Soc., **92**, 4809 (1970).
138. N.Filipescu, J.P.Pinion, and E.L.Minn, Chem.Comm., 1413 (1970).
139. P.Margaretha, J.Gloor, and K.Schaffner, Chem.Comm., 565 (1974).
140. G.Gauglitz and U.Kolle, J.Photochem., **4**, 309 (1975).
141. J.Dedinas, J.Amer.Chem.Soc., **95**, 7172 (1973).
142. J.S.Chang, J.T.Price, A.J.Tomlinson, and C.J.Willis, Canad.J.Chem., **50**, 512 (1972).
143. D.V.Gendin, O.Ya.Kruglaya, T.I.Vakul'skaya, L.P.Petukhov, and N.S.Vyazankin, Zhur.Obshch.Khim., **47**, 1427 (1977).

144. J.R.Majer, S.-A.M.A.Naman, and J.C.Robb, Trans. Faraday Soc., **65**, 1846 (1969).
145. G.G.Yakobson, T.D.Petrova, and L.S.Kobrina, Fluorine Chem.Rev., **7**, 115 (1974).
146. M.Kulka, J.Amer.Chem.Soc., **76**, 5469 (1954).
147. T.N.Gerasimova, N.V.Semikolenkova, N.A.Orlova, T.V.Fomenko, and E.P.Fokin, Izv.Sibir.Otd.Akad.Nauk SSSR, Ser.Khim.Nauk, No.14, Issue 6, 54 (1975).
148. N.A.Orlova, L.L.Dmitrieva, T.N.Gerasimova, and E.P.Fokin, Izv.Sibir.Otd.Akad.Nauk SSSR, Ser.Khim. Nauk, No.7, Issue 3, 109 (1976).

Novosibirsk Institute of Organic Chemistry, Siberian Division of the USSR Academy of Sciences

Translated from *Uspekhi Khimii*, 49, 1079-1105 (1980) U.D.C. 547.933

The Synthesis of Carbohydrates from Formaldehyde

T.I.Khomenko, M.M.Sakharov, and O.A.Golovina

The problems of the synthesis of carbohydrates from formaldehyde are examined and the catalysts and conditions of the synthesis are described. The kinetics and current ideas concerning the mechanism of this process as well as different versions of its application in the regeneration of food products in manned spacevessels are discussed. The bibliography includes 141 references.

CONTENTS

I. Introduction 570
II. Catalysts and conditions for the condensation of formaldehyde to carbohydrates 571
III. General characteristics of the condensation reaction 571
IV. Current studies on the kinetics and mechanism of the synthesis of carbohydrates 573
V. The possible versions of the condensation of formaldehyde to carbohydrates in life support systems in spacevessels 580

I. INTRODUCTION

The rapid growth of the duration of space flights has given rise to new problems in the field of the construction of life support systems for the crews of space vessels. It is already insufficient merely to eliminate harmful substances from the atmosphere of the cabin in the space vessels and to provide stores of substances ready for consumption—water, oxygen and food. In the flights of manned spaceships and stations not less than 4–5 litres of water[1], approximately 1 kg of oxygen[2], and 1–1.3 kg of food[3] is the daily requirement per member of the crew. These figures show that space flights lasting several months require at least partial regeneration of water and oxygen, so that the starting weight of manned space vessels is not unduly large; for flights lasting more than a year the problem of the regeneration of food products becomes of urgent importance.

There is a possibility of two fundamentally different ways of constructing a life support system in space vessels: on physicochemical and biotechnical bases. Studies in both fields are in the initial stage.

Table 1. The compositions and caloric values of the diet of cosmonauts.

Spacevessel	Content of food products			Moisture, ml	Caloric value, kcal
	proteins, g	fats, g	carbohydrates, g		
Soyuz-3	120.9	118.5	267.1	521.5	2755.0
Soyuz-4, Soyuz-8	110.7	98.2	297.0	672.0	2586.0
Soyuz-9	109.7	100.3	339.2	756.3	2852.0
Soyuz-10, Soyuz-23	126.5	116.7	338.3	697.8	2992.3
Soyuz-19	129.2	135.1	289.5	747.6	2975.7
Salyut-3, Salyut-5	129.2	135.1	289.5	747.6	2975.7

Table 1 presents data[3] concerning the composition and caloric value of the food consumed by cosmonauts in Soviet spaceships and stations. Evidently the fraction of carbohydrates in the cosmonauts' food ration is more than 60% of the entire dry weight of the food, reaching in terms of weight 270–350 g per day. In view of the dominant carbohydrate content in the food, the attention of investigators should be devoted to the search for physicochemical or biotechnical methods of synthesis of carbohydrates from the main final products of the vital activity of the human organism—carbon dioxide and water.

At the present time only one suitable chemical synthesis of carbohydrates from simple molecules is know—the condensation of formaldehyde in aqueous solutions in the presence of a number of organic bases as process catalysts. This procedure was discovered by Butlerov as early as 1861.[4,5]

The synthesis of formaldehyde from CO_2 and H_2O under the conditions of the spaceship could be achieved in the following two ways[2]: by hydrogenating carbon dioxide to methane and by oxidising the latter to formaldehyde:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad ,$$
$$CH_4 + O_2 \rightarrow HCHO + H_2O \quad ,$$

or by hydrogenating carbon dioxide to methanol, the oxidation of which can also yield formaldehyde:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \quad ,$$
$$CH_3OH + {}^1/_2O_2 \rightarrow HCHO + H_2O \quad .$$

The first procedure can be achieved under atmospheric pressure, which is extremely important in relation to the conditions in space vessels. However, it is not so far been possible to overcome a number of significant disadvantages of this method of synthesis of formaldehyde—low selectivity in the oxidation of methane to formaldehyde and low yields of the latter under optimum process conditions. The second method is free from these disadvantages, but the need to use high pressures in order to obtain methanol at the present level of technology precludes its employment in space vessels.

Since the synthesis of formaldehyde by the above methods in space vessels is in principle feasible, the interest in the synthesis of carbohydrates from formaldehyde as an acceptable concluding stage in the conversion of the final products of the vital activity in a manned spaceship to food products is understandable. Hexoses, which are the most valuable carbohydrates as regards food, can be obtained by the condensation of six formaldehyde molecules:

$$6HCHO \rightarrow C_6H_{12}O_6 \quad .$$

However, a significant disadvantage of the synthesis of carbohydrates from formaldehyde, which has still not been overcome, is the low selectivity of this process. Apart from the small fraction of hexoses which can be assimilated by the human organism (D-modifications of glucose, fructose,

galactose, and mannose), the main bulk of the products of the synthesis consists of non-assimilable carbohydrates. This disadvantage of the method is aggravated by the formation of appreciable amounts of branched carbohydrates[6], which, according to some hypotheses, may exhibit a toxic activity when taken with food. Therefore, despite the fact that the synthesis of carbohydrates from formaldehyde takes place under readily realisable conditions—in aqueous solutions at atmospheric pressure and temperatures only a little above room temperature—it is not so far used in practice.

For the synthesis to be carried out in practice, it is necessary to increase greatly its selectivity, which requires detailed information about the kinetics and mechanism of the process. Particular attention has been devoted to these problems in studies during the last decade, in which the classical kinetic methods have been supplemented by an improved chromatographic technique for the analysis of products and by isotopic and spectroscopic methods. The use of a gradient-free reactor made it possible to obtain particularly valuable information about the kinetics of the synthesis. The search for optimum catalysts and conditions for the synthesis of carbohydrates is being vigorously prosecuted.

This review deals with the following problems: catalysts and conditions of the synthesis of carbohydrates from formaldehyde and the kinetics and mechanism of the process. In the concluding section of the review different versions of the application of this process in the regeneration of food products in manned space vessels are discussed.

II. CATALYSTS AND CONDITIONS FOR THE CONDENSATION OF FORMALDEHYDE TO CARBOHYDRATES

As already mentioned, sugars were obtained from formaldehyde for the first time by Butlerov[4,5]. The reaction took place in an aqueous solution at 100 °C using $Ca(OH)_2$, $Ba(OH)_2$, Na_2CO_3, and K_2CO_3 as catalysts. Subsequently a wide range of inorganic compounds were tested for catalytic activity in this process. Thus Loew[7-12] used in 1886 calcium hydroxide with added NaCl, KNO_3, and CH_3COONa as catalyst and observed that among these salts only NaCl has no inhibiting effect. According to Loew's data, sugars are formed when formaldehyde is acted upon by alkaline earth metal carbonates and lead oxide. In subsequent studies DL-fructose, DL-glucose, DL-sorbose, and DL-arabinose were isolated from syrups obtained by Loew's method[13-15].

The influence of calcium, barium, sodium, and iron hydroxides as well as $CaCO_3$ on the condensation of formaldehyde was investigated[16-18] and it was established that calcium hydroxide is the best catalyst. The use of potassium, sodium, and calcium phosphates[19] did not yield a positive result; when $MgSO_4$ was employed, it was possible to obtain a syrup in which fructose, sorbose, and arabinose were identified.

Schmalfuss[20-22] achieved for the first time the condensation of formaldehyde to carbohydrates at a high pressure and temperature (2 atm, 120 °C). MgO, Al_2O_3, CaO, $Ca(OH)_2$, NaOH, and $Al(OH)_3$ were used as catalysts. The carbohydrates were formed in all cases except when Al_2O_3 and $Al(OH)_3$ were used. In the presence of NaOH carbohydrates were formed 2 min after the start of the experiment but then began to decompose very rapidly. In the 1950's[23] a new highly active catalyst (TlOH) was introduced, the synthesis of carbohydrates in its presence being completed after 20 min at 60 °C. The activity of magnesium, calcium, zinc, cadmium, mercury, aluminium, lead, tin, antimony, bismuth, and manganese oxides has been investigated[24,25] in the condensation reaction. It was noted that only magnesium, calcium, and lead oxides exhibit a catalytic activity in the temperature range 75–100 °C.

Thus by the end of the 1960's it was established that the most active catalysts in the condensation of formaldehyde to carbohydrates are fairly strong bases—alkaline earth metal hydroxides and oxides, thallium hydroxide, and lead oxide. In subsequent years it was observed that certain tertiary amines[26], lanthanice hydroxides[27,28] and aluminosilicates[29,30] can function as condensation catalysts.

The catalytic activities of the following tertiary amines have been demonstrated[26]: triethanolamine, dimethylaminoethanol, pyridine, *N*-methylpiperidine, α-picoline, collidine, *N*-methylmorpholine, tetraethylammonium hydroxide, and a mixture consisting of β and γ-picolines. Their activities are appreciably lower than those of alkaline earth metal hydroxides. When the above organic bases are used as catalysts, the synthesis must be carried out at high temperatures (100 °C) and as a rule in the presence of a large excess of the base relative to formaldehyde. The catalytic activities of the organic bases have been confirmed[31]. Berlin and coworkers[27,28] observed a catalytic activity of lanthanide (La, Tb, Ho, Tm, Gd, Dy, Er, Sm, and Yb) hydroxides in the synthesis of carbohydrates at high temperatures (optimum process conditions 110 °C and 1.8 atm).

In contrast to early studies, Gable and Ponnamperuma[29] found that appreciable amounts of carbohydrates are obtained after a boiling solution of formaldehyde has been in contact with Al_2O_3 for 5 h. According to their data, the formation of hexoses in the presence of Al_2O_3 is favoured by the use of low formaldehyde concentrations (10^{-2} M). They also showed[29] that aluminosilicates such as kaolinite and illite are catalytically active in the synthesis of carbohydrates. Appreciable amounts of carbohydrates are formed in their presence after many hours of contact with a boiling solution of formaldehyde. It has been shown[30] that the NaX zeolite exhibits an appreciable catalytic activity in the synthesis of carbohydrates at 95 °C when the pH of the solution is sufficiently high (>10 at the outlet from the flow reactor).

Appreciable formation of carbohydrates has been observed[32] on prolonged refluxing of formaldehyde with a suspension of a carbonate-containing apatite.

III. GENERAL CHARACTERISTICS OF THE CONDENSATION REACTION

In the very earliest studies[8-12] it was already observed that the condensation of formaldehyde to carbohydrates is accompanied by the dismutation reaction

$$2CH_2O + H_2O \rightleftarrows CH_3OH + HCOOH$$

which leads to the formation of formic acid and methanol (the Cannizzaro reaction).

In 1895 Henry[33] identified glyceraldehyde and dihydroxyacetone in the formaldehyde condensation products and suggested that they are intermediates in the formation of hexoses. Neuberg[34] suggested in 1902 that glycolaldehyde is the first condensation product and is formed from formaldehyde at a low rate. According to Neuberg, the reaction is autocatalytic and heavier carbohydrates (starting from C_3) are formed at high rates.

In 1915 Franzen and Hauck[35] isolated salt-like compounds resulting from the combination of formaldehyde and calcium hydroxide and investigated the possibility of their presence as intermediates in the condensation reaction. They suggested

that in dilute solutions the first stage involves the interaction of methylene glycol (the main form of monomeric formaldehyde in aqueous solutions) with calcium hydroxide:

$$CH_2(OH)_2 + Ca(OH)_2 \rightarrow HOCH_2OCaOH + H_2O \quad .$$

In the next stage the interaction of two such molecules leads, in their view, to the formation of glycolaldehyde:

$$2HOCH_2OCaOH \rightarrow HOCH_2CHOHOCaOH + Ca(OH)_2.$$

However, Franzen and Hauck do not present any data in support of their ideas concerning the process mechanism apart from the possible composition of the salt-like products.

Schmalfuss[20-22] used for the first time as the catalyst the product of the condensation of formaldehyde carried out in the presence of MgO and observed its high catalytic activity. He also noted that the rate of condensation increases greatly following the addition of glucose to the reaction mixture. On the basis of these experiments, Schmalfuss arrived at the conclusion, reached previously by Neuberg, that the condensation is autocatalytic. This view was subsequently expressed by Trigerman et al. [36] Orther and Gerisch[37] analysed the composition of the products in the reaction carried out in the presence of lead hydroxide: after hydrogenation and subsequent fractionation of the condensate, it was possible to isolate glycerol, tetritols, pentitols, and hexitols. According to their reaction mechanism, carbohydrates ranging from C_3 to C_6 are formed via the self-condensation of formaldehyde, for example:

$$3CH_2O \rightarrow \text{trioses},$$

$$4CH_2O \rightarrow \text{tetroses, etc.}$$

Kuzin[38-44] continued Schmalfuss's experiments to elucidate the role of organic compounds added to the reaction mixture. He established that the addition of compounds such as polyhydric alcohols, acetone, penta-acetylfructose, and polysaccharides does not affect the rate of condensation when $Ca(OH)_2$ is used as for the catalyst. On the other hand, compounds such as hydroxyoxosuccinic acid, ethoxyacetaldehyde, benzoin, and acetoin eliminated or at least shortened the induction period on being added together with the hydroxide. Nowadays such compounds are regarded as cocatalysts. Kuzin attributed their catalytic activity to their ability to form enediols:

$$-\underset{\underset{OH}{|}}{CH}-\underset{\underset{O}{\|}}{C}- \rightleftarrows -\underset{\underset{OH}{|}}{C}=\underset{\underset{OH}{|}}{C}- \quad .$$

He regarded enolisation as a preliminary condition for the appearance of the activity of the cocatalyst.

Langenbeck[45-51] used as cocatalysts higher and lower monosaccharides, benzoylcarbinol, and a number of its derivatives. The kinetic measurements quoted by the authors show that the individual cocatalysts differ only by the induction period, and the corresponding kinetic curves are almost parallel. It was shown that glycolaldehyde and dihydroxyacetone are the most active cocatalysts. According to Langenbeck[47], the role of other cocatalysts, with a long induction period, reduces to the formation of glycolaldehyde or dihydroxyacetone with their participation. Langenbeck[51] suggested that the organic cocatalyst behaves as an activator of formaldehyde, which gives rise to glycolaldehyde on combining with a non-activated formaldehyde molecule:

$$R-CHOH-CO-R + CH_2O \rightarrow R-\underset{\underset{OH}{|}}{\overset{\overset{CH_2OH}{|}}{C}}-CO-R \rightarrow R-CHOH-CO-R + CH_2O^* \quad ;$$

$$CH_2O^* + CH_2O \rightarrow CH_2OHCHO \quad .$$

Here CH_2O^* is an activated formaldehyde molecule. Like, incidentally, Kuzin, Langenbeck assumed that the hydroxide plays only a secondary role. According to Kuzin's views, the hydroxide promotes the formation of enediol groups, ensuring the required pH and interacting with the hydrated forms of the carbohydrates and formaldehyde. However, this treatment conflicts with the specific catalytic action of a number of cations, which has now been demonstrated.

The formaldehyde condensation reaction has been thoroughly investigated in a series of studies[23,52-52] using alkali and alkaline earth metal hydroxides as catalysts. The kinetics and mechanisms of the Cannizzaro reaction were especially considered. The experimental results showed that the weaker the base the more effectively does it catalyse the Cannizzaro reaction:

$$Ca(OH)_2 \gg Tl(OH)_3 > Ba(OH)_2 > LiOH > NaOH,\ KOH.$$

It was also shown that low-molecular-weight alcohols, ethylene glycol, glycerol, dioxan, and tetrahydrofuran, added to the reaction mixtures, suppress the Cannizzaro reaction and increase thereby the yield of sugars. On the basis of paper chromatographic analyses of the products, the authors concluded that the primary reaction products is glycolaldehyde, which then condenses either with itself or with formaldehyde to give a wide range of reaction products—from trioses to hexoses. A stepwise mechanism of the formation of higher carbohydrates by the successive addition of a formaldehyde molecule to molecules of lower carbohydrates was put forward for the first time taking into account the keto–enol tautomerism and epimerisation[55]. Furthermore, the authors took into account in their scheme the fact that higher carbohydrates can be formed from lower carbohydrates as a result of the self-condensation of the latter:

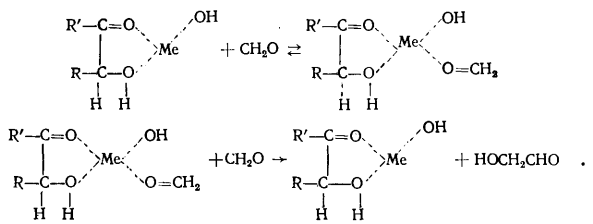
$$2CH_2OHCHO \rightarrow \text{tetroses},$$

$$2CH_2OHCHOHCHO \rightarrow \text{hexoses},$$

$$CH_2OHCHO + CH_2OHCHOHCHO \rightarrow \text{pentoses}.$$

It has been shown by a number of workers[56-62] that the carbohydrate self-condensation reactions proceed at a fairly high rate in alkaline solutions and should therefore play an important role in the mechanism of the formation of higher carbohydrates.

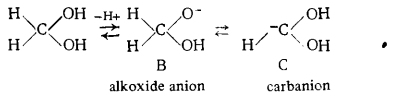
Pfeil and coworkers[56] suggested that the condensation proceeds at a complex of the undissociated metal hydroxide, the hydroxyoxo-compound, and formaldehyde:



Despite the fact that the existence of the complex of the hydroxyoxo-compound has not been demonstrated by any direct methods, one should note that Pfeil and coworkers were the first to draw attention to the possible decisive role of complexes of this kind in the synthesis of carbohydrates.

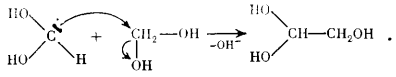
Other ideas about the mechanism of the action of bases on the condensation reaction were put forward by Runge and Mayer[26]. They established that in the presence of organic bases the Cannizzaro reaction does not take place. At the same time, under the influence of both inorganic and organic

bases (pyridine, dimethyl-aminoethanol, etc), the condensation reaction is characterised by an induction period and an autocatalytic period. The reaction time falls appreciably also after the addition of substances capable of forming enediol groups. The reaction mass, analysed by paper chromatography, does not differ in composition from the condensate obtained under the influence of an inorganic catalyst. On the basis of these extremely qualitative data, it was concluded that the mechanisms of the condensation reaction catalysed by organic and inorganic bases should be similar. Bearing in mind that organic catalysts such as tertiary amines cannot form complexes, Krylov et al.[27] proposed a mechanism in which a secondary role is assigned to the base. In the first stage a proton is abstracted in the presence of the base from the hydrated formaldehyde molecule with formation of structures corresponding to alkoxide and carbanionic forms:

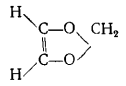


B alkoxide anion C carbanion

In such a system there is a possibility, albeit with a low probability, of the interaction of the carbanions of formaldehyde and its hydrated molecules to form a glycolaldehyde molecule:



The autocatalytic nature of the process is caused, according to the authors[27], by the intermediate formation of the five-membered ring



from the enediol form of glycolaldehyde and formaldehyde and by the ease of the successive interaction of this ring with two other formaldehyde molecules to form a new glycolaldehyde molecule with regeneration of the ring.

This mechanism suffers from the same significant disadvantage as those of Kuzin and Langenbeck. It cannot explain the dependence, observed by Pfeil as early as 1952, of the rate of reaction on the nature of the cation. The possibility of the formation of a ring of the above type is also doubtful.

IV. CURRENT STUDIES ON THE KINETICS AND MECHANISM OF THE SYNTHESIS OF CARBOHYDRATES

The kinetics of the synthesis of carbohydrates have been investigated by Krylov, Sinyak, and others[63–67] using alkaline earth metal hydroxides as catalysts. According to these workers, calcium and strontium hydroxides are much more active than $Ba(OH)_2$ and $Mg(OH)_2$; no catalytic activity has been found in $Be(OH)_2$. It has been discovered that only at a CH_2O concentration below 0.5% is there a linear relation between the rate of reaction and the CH_2O concentration; on the other hand, in the range 2.5–10% the rate is independent of the CH_2O concentration. Experiments carried out in the presence of various monosaccharides (C_3–C_6) showed that the variation of the rate of reaction with the cocatalyst concentration is also non-linear. At a monosaccharide concentration below $(3–4) \times 10^{-2}$ M and for degrees of conversion of formaldehyde up to 50%, the reaction kinetics in the presence of $Ca(OH)_2$ and $Sr(OH)_2$ can be described satisfactorily by the autocatalytic equation[64,65]

$$\frac{dx}{dt} = K(c_0 - x)(x_0 + x),$$

where c_0 and x_0 are the initial concentrations of formaldehyde and the monosaccharide and x is the current concentration of the reaction products. It was found[65] that the autocatalytic effect diminishes with increase of the number of carbon atoms in the monosaccharide and also that ketoses are more active than aldoses.

On the other hand, comparative experiments on the kinetics of the condensation of formaldehyde in the presence of a specific amount of $Ca(OH)_2$ in the form of a suspension and after filtering off the insoluble calcium hydroxide, carried out by the same workers[68], showed that the kinetic curves for the consumption of formaldehyde coincide. These experiments demonstrated the homogeneity of the reaction involving the condensation of formaldehyde to a sugar in the presence of $Ca(OH)_2$. Evidence for the homogeneous-catalytic nature of the process in the presence of $Ca(OH)_2$ was also obtained in other investigations[69–72].

The observed appreciable increase of the solubility of $Ca(OH)_2$ under the conditions of the synthesis has been explained[68] by the formation of a complex of the Ca^{2+} ion with formaldehyde and the reaction product—monosaccharides. The authors concluded that the elementary stages of the reaction take place in the coordination sphere of the catalytically active cation and put forward the following general kinetic equation for the reaction:

$$-\frac{d[CH_2O]}{dt} = k[Ca(OH)_2] \cdot \frac{b[CH_2O]}{1 + b[CH_2O]} \cdot \frac{b'[Pr]}{1 + b'[Pr]},$$

where b and b' are the complex formation equilibrium constants analogous to adsorption coefficients and Pr are reaction products. Different stages of the reaction are characterised by different reaction orders:

(1) For low conversions, when the concentration of CH_2O is low $\{b[CH_2O] \gg 1\}$ and

$$-\frac{d[CH_2O]}{dt} = k[Ca(OH)_2]\, b'[Pr]$$

the kinetics are described by the autocatalytic equation;

(2) For high conversions $\{b'[Pr] \gg 1\}$ and

$$-\frac{d[CH_2O]}{dt} = k[Ca(OH)_2]\, b[CH_2O]$$

the reaction is of first order with respect to formaldehyde:

(3) For moderate conversions $\{b[CH_2O] > 1;\ b'[Pr] > 1\}$, we have

$$-\frac{d[CH_2O]}{dt} \simeq k[Ca(OH)_2],$$

i.e. the reaction is of zero order with respect to formaldehyde.

Another important result of the investigations by the same workers was the discovery of a new class of catalysts—lanthanide hydroxides[27,28,73,74]. The authors suggested that new catalysts should be sought among the hydroxides of metals whose ionic radius is close to that of the metals in the catalysts already known. According to this hypothesis, the hydroxides of elements whose ionic radii is between 0.98 and 1.15 Å (Ca^{2+}–1.06 Å, Tl^{3+}–1.05 Å) should catalyse the condensation of formaldehyde to sugars. In this instance the groups of catalytically active cations includes those of lanthanide metals. Indeed, in the presence of La, Tb, Ho, Tm, Gd, Dy, Er, Sm, and Yb hydroxides, 100% conversion of formaldehyde was reached in the process after 5–6 h in an autoclave at 110 °C and a pressure of 1.8 atm. As for other catalytically active bases, the kinetics of the decrease

of the amount of formaldehyde were characterised by an induction period and auto-catalytic acceleration. The fact that the reaction proceeds wholly in an acid medium (the pH of the initial solutions at 110 °C in the presence of various catalysts varied in the range from 7 to 4) is of great interest. The conversion of formaldehyde via the Cannizzaro reaction takes place to an insignificant degree and the selectivity of the synthesis of carbohydrates in the presence of these catalysts is therefore greater than in the presence of $Ca(OH)_2$. These studies showed that the region where the condensation reaction can occur is not limited to an alkaline medium.

A kinetic equation analogous to that quoted by Krylov et al.[27] was obtained simultaneously and independently by Weiss et al.[75]. In a series of studies, carried out under Weiss's supervision, a detailed investigation was made of the kinetics of the condensation of formaldehyde in the presence of $Ca(OH)_2$ in a gradient-free reactor. At the same time a study was made of the Cannizzaro reaction[76]. The authors[75] began with the hypothesis that the following reactions take place in the formation of carbohydrates:

$$A_1 + Ca(OH)_2 \rightleftarrows A_1^* \quad , \qquad (1)$$

$$A_n + Ca(OH)_2 \rightleftarrows A_n^* \quad , \qquad (2)$$

$$A_n^* + A_1^* \rightleftarrows A_{n+1}^* + Ca(OH)_2 \quad , \qquad (3)$$

$$A_{n+1}^* \rightarrow A_{n+1} + Ca(OH)_2, \qquad (4)$$

where A_1 is formaldehyde, A_n a carbohydrate with n carbon atoms in the chain, and A_1^* and A_n^* are complexes of $Ca(OH)_2$ with formaldehyde and the carbohydrate respectively. In conformity with literature data[35,77], according to which formaldehyde and low-molecular-weight carbohydrates form complexes relatively readily, the authors[75] believe that stages (1) and (2) cannot be rate-limiting. The relatively low activation energy (16 kcal mol^{-1}) found by the authors made it possible to assume that stage (3) is likewise not rate-limiting. Assuming that stage (4) is rate-limiting, the authors derived the following equation:

$$r_F = k_4 K_1 K_2 K_3 S A_1 A_n / (1 + K_1 A_1 + K_2 A_n + K_1 K_2 K_3 A_1 A_n),$$

where r_F is the rate of reaction, K_1, K_2, and K_3 are the equilibrium constants of stages (1), (2), (3), k_4 is the rate constant for stage (4) in the forward direction, A_1 and A_n are the concentrations of formaldehyde and the carbohydrate respectively, and S is the concentration of $Ca(OH)_2$ equal to the sum of the concentrations of the hydroxide in a free state and in the form of a complex.

The equation obtained gives a formally satisfactory description of the observed kinetic relations for the reaction: autocatalysis for low conversions, zero order for intermediate conversions, and first order with respect to formaldehyde for high conversions. However, the above mechanism does not include the slowest stage, involving the dimerisation of formaldehyde, and cannot therefore explain the nature of the autocatalysis. In their purely kinetic study, Weiss and coworkers did not have as their aim a special investigation of the nature of the intermediate complexes. At the same time, the authors first complete analysis of the reaction products by a combination of gas chromatography and mass spectrometry[6,78,79] was a major step forward in this field. An important result of their investigation was the detection of a considerable content of branched carbohydrates in the reaction product.

Following Breslow[80,81], Weiss et al.[75] attribute an important role in the process to the Lobry de Bruyn–van Ekenstein rearrangement, the occurrence of which determined the ratio of the aldoses and ketoses in the reaction products. The rearrangement is based on the formation of the enediol form from the carbonyl form. As a result of the reversibility of this process, there is a possibility of the reformation of the carbonyl form together with its epimer and the ketose. The reaction is catalysed by both acids and bases. This rearrangement therefore always accompanies the condensation reaction, complicating the composition of the final products.

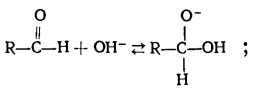
Weiss and coworkers[75,76] also investigated the ratio of the rates of the condensation and Cannizzaro reactions. The rate of the latter passes through a maximum near 50% conversion.

A single mechanism has been proposed for the Cannizzaro reaction and the reaction involving condensation to sugars[82]. On the grounds that the reaction does not require high concentrations of calcium cations, the authors conclude that the entire process is catalysed by the singly dissociated form of the calcium hydroxide formed on dissolution of $Ca(OH)_2$:

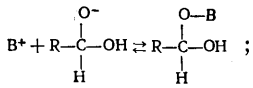
$$Ca(OH)_2 \rightleftarrows CaOH^+ + OH^- \quad ,$$
$$CaOH^+ \rightleftarrows Ca^{2+} + OH^- \quad .$$

The overall mechanism is based on the hypothesis of the decisive role of the interaction of the carbonion and the carbonium ion formed from formaldehyde molecules via the following mechanism:

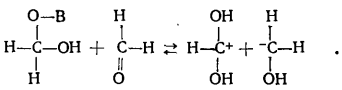
(a) the aldose or formaldehyde interacts with a hydroxide ion to form the anionic form:



(b) the anionic form interaction with the hydroxide cation (in the present instance, with $CaOH^+$), giving rise to a salt-like complex:

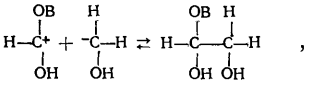


(c) the initiation of the condensation begins with the transfer of a hydride ion from the salt-like formaldehyde complex to a free formaldehyde molecule:

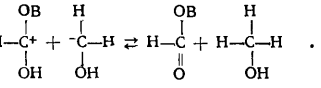


After this, two reactions pathways are possible:

(d) either recombination of the ions with formation of carbohydrate molecules—condensation (in the simplest case a salt-like complex of glycolaldehyde is produced):



(e) or proton transfer from the carbonium ion with formation of methanol (or a polyol) and a formate (the Cannizzaro or cross-Cannizzaro reactions):



It is believed[82] that the nature of the base affects the ratio of the rates of the last two stages and is therefore responsible for the process selectivity. The authors think that stage (d) is highly reversible on the grounds that, for low conversions, small amounts of glycolaldehyde are formed, while stage (e) is almost irreversible. Stage (d) explains the formation of the first condensation products. Further formation of carbohydrates proceeds mainly as a result of the aldol condensation, which the authors believe is also based on stage (d). However, the transfer of a hydride ion is inconsistent with modern ideas concerning the mechanism of the aldol condensation and requires at least special demonstration.

In the same study[82] the authors observed instances of instability of the rate of reaction for slight changes in the concentrations of the hydroxide and the components of the reaction, the pH, or temperature. The authors attribute this instability to the specific features of the autocatalytic reaction in a gradient-free reactor. The possibility of concentration instabilities in autocatalytic processes has been accounted for theoretically[83].

An interesting phenomenon—the inhibiting effect of transition metal hydroxides on the condensation of formaldehyde in the presence of calcium hydroxide—has been observed by Morozov and Levanevskii[84]. In their experiments $\sim 10^{-4}$ M transition metal hydroxide was introduced into the reaction mixture in the presence of a $Ca(OH)_2$ concentration of $\sim 10^{-2}$ M. As a rule, an appreciable increase of the induction period was observed. The induction period was longest in the presence of Fe^{2+} and Mn^{2+}. Under these conditions, the Cannizzaro reaction was not inhibited. It was established that the nature of the kinetic curves depends on the instant when the inhibitor is introduced and on the nature of the cocatalyst. The introduction of monosaccharides, such as C_2 and C_3, into the reaction mixture reduces the inhibition.

It was later established[85] that the inhibiting effect on the synthesis in the presence of $Ca(OH)_2$ can also be shown by lanthanide hydroxide. The experiments were performed at 60 °C and a concentration of hydroxides of $\sim 10^{-4}$ M. Praseodymium(III), gadolinium(III), terbium(III), and ytterbium(III) hydroxides have the strongest inhibiting effect. Lanthanum(III), europium(III), dysprosium(III), and erbium(III) hydroxides are weak inhibitors. Cerium(III), neodymium(III), samarium(III), holmium(III), and thulium(III) hydroxides exhibit an intermediate inhibiting activity. The composition of the condensation products is in all cases almost the same as in the presence of pure calcium hydroxide. The main reaction products are pentoses and hexoses. The addition of glyceraldehyde to the initial mixture reduced the inhibiting effect of lanthanide hydroxides. On the basis of these results, the authors conclude that the inhibiting effect of transition metal and lanthanide hydroxides is associated with the inhibition of the slowest stage—involving the formation of a molecule of glycolaldehyde from two formaldehyde molecules. The authors do not discuss the reasons why lanthanide cations, which are catalytically active in the synthesis of carbohydrates in the absence of calcium hydroxide, exhibit an inhibiting effect when the latter is introduced. In the same study[85] inhibitors of another type, inhibiting the condensation proper, were investigated. They include nitrobenzene and copper hydroxide. The inhibition at this stage is associated with the oxidative breakdown of the organic cocatalyst—the carbohydrate formed during the induction period. Such inhibition was first discovered by Langenbeck[47].

The condensation of formaldehyde to carbohydrates has been investigated in the presence of lead oxide[72,86-90]. The authors found that, in the presence of PbO, the rate of conversion of CH_2O into carbohydrates is independent of the surface area of the catalyst. As in the experiments with alkaline earth metal hydroxides, sugars greatly accelerate the reaction. The authors believe that these findings indicate a homogeneous autocatalytic mechanism of the condensation of CH_2O in the presence of PbO, which forms a soluble catalytically active complex with carbohydrates.

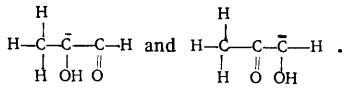
The influence of added alkaline earth and lanthanide oxides [MgO, CaO, BaO, Dy_2O_3, Sm_2O_3, and $Eu(OH)_3$] as well as the oxides of variable-valence metals tending to form complexes (Fe_2O_3, Co_2O_3, ZnO, and CuO) on the rate of condensation under the influence of the lead catalyst has been investigated[87]. The oxides were introduced at concentrations of 10 wt.% relative to the weight of PbO and 1 wt.% relative to the weight of CH_2O. It was found that BaO, CaO, and MgO intensify the effect of lead oxide, a synergistic and not an additive effect being produced. Lanthanide oxides have an inhibiting effect, while the oxides of effective complex-forming metals, cobalt(III) and copper(II), are still more powerful inhibitors. The addition of Fe_2O_3, and NiO, and ZnO has almost no influence on the condensation reaction.

One should also note that the condensation in the presence of both pure PbO and a mixture of oxides proceeds at comparatively low pH values. Thus, for conversions α not exceeding 25% in an experiment with pure PbO, the pH is 6.8 ($\alpha = 16\%$), while in the presence of added MgO ($\alpha = 7\%$), CaO ($\alpha = 25\%$) and BaO ($\alpha = 20\%$) the pH values are 8.9, 7.5, and 6.7 respectively. The condensation does not begin at pH values below 5 and is appreciably accelerated when the initial pH is raised to 8.0, while in the presence of $Ca(OH)_2$[71,72] at 50 °C the synthesis no longer occurs even at pH less than 9.5. According to the authors[87], the action of metal oxide added to PbO consists both in altering the pH and in the involvement of the dissolving metal ions in complex formation, which promotes or hinders the formation and subsequent reactions of complexes capable of propagating the condensation process. It has been suggested that the synergism may be associated with the formation of polynuclear complexes with a higher catalytic activity than the complexes of lead alone. The inhibiting effect of a number of oxides is attributed to the possibility of the decomposition of catalytically active complexes on the surface of these oxides.

The attempt to demonstrate with the aid of ultraviolet spectroscopy the formation of complexes of glucose and the products of condensation with PbO did not yield clearcut results[88,89]. In a study over a comparatively narrow spectral range (40000–54000 cm^{-1}), adjoining the far ultraviolet, the authors observed in the spectra of solutions of PbO containing glucose and the condensate an intense band having a maximum at ~ 48000 cm^{-1}, corresponding to the Pb^{2+} ion. The appearance of this band, which is absent from the spectra of aqueous solutions of PbO owing to the low solubility of the latter, was attributed to the formation of lead complexes with glucose and other carbohydrates. The absence of other specific bands in this part of the spectrum did not allow the authors to put forward a hypothesis concerning the possible structure of the complexes.

Other ideas about the mechanism of the condensation of formaldehyde have been put forward[91-97]. The mechanism proposed by the above workers is based on the hypothesis that the active intermediate compounds are the carbanionic forms of formaldehyde and the carbohydrates. For glyceraldehyde and dihydroxyacetone, this form is, according to the authors, the carbanion R^-, having the following limiting

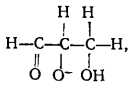
structural formalae:



The mechanism of the condensation of formaldehyde in the absence of an organic cocatalyst is not considered by the investigators. The following pathways leading to the formation of carbanions R^- are postulated: (a) via the interaction with hydroxide ions ($C_{3A} + OH^- \rightarrow R^- + H_2O$) and (b) as a result of the interaction with formaldehyde or glyceraldehyde alkoxide anions:

$$C_{3A} + C_{3A}^- \rightarrow R^- + C_{3A}\ , \quad C_{3A} + F^- \rightarrow R^- + F\ ,$$

where C_3A is a molecule of glyceraldehyde and C_{3A}^- is its alkoxide anion having the structure



F^- is the alkoxide anion derived from formaldehyde, and R' is the glyceraldehyde carbanion.

The carbanion is consumed in the condensation reaction, in isomerisation to a dihydroxyacetone molecule, and in the formation of alkoxide anions derived from formaldehyde and trioses. The proposed overall mechanism consists of eleven stages, taking into account the processes enumerated above, and of four possible processes involving the formation of alkoxide anions:

$$OH^- + F \rightleftarrows F^- + H_2O,\ OH^- + C_{3A} \rightleftarrows C_{3A}^- + H_2O\ ,$$
$$OH^- + C_6 \rightleftarrows C_6^- + H_2O\ ,\quad OH^- + C_4 \rightleftarrows C_4^- + H_2O\ .$$

The authors were the first to take into account the equilibrium between the monomeric formaldehyde and its polymeric forms[94]. Applying the principle of steadystate values in relation to R^-, the authors determined the ratio of the rate constants for the following stages:

$$R^- + C_{3A} \xrightarrow{k_1} C_{3K} + C_{3A}^-\ ,\quad R^- + H_2O \xrightarrow{k_2} C_{3K} + OH^-\ ,$$
$$R^- + F \xrightarrow{k_3} C_4^-\ ,\quad R^- + C_{3A} \xrightarrow{k_4} C_6^-\ .$$

where C_3K is a dihydroxyacetone molecule. The following values were obtained: $k_3/k_4 = 0.6$, $k_2/k_4 = 0.15$ mol litre^{-1}, and $k_1/k_4 = 0.03$.

Salt-like compounds of formaldehyde and hydrocarbons with calcium hydroxide, analogous to the compounds isolated by Franzen and Hauck[35], were isolated in two investigations[95,96]. However, the authors[95,96] believe that these compounds do not play a significant role in the condensation mechanism. The possible causes of the specific action of the cations derived from the hydroxides on the rate and selectivity of the synthesis have not been considered[91-97].

Towards the end of the 1960's and the beginning of the 1970's, studies on the reaction mechanism as well as those designed to elucidate the possible practical applications of the carbohydrates obtained were initiated by Japanese investigators. Nakai et al.[98] investigated the condensation in the presence of $Ca(OH)_2$ at 50 °C and found that the yield of sugars per gram of formaldehyde is a maximum when solutions with formaldehyde concentrations in the range of 0.81–4.05% are used. The employment of small amounts of monosaccharides as cocatalysts tends to increase the yield of sugars and decrease the reaction time. As in an earlier study[65], it was found that ketoses are more effective as cocatalysts than aldoses.

Mizuno et al.[31] investigated the catalytic activity of a number of inorganic and organic bases in the condensation reaction: $Ca(OH)_2$, $Ba(OH)_2$, $Sr(OH)_2$, $Mg(OH)_2$, $Pb(OH)_2$, KOH, TlOH, pyridine, picoline, collidine, *N*-methylpiperidine, *N*-methyl-morpholine, 2-(dimethylamino)ethanol, triethanolamine, and tetraethylammonium hydroxide. According to their data[31], the best catalyst at 50 °C is $Ca(OH)_2$ (the yield of carbohydrates is 55%). The sugars were analysed by all possible chromatographic methods: paper, thin-layer, gas–liquid, and liquid adsorption chromatography[99,100]. The authors were able to identify 33 carbohydrates ranging from C_2 to C_7, the main components being hexoses and pentoses. Methods for the isolation of various carbohydrates for subsequent toxicological tests have been developed[101,102].

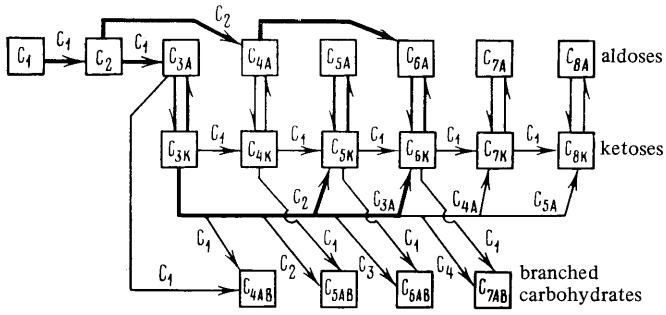


Figure 1. Schematic illustration of the formation of carbohydrate products in the formaldehye condensation reaction (according to Mizuno[103]); C_iA = aldoses with i carbon atoms; C_iK = ketoses with i carbon atoms; C_iAB = branched carbohydrates with i carbon atoms.

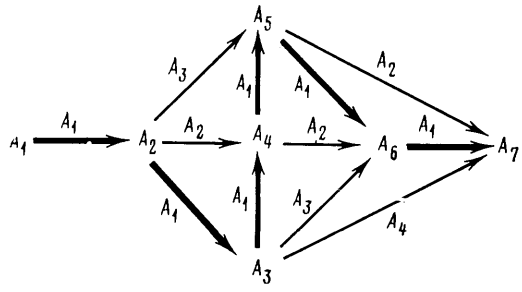
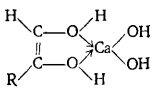


Figure 2. Schematic illustration of the formation of carbohydrate products in the formaldehyde condensation reaction (according to Weiss et al.[75]); A_i = carbohydrate with i carbon atoms. Thick arrows—tentative pathway leading to the formation of carbohydrates.

On the basis of gas-chromatographic and mass-spectrometric analyses of the reaction products, a new condensation mechanism (Fig.1), differing appreciably from Weiss's scheme[75] (Fig.2), has been proposed[103]. The controversial hypothesis has been put forward that, among all the carbohydrates, starting from C_3, only ketoses undergo cocondensation with formaldehyde. However, according to Mizuno, this is not

the main reaction pathway. According to the scheme in Fig.1, C_4 aldoses are formed mainly as a result of the self-condensation of glycolaldehyde, while C_6 aldoses are produced by its cocondensation with tetroses. Among ketoses, the highest reactivity is attributed to dihydroxyacetone. Its cocondensation with glycolaldehyde is regarded as the main pathway leading to the formation of pentoses and its cocondensation with glyceraldehyde is believed to be the main pathway to the ketohexoses. In the transformations of tetroses the Lobry de Bruyn–van Ekenstein equilibrium is not considered (without adequate justification). The controversial nature of a number of postulates of the above mechanism is evidently due to the limited amount of experimental data on which it is based.

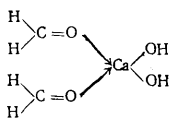
Fujino and Kobayashi[69,70] were the first to draw attention to the structure of the intermediate compounds of carbohydrates with hydroxides, which apparently play the role of condensation catalysts. The existence of these compounds has been postulated but has been in no way demonstrated in the series of the above studies. Fujino and Kobayashi[69,70] investigated the physicochemical properties of homogeneous systems such as CaO–glucose and CaO–xylose obtained after prolonged mixing of CaO with the carbohydrates at 10 °C and after filtering off the undissolved CaO. The study was carried out by NMR and infrared spectroscopy. On the basis of the results, the authors concluded that complexes of the calcium hydroxide with carbohydrates, having the structure



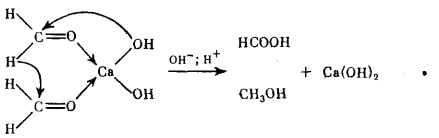
(I)

are formed.

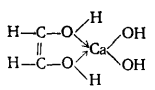
Fujino and Kobayashi[69,70] performed experiments on the condensation of formaldehyde at 50 °C in the presence of complexes of calcium hydroxide with glucose and xyloses and also with formaldehyde, prepared beforehand by the method indicated above. The results of these experiments led to the conclusion that, under the formaldehyde condensation conditions, two types of calcium hydroxide complexes are formed: (1) with the carbohydrate in the enediol form, having the structure given above and (2) with formaldehyde. having the structure



The complexes of the first type catalyse the condensation to carbohydrates and those of the second type catalyse the Cannizzaro reaction via the mechanism

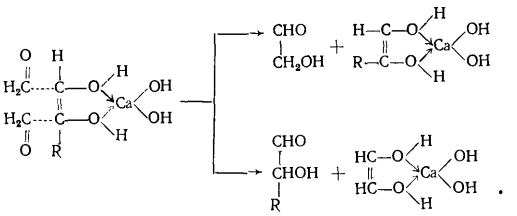


In the absence of an organic cocatalyst, there is, however, a possibility of the formation of the complex



(II)

This complex of glycolaldehyde and the hydroxide has an enediol group and, like complex (I), is the catalyst of subsequent condensation, which proceeds via the following mechanism according to the authors:



The rate constants for the synthesis of carbohydrates and the Cannizzaro reaction in the presence of alkaline earth metal hydroxides have also been determined[70]. When glucose was used as the cocatalyst, their activity in the synthesis of carbohydrates fell in the sequence

$$Ca(OH)_2 > Sr(OH)_2 > Ba(OH)_2.$$

An analogous activity series had been established earlier[64]. The activity series of the above hydroxides for the Cannizzaro reaction in the presence of glucose is the opposite to that found for the synthesis of carbohydrates, while in the absence of glucose it is identical. The authors[70] also found the ratios of the zero-order rate constants for the synthesis of carbohydrates and the Cannizzaro reaction at 50 °C:

$Ca(OH)_2$	$Sr(OH)_2$	$Ba(OH)_2$
4.1	2.1	0.73

These ratios virtually agreed with the ratios of the degrees of involvement, determined previously[26], of CH_2O in the synthesis of carbohydrates and in the Cannizzaro reaction (4.0 : 2.3 : 0.8).

In recently published studies[104–106] an attempt was made to use the potentiometric method for the investigation of the kinetics of the synthesis of carbohydrates in the presence of $Ca(OH)_2$. The authors determined the end of the induction period from the time required for the attainment of a minimum in the oxidation-reduction potential of the reaction system, while the time required to reach its maximum corresponded, according to their data, to the complete conversion of formaldehyde. Using this relatively insensitive method, the authors found that, after the end of the induction period, the kinetics of the syntheses correspond to first order with respect to CH_2O and zero order with respect to $Ca(OH)_2$. Like Weiss and coworkers[82], they concluded that the true process catalyst is $CaOH^+$. Despite the contradictory nature of the kinetic relations found by these workers and by Weiss et al.[75], the former[104–106] believe that their investigation confirmed the mechanism of the synthesis of carbohydrates proposed by Weiss[82].

The result obtained[107] on precipitation of Ca^{2+} ions by oxalic acid at the end of the induction period is of interest. It was observed that, following the subsequent addition of KOH and the adjustment of pH to 12, the synthesis at 60 °C can be carried out selectively in the direction of the formation of a few branched carbohydrates and the corresponding alcohols (the alcohols 2-hydroxymethylglycerol, 2,4-hydroxymethylpentitol, and 3-hydroxymethylpentitol are formed preferentially).

Harsch et al.[108] used for the first time high-pressure liquid chromatography to obtain kinetic data for the change in the content of products during the synthesis of carbohydrates from formaldehyde. They studied model reactions

involving the cocondensation of formaldehyde with glycolaldehyde, glyceraldehyde, and dihydroxyacetone in the presence of $Ca(OH)_2$. The results confirmed the stepwise mechanism of this synthesis of carbohydrates[55]. In view of the absence of even traces of octoses in experiments with glyceraldehyde, the authors[108] regard as unlikely the mechanism proposed by Mayer and Jaschke[59], according to which the reactions involving the dimerisation of tetroses to octoses and their subsequent cleavage to dihydroxyacetone and aldopentose play and important role in the formation of the final products. They also criticise Breslow's mechanism of autocatalysis[81] which is based on the hypothesis of the ready cleavage of tetroses under the conditions of the synthesis. Such cleavage leads to a rapid increase of the content of glycolaldehyde in the reaction system. The secondary role of this mechanism follows from the evidence obtained by the authors[108] for the high rates of cocondensation of tetroses with formaldehyde and the extremely low rates of cleavage of tetroses.

Guillot et al.[109] investigated the kinetics of the synthesis of carbohydrates in the presence of TlOH using a number of aromatic α-ketols (benzoyl-carbinol, 1-phenyl-2-hydroxy-1-butanone, and 1-phenyl-1-hydroxy-2-butanone) as cocatalysts. It was found that, for degrees of conversion of formaldehyde of 5–95%, the kinetics are described satisfactorily by the autocatalytic equation

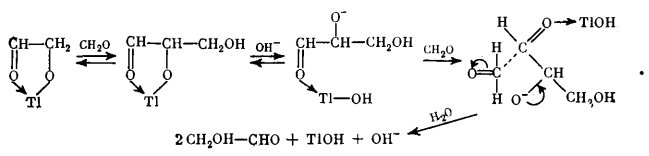
$$\lg\left[\frac{x}{a-x}\right]_{x_1}^{x_2} = k(t_2 - t_1),$$

where a is the initial concentration of formaldehyde, x_1 and x_2 are the amounts of formaldehyde in mol litre^{-1} which have reacted at times t_1 and t_2, and $k = k_0\,[Tl^+][OH^-]$. Benzoylcarbinol proved to be the most active cocatalyst (more active than glycolaldehyde) and phenylhydroxybutanones proved to be the least active. The induction period increased with increasing formaldehyde concentration.

In their explanation of the experimental results the authors[109] began with the hypothesis that a complex of formaldehyde with Tl^+ having the following structure can be formed in an alkaline medium:



The interaction of this complex with a second formaldehyde molecule leads in their view to the slow formation glycolaldehyde. They explain the autocatalysis by the much faster formation of glycolaldehyde on interaction of two formaldehyde molecules with the alkoxide anion derived from glycolaldehyde (or α-ketol) and coordinated to Tl^+, via the following mechanism:



The literature data considered above show that, despite much attention devoted to the study of the kinetics of the synthesis of carbohydrates and the considerable progress achieved in the analysis of the composition of the products of the synthesis during the last decade, many aspects of the mechanisms of this process remain obscure. There has been no lack of attempts to put forward new mechanisms. Such mechanisms, developed on the basis of only kinetic data and the results of the analysis of the composition, cannot be regarded as sufficiently well founded and it is not surprising that several mutually exclusive mechanisms have been proposed recently. The mechanism of the first stage of the synthesis—the dimerisation of formaldehyde to glycolaldehyde—remains completely obscure. There is no satisfactory explanation of the autocatalytic nature of the process. An important theoretical and practical task is the elucidation of the conditions for the complete suppression of the formation of branched carbohydrates. Weiss's studies in this field constitute only the first steps. Evidently success in the solution of the above problems in the synthesis of carbohydrates will be possible only by combining kinetic research techniques with modern physicochemical and physical methods.

A combined study of the mechanism of the synthesis was therefore undertaken at the Institute of Chemical Physics of the USSR Academy of Sciences in 1969[111–116] in which ultraviolet and NMR spectroscopy as well as radioactive tracers were used in addition to kinetic methods. The kinetics were studied in a static reactor in the presence of alkaline earth metal hydroxides (calcium, strontium, and barium). Gas-chromatography[6] made it possible to carry out a complete group analysis of the carbohydrates with separate determination of the linear and branched components in each carbohydrate fraction with the given number of carbon atoms in their molecules.

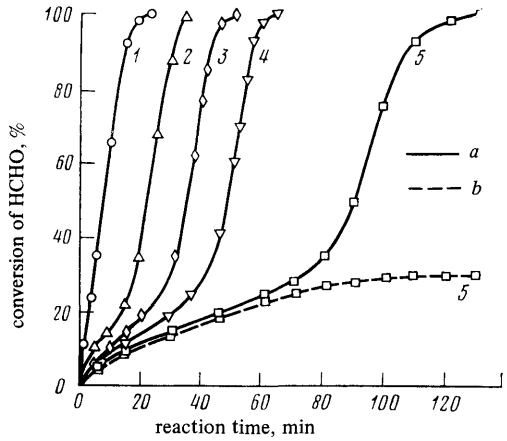


Figure 3. Kinetic curves for the overall conversion of formaldehyde (*a*) and the conversion via the Cannizzaro reaction[12] (*b*) for different molar concentrations of glycolaldehyde: 1) 0.042; 2) 0.008; 3) 0.0017; 4) 0.0008; 5) 0.0; $c_{H_2CO} = 1.53$ M; $c_{Ca(OH)_2} = 0.19$ M; $t = 40$ °C.

Fig. 3 presents the kientic curves obtained[112] for the condensation of formaldehyde (1.53 M) at 40 °C in the presence of $Ca(OH)_2$ (0.18 M) and variable amounts of glycolaldehyde used as the cocatalyst. Evidently a decrease of the induction period corresponds to an increase of the concentration of glycolaldehyde. At a concentration of this cocatalyst of 4.2×10^{-2} M the induction period disappeared altogether and, up to almost complete conversion of formaldehyde (~90%), the condensation proceeded as a zero-order reaction with respect to formaldehyde. Analogous kinetics were observed when glucose was used as the catalyst, but the induction period did not disappear completely even at a glucose concentration of 1×10^{-1} M. When $Ca(OH)_2$ was used as the catalyst

and glucose as a cocatalyst, it was established[113,115] that the induction period passes through a minimum with increasing NaOH content (from 0.1 to 1.0 M). In the range of conversions α from 20–30 to 80–90% the rate of condensation of formaldehyde was found to be constant but increases linearly with increasing concentration of OH^- ions. This is consistent with the zero order with respect to formaldehyde and the first order with respect to $Ca(OH)_2$ found in earlier studies[27,75] for moderate conversions.

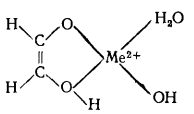
The observed minimum in the induction period with increasing NaOH concentration in solution must be regarded as confirmation of the earlier conclusion[82] that the catalytically active form of $Ca(OH)_2$ is the cation $CaOH^+$.

It has been observed[116] by means of the radioactive tracer method, using glucose labelled with ^{14}C, that, under the conditions of the synthesis, the carbohydrates undergo the disproportionation reactions

$$C_mH_{2m}O_m + C_nH_{2n}O_n \rightarrow C_{m-k}H_{2(m-k)}O_{m-k} + C_{n+k}H_{2(n+k)}O_{n+k},$$

known previously solely as biocatalytic reactions[117]. At the same time radioisotope data show that the rates of these reactions, as well as secondary reactions in the synthesis of carbohydrates such as retroaldol cleavage, are much lower than the rate of growth of carbohydrate molecules.

Analysis of the ultraviolet spectra of alkaline solutions of carbohydrates in the presence and absence of alkaline earth metal ions[111] as well as ultraviolet spectra of samples of the solution removed from the reactor during the synthesis of carbohydrates[113–118] made it possible to attribute the appearance of the band in the range 300–340 nm in these spectra to the formation of complexes of the enediol forms of carbohydrates and hydroxides of the type



.

It was found that the position of the absorption maximum depends on the nature of the cation forming the complex. When glucose was used as the ligand, the absorption maximum was found at 342 nm for $Ca(OH)_2$, 332 nm for $Sr(OH)_2$, and 322 nm for $Ba(OH)_2$.

An important result of the ultraviolet spectroscopic study was the observation that the kinetics of the increase of the optical density of this band for different carbohydrates (glycolaldehyde, dihydroxyacetone, glyceraldehyde, arabinose, glucose, and fructorse) are similar to the initial kinetics of the synthesis using the same carbohydrates as cocatalysts. This suggested that the complexes of the above type are capable of manifesting autocatalytic activity.

In view of this conclusion, the results of the chromatographic analysis (carried out immediately after preparing the solution) of the complex of α-D-glucose and $Ca(OH)_2$ are of interest[71,72,119]. Analysis demonstrated the presence in solution of a number of other hexoses (fructose, mannose, etc.) together with glucose. This enabled Weiss[119] to conclude that the catalytically active complex is a dynamic mixture of carbohydrate complexes of different structures and not the complex of an individual carbohydrate. The application of photoelectron X-ray spectroscopy to obtain information about the structure of the catalytically active complexes of calcium hydroxide with glucose and dihydroxyacetone, isolated from solution by the method of Roy and Mitra[121], showed[120] that the corresponding complexes consist of adducts with weakly polarised bonds between Ca^{2+} and the carbohydrate molecule.

The results of this study justified the conclusion that the autocatalytic nature of the synthesis of carbohydrates is due to the possibility of the formation of glycolaldehyde via two pathways having sharply different rates: (a) via the slow dimerisation of the formaldehyde in the coordination sphere of the calcium cation and (b) via the much faster dimerisation in the coordination sphere of the calcium cation where two coordination sites are occupied by the enediol form of glycolaldehyde formed previously.

The multistage mechanism of the synthesis of glycolaldehyde from formaldehyde, which accounts for the autocatalytic nature of its formation, can be formulated as follows in accordance with the evidence presented above:

$$A + K \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} AK \quad , \tag{1}$$

$$AK + A \xrightarrow{k_2} EK \quad , \tag{2}$$

$$EK \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} K + C_2 \quad , \tag{3}$$

$$EK + A \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} EKA \quad , \tag{4}$$

$$EKA + A \xrightarrow{k_5} EK + C_2 \quad , \tag{5}$$

where A is formaldehyde, K the catalyst [the $CaOH^+$ cation for $Ca(OH)_2$], C_2 glycolaldehyde (in the non-hydrated form), EK the complex of the catalyst with the enediol form of glycolaldehyde, and EKA the complex EK whose coordination sphere contains formaldehyde A.

^1H and ^{13}C NMR showed[113,122] that, under the conditions of the synthesis, formaldehyde exists mainly in the form of unionised and singly ionised methyleneglycol. However, these data do not rule out the possibility of the involvement of formaldehyde in the proposed stages in the non-hydrated form. One should bear in mind that the concentration of this form under the conditions of the synthesis cannot exceed several hundredth per cent of the overall formaldehyde concentration[123].

The elucidation of the problem of the form in which formaldehyde participates in the proposed stages is difficult and requires additional studies.

The equation derived on the basis of the above mechanism for the rate of the initial stage of the reaction [until the attainment of a degree of conversion of formaldehyde of ~20% when part of $Ca(OH)_2$ still remains in the precipitate] has the following form[113,118]:

$$w = (k_2K_I[A]^2 + k_5K_{III}K_{IV}[A]^2[C_2])[Ca(OH)_2]_0 \times \\ \times (1 + K_w/K_I'[H^+] + K_{II}'[H^+]/K_w)^{-1} \quad ,$$

where k_2 and k_5 are the rate constants for stages (2) and (5), K_I, K_{III}, and K_{IV} are the rate constants for the formation of complexes in stages (1), (3), and (4), K_W is the ionic product of water, and K_I' and K_{II} are the first and second dissociation constants of $Ca(OH)_2$. Since $k_5 \gg k_2$, the term $k_2K_I[A]^2$ in the expression for the rate of reaction can be neglected, whereupon the above expression reduces to the form typical for autocatalytic reactions:

$$w = k_5K_{III}K_{IV}[A]^2[C_2][Ca(OH)_2]_0(1 + K_w/K_I'[H^+] + K_{II}'[H^+]/K_w)^{-1} \quad .$$

At a constant pH and in the presence of $Ca(OH)_2$ in the precipitant, we obtain

$$w = k[A]^2[C_2] \quad .$$

The constancy of the rate of reaction in the range of values of α from 20–30% to 80–90% has been attributed[113] to the fact that, starting from $\alpha = 20$–30%, the main pathway followed in the consumption of formaldehyde is its aldol condensation with C_2–C_4 carbohydrates. According to Ingold[124], the rate-limiting stage in this process is the formation of carbanions from C_2–C_4 carbohydrates, which sould lead to the first reaction order with respect to OH^-. The rate of formation of carbanions from glycolaldehyde has been estimated by NMR[125]. The observed overall zero order of the synthetic reaction for a slight change in pH in the range of values of α from 20–30% to 80–90% shows that the rate constants for the formation of carbanions from the C_2–C_4 carbohydrates differ little and that the overall C_2–C_4 concentration hardly changes in the above range of values of α.

The first information about the significant influence of the nature of the catalyst cation on the ratio of the linear and branched carbohydrates formed has been obtained in a number of studies[112–115]. Table 2 presents the corresponding data for 100% conversion of formaldehyde using glycolaldehyde (4.2×10^{-2} M) as the cocatalyst. The data for the C_4 fraction, whose composition should be closer to that for the primary products than the composition of the C_5 and C_6 fractions, are particularly instructive. The proportion of linear carbohydrates in this fraction is 81% for $Ca(OH)_2$, 37% for $Sr(OH)_2$, and 21% for $Ba(OH)_2$. It follows from the data in Table 2 that $Ca(OH)_2$ is most selective in relation to the synthesis of linear carbohydrates but even for this hydroxide the proportion of branched carbohydrate is high.

Table 2. Fractional composition (%) of the carbohydrates[112] formed in the condensation of formaldehyde (1.53 M) in the presence of calcium, strontium, and barium hydroxides (0.19 M); cocatalyst—glycolaldehyde (4.2×10^{-2} M).

Carbohydrates	Condensation conditions*			
	$Ca(OH)_2$; 40°; 20 min; 7.2%	$Ca(OH)_2$; without cocat., 40°; 135 min; 35.5%	$Sr(OH)_2$; 40° 23 min; 6.0%	$Ba(OH)_2$; 50°; 50 min; 18%
C_3	6.6	11.1	4.5	3.6
C_4 (branched)	1.3	6.2	4.6	9.1
C_4 (lin.)	5.6	9.9	2.7	2.4
ΣC_4	6.9	16.1	7.3	11.5
C_5 (branched)	5.1	5.6	4.2	2.4
C_5 (lin.)	15.2	21.6	9.7	5.2
ΣC_5	20.3	27.2	13.9	7.6
C_6 (branched)	31.5	19.7	21.8	22.8
C_6 (lin.)	16.6	15.4	16.7	10.1
ΣC_6	48.1	35.1	35.8	32.9
C_7	18.1	10.5	35.4	44.5
Σ branched without C_7	38	35.5	31	34
Σ lin. without C_7	44	58	34	21

* The catalyst, temperature, reaction time, and the degree of conversion via the Cannizzaro reaction are quoted.

The results obtained can be regarded as promising in the sense that they indicate the possibility of a considerable alteration of the proportion of linear carbohydrates when one catalyst is replaced by another or when the temperature is altered, i.e. they give rise to the hope that it may be possible to select optimum catalysts and conditions whereby the content of branched carbohydrates in the products of synthesis can be reduced to an acceptable minimum or fully eliminated. The latest results[126] show that, in principle, one can achieve a very high selectivity of the synthesis in favour of linear hexoses, provided that the synthesis is carried out at sufficiently high temperatures. Thus, at 98 °C and using $Ca(OH)_2$ as the catalyst, the proportion of hexoses reaches 84% of all the products (by weight) for a degree of conversion of 18%; 90% of the hexoses then consist of a mixture of approximately equal amounts of glucose and idose.

The data discussed above show that, despite certain advances in the elucidation of the mechanism of the synthesis of carbohydrates from formaldehyde and promising indications of a possibility of achieving a highly selective process, it is necessary to continue research into the mechanism and to develop ways of increasing the process selectivity. In particular, it is necessary to refine the structure of catalytically active complexes of carbohydrates and formaldehyde with hydroxides. As already mentioned, the problem of the form (hydrated or non-hydrated, ionised or unionised) in which formaldehyde is involved in the formation of glycolaldehyde remains unelucidated. Exhaustive kinetic information (the reaction order with respect to formaldehyde, the concentration of calcium hydroxide ions and OH^- ions, and the activation energy) for the induction period is so far lacking. The problem of the extent to which branched carbohydrates can be involved in secondary disproportionation and retroaldol cleavage reactions remains completely obscure. This evidently does not complete the list of the obscure problems of the mechanism. It is no less important to continue the search for optimum catalysts and conditions for a highly selective synthesis of assimilable carbohydrates. The results obtained hitherto in attempts to increase the process selectivity constitute only the first steps in this practically important field of study.

V. THE POSSIBLE VERSIONS OF THE CONDENSATION OF FORMALDEHYDE OF CARBOHYDRATES IN LIFE SUPPORT SYSTEMS IN SPACE VESSELS

It follows from the foregoing that the selectivity of the synthesis of carbohydrates from formaldehyde is as yet insufficient for this process to be used without significant improvement in life support systems at the concluding stage of the conversion of the final products of the vital activity of the human organism into food products. When formaldehyde is fully converted into carbohydrates in the presence of $Ca(OH)_2$, one of the most effective catalysts of this process, the proportion of hexoses in the carbohydrate products is only ~50%.[76] On the other hand, the proportion of assimilable hexoses must be less than 25% since, in view of the characteristics of the process examined above, half of all the carbohydrates should apparently be formed in the non-assimilable L-form. Furthermore, the non-assimilable carbohydrates include also all the branched and certain linear D-hexoses produced.

The low process selectivity is apparently the main cause of the negative results of toxicological assessments of the carbohydrates synthesised. After a most careful purification of the carbohydrates [precipitation of $Ca(OH)_2$, treatment of the filtered solution with a cation exchanger, an anion exchanger, and activated charcoal], prolonged feeding of rats with the product led to weight loss by the animals accompanied by a number of pathological phenomena and terminating in their death[127]. Therefore, together with the search for ways of improving significantly the selectivity of the synthesis of assimilable hexoses from formaldehyde,

it is desirable to carry out also studies designed to elucidate the possibility of employing this process in other more promising versions.

A 50 day experiment[128], showing that human diet can contain considerable amounts of glycerol (110 g per day) without any harmful consequences of health, was carried out recently. Later studies[129] showed that glycerol in the diet can constitute more than half, by weight, of the entire daily ration for man (up to 300 g per day).

On the other hand, it is known[130] that hydrogenolysis can yield glycerol as the main reaction product. At the beginning of the 1940's the first patents were taken out[131–133] for the synthesis of glycerol by the hydrogenolysis of a mixture of carbohydrates synthesised from formaldehyde.

Bearing in mind these data, Weiss et al.[134] suggested that at the end of the synthesis of carbohydrates the reaction mixture be hydrogenated and hydrogenolysed under conditions ensuring the preferential formation of glycerol. This application of the formaldehyde condensation process can ensure the recycling under the conditions of the space vessel of at most between 20 and 50% of carbon dioxide in the form of glycerol which is assimilable by the human organism.

In view of the low selectivity of the condensation of formaldehyde to assimilable carbohydrates, this verion of the process makes it possible to obviate difficulties associated with the toxic effect of complex mixtures of the carbohydrates synthesised. However, at present one can only speak of the possibility, in principle, of using this version of the formaldehyde condensation process. Comparatively few studies have been made on these lines and the selectivity achieved in the synthesis of glycerol is insufficient. Thus it can be shown[135,136] that the selectivity of the hydrogenolysis of sucrose (200–225 °C, 200 atm) in relation to the formation of glycerol is only 31%. A disadvantage of this version of the process is also the necessity to employ severe conditions—high temperatures and pressures.

Another way of obtaining glycerol from formaldehyde may therefore be more promising for the conditions in space vessels: preliminary synthesis of carbohydrates from formaldehyde under conditions ensuring the preferential formation of trioses and subsequent hydrogenation of the latter to glycerol. Studies by Weiss and coworkers[137] showed that the selective synthesis of trioses is in principle possible if the process is terminated at low degrees of conversion of formaldehyde. Thus, at 40 °C in the presence of $Ca(OH)_2$ for degrees of conversion of ~10%, the content of trioses in the carbohydrate products can be close to 80% according to the above authors' data. We obtained similar results[112]. Direct data indicating the possibility of the selective synthesis of trioses from formaldehyde have also been obtained. According to Shapira[138], in the presence of the $CaO-Al_2O_3$ catalyst and after the addition of 5% of glyceraldehyde as the cocatalyst, it is possible to obtain trioses with a selectivity of 73% for an overall conversion of formaldehyde of 71%.

The hydrogenation of trioses in the presence of fairly active catalysts (for example, ruthenium catalysts) could be carried out at a much lower temperature and pressure compared with those indicated above for hydrogenolysis; a very high hydrogenation selectivity is then achieved[138].

The above advantages of this version of the synthesis of glycerol evidently make it desirable to carry out special studies in order to elucidate the possibility of its practical application.

The selective synthesis of trioses from formaldehyde may be of particularly great interest in view of the fact that trioses can be converted with the aid of an immobilised enzyme (aldolase) into D-glucose, nutritionally the most valuable carbohydrate, with a selectivity close to 100%.[117] However, despite the known advantages of this version of the synthesis of D-glucose (not only under conditions of space vessels but also for terrestrial purposes), there have been almost no studies designed to elucidate the possibility of the practical realisation of this synthesis.

The difficulties associated with the low selectivity of the synthesis of carbohydrates and the possible toxicity of individual products can also be avoided by employing solutions of synthetic carbohydrates as the nutrient medium for the growing of yeast. This method of using synthetic carbohydrates has been proposed by Soviet and American investigators[68,139]. The yeast grown in this way can evidently serve under the conditions of prolonged space flights as a valuable additional source of food protein and vitamins. The protein content in yeast is 45% and yeast is capable of synthesising also other valuable food components: lipids, glycolipids, and sugars[140].

Yeast (or at any rate some of their species) have less stringent requirements as regards the composition of carbohydrates than the human and animal organism and the extent to which they can utilise synthetic carbohydrates can be fairly high. Thus the degree of utilisation of carbohydrates reached 30–40% in a study[68] where yeast was cultured on synthetic carbohydrates. Table 3 presents qualitative data from the study of Chermside et al.[139] for the utilisation of various sources of carbon by certain yeast species. They show that certain yeast species are capable of effectively assimilating synthetic carbohydrates.

Table 3. The utilisation of various sources of carbon by certain yeast species*.

Yeast species	Glucose	Mannitol	Glycerol	Dihydroxyacetone	Synthetic carbohydrates		
					1%	3%	5%
Candida krusoides	++	++	++	++	+	—	—
Lipolytica	++	++	++	++	+	—	—
Atilis	++	++	++	++	+	+**	—
Rhodotorula pilimanae	++	++	++	++	++	+**	—
Saccharomyces carlsbergensis	++	—	—	++	+	+**	+**
Cerevisiae	++	—	—	++	—	—	—

* Notation: ++ effective utilisation; + utilisation; — no utilisation.

** The utilisation was greater in a 14 day experiment than in a 7 day experiment.

Data obtained in a study[141] where it was shown that good results can be secured in the growing of yeast (*Candida tropicalis* CK-4) using as a source of carbon complex mixtures of organic acids obtained by oxidising synthetic carbohydrates are of interest in connection with the problem under discussion.

The literature data considered in this Section show that there are a number of promising versions of the formaldehyde condensation process for the recycling of food under the conditions of prolonged space flights. At the same time it is evident that only preliminary studies have so far been

carried out in each of the relevant fields and that extensive and thorough research is necessary before the practical application of these procedures will become possible.

REFERENCES

1. Yu.E.Sinyak and S.V.Chizhov, Khimiya i Zhizn', No.5, 23 (1975).
2. O.V.Krylov, V.A.Naumov, and Yu.E.Sinyak, Priroda, No.10, 2 (1973).
3. O.G.Gazenko and A.S.Ushakov, Priroda, No.10, 44 (1977).
4. A.M.Butlerov, Compt.rend., **5**, 145, 247 (1861).
5. A.M.Butlerov, Annalen, **120**, 295 (1861).
6. R.D.Partridge, A.H.Weiss, and D.Todd, Carbohydr. Res., **24**, 29 (1972).
7. O.Loew, J.prakt.Chem., **33**, 321 (1886).
8. O.Loew, Chem.Z., 21, 131 (1897).
9. O.Loew, Ber., **22**, 470 (1889).
10. O.Loew, Ber., **22**, 478 (1889).
11. O.Loew, Ber., 22, 482 (1889).
12. O.Loew, Ber., 39, 1592 (1906).
13. E.Fischer, Ber., **21**, 988 (1888).
14. E.Fischer, Ber., 22, 359 (1889).
15. E.Fischer, Ber., **23**, 370 (1890).
16. H.Euler, Ber., **33**, 2551 (1905).
17. H.Euler and A.Euler, Ber., **39**, 39 (1906).
18. H.Euler and A.Euler, Ber., **39**, 45 (1906).
19. W.Kuster and F.Schoder, Z.physiol.Chem., **141**, 113 (1924).
20. H.Schmalfuss, Ber., **57**, 2101 (1924).
21. H.Schmalfuss, Biochem.Z., **185**, 70 (1927).
22. H.Schmalfuss, Ber., 60, 1035 (1927).
23. E.Pfeil and G.Schroth, Ber., **85**, 293 (1952).
24. S.Malinowski and J.Kehl, Roczniki Chem., **34**, 291 (1960).
25. S.Malinowski and J.Kehl, Roczniki Chem., **36**, 1039 (1962).
26. K.Runge and R.Mayer, Annalen, **707**, 161 (1967).
27. O.V.Krylov, Yu.E.Sinyak, A.A.Berlin, and I.L. Shul'gina, Dokl.Akad.Nauk SSSR, **199**, 643 (1971).
28. A.A.Berlin, Candidate's Thesis, Institute of Medico-Biological Problems, The Ministry of Health of the USSR, Moscow, 1970.
29. N.W.Gabel and C.Ponnamperuma, Nature, **216**, 453 (1967).
30. S.Trigerman, E.Biron, and A.H.Weiss, React.Kinet. Catal.Letters, **6**, 269 (1977).
31. T.Mizuno, T.Mori, N.Shiomi, and N.Nakatsuji, Nippon Nogei Kagaku Kaishi, **44**, 324 (1970).
32. C.Reid and L.E.Orgel, Nature, **216**, 455 (1967).
33. L.Henry, Compt.rend., **121**, 210 (1895).
34. C.Neuberg, Ber., **35**, **2626** (1902).
35. H.Franzen and L.Hauck, J.prakt.Chem., **91**, 261 (1915).
36. É.Katschmann, Ber., **77B**, 579 (1944).
37. L.Orther and E.Gerisch, Biochem.Z., **259**, 30 (1935).
38. A.M.Kuzin, Zhur.Obshch.Khim., **5**, 1373 (1935).
39. A.M.Kuzin, Zhur.Obshch.Khim., **7**, 2954 (1937).
40. A.M.Kuzin, Biokhimiya, **2**, 127 (1937).
41. A.M.Kuzin, Zhur.Obshch.Khim., **8**, 8 (1938).
42. A.M.Kuzin, Zhur.Khim.Farm.Prom., **5**, 257 (1938).
43. A.M.Kuzin, Zhur.Obshch.Khim., **8**, 759 (1938).
44. A.M.Kuzin, Ber., **68**, 619, 1494, 2169 (1935).
45. W.Langenbeck, Naturwiss., **30**, 1942.
46. W.Langenbeck, Oel und Kohle, **40**, 206 (1944).
47. W.Langenbeck, W.Sander, F.Kuhn, S.Hunig, and E.Katzschmann, Angew.Chem., **61**, 186 (1949).
48. W.Langenbeck, J.prakt.Chem., 3, 196 (1956).
49. W.Langenbeck, Angew.Chem., **66**, 151 (1954).
50. W.Langenbeck, Tetrahedron, **3**, 185 (1958).
51. W.Langenbeck, "Organic Catalysts" (Translated into Russian), Inostr.Lit., Moscow, 1961.
52. S.Hunig, Biochem.Z., **313**, 31 (1942).
53. E.Pfeil, Ber., 84, 229 (1951).
54. E.Pfeil and G.Schroth, Z.anal.Chem., 134, 333 (1952).
55. E.Pfeil and H.Ruckert, Annalen, **641**, 121 (1961).
56. H.Ruckert, E.Pfeil, and G.Scharf, Ber., 98, 2558 (1965).
57. H.O.L.Fisher and E.Baer, Helv.Chim.Acta, 19, 519 (1935); 20, 1213 (1937).
58. R.Mayer, K.Runge, and H.Drechsel, Z.Chem., 224, 134 (1963).
59. R.Mayer and L.Jaschke, Annalen, **635**, 145 (1960).
60. R.Mayer and L.Jaschke, Angew.Chem., **72**, 635 (1960).
61. C.D.Gutsche, D.Redmore, R.S.Buriks, K.Novotny, H.Grassner, and C.W.Armbruster, J.Amer.Chem. Soc., 89, 1235 (1967).
62. W.G.Berg and C.E.Feasel, J.Amer.Chem.Soc., **50**, 486 (1928).
63. Yu.E.Sinyak and A.A.Berlin, Kosmicheskaya Biologiya i Meditsina, No.6, 9 (1968).
64. O.V.Krylov, Yu.E.Sinyak, V.A.Uspenskaya, and I.L.Shul'gina, Kosmicheskaya Biologiya i Meditsina, No.1, 6 (1970).
65. V.A.Uspenskaya, O.V.Krylov, and Yu.E.Sinyak, Kosmicheskaya Biologiya i Meditsina, No.4, 9 (1971).
66. V.A.Uspenskaya and G.M.Petrova, Kosmicheskaya Biologiya i Meditsina, No.8, 20 (1974).
67. V.N.Demishev, N.B.Berlin, L.A.Sidovnikova, and Yu.E.Sinyak, Symposium, "Sinteticheskie Polielektrolity i Dispersnye Sistemy (Fizicheskaya Khimiya i Reologiya)" [Synthetic Polyelectrolytes and Disperse Systems (Physical Chemistry and Rheology)], Moscow, 1973, p.9.
68. Yu.E.Sinyak, O.V.Krylov, A.A.Berlin, I.L.Shul'gina, L.V.Lugovaya, and T.I.Khomenko, "Trudy VI Chtenii, Posvyashchennykh Razrabotke Nauchnogo Naslediya i Razvitiyu Idei K.E.Tsiolkovskogo (Kaluga 9–13 Sentyabrya 1971 g.)" [Data presented in the VIth Series of Lectures Devoted to the Development of the Scientific Heritage and Ideas of K.E.Tsiolkovskii (Kaluga, 9–13, September, 1971)], Moscow, 1972, p.22.
69. K.Fujino and J.Kobayashi, Nippon Kagaku Kaishi, **12**, 2282 (1972).
70. K.Fujino and J.Kobayashi, Nippon Kagaku Kaishi, **12**, 2992 (1972).
71. A.H.Weiss, V.A.Seleznev, and R.Partridge, "Catalysis in Organic Synthesis", Acad.Press, New York, 1977, p.153.
72. A.H.Weiss, V.A.Seleznev, M.M.Sakharov, J.B. Gorokhovatsky, and N.P.Evmenenko, J.Catalysis, **48**, 354 (1977).
73. A.A.Berlin, O.V.Krylov, and Yu.E.Sinyak, Izv. Akad.Nauk SSSR, Ser.Khim., 1679 (1970).

74. A.A.Berlin, O.V.Krylov, and Yu.E.Sinyak, Kosmicheskaya Biologiya i Meditsina, No.1, 33 (1971).
75. A.H.Weiss, R.B.LaPierre, and J.Shapira, J.Catalysis, **16**, 332 (1970).
76. H.Tambawala and A.H.Weiss, J.Catalysis, **26**, 338 (1972).
77. S.A.Balezin, Zhur.Obshch.Khim., **17**, 2288 (1947).
78. R.D.Partridge and A.H.Weiss, J.Chromatrog.Sci., **8**, 553 (1970).
79. H.Tambawala and A.H.Weiss, J.Chromatog.Sci., **10**, 120 (1972).
80. R.Breslow, J.Amer.Chem.Soc., **80**, 3719 (1958).
81. R.Breslow, Tetrahedron Lett., 22 (1959).
82. A.H.Weiss and T.John, J.Catalysis, **32**, 216 (1974).
83. T.Matsuure and M.Kato, Chem.Eng.Sci., **22**, 171 (1967).
84. A.A.Morozov and O.E.Levanevskii, Kinetika i Kataliz, **14**, 793 (1973).
85. A.A.Morozov and O.E.Levanevskii, Dokl.Akad.Nauk SSSR, **216**, 350 (1974).
86. A.N.Surzhenko, G.P.Kornienko, and Ya.B.Gorokhovatskii, All-Republic Inter-Departmental Symposdium, "Kataliz i Katalizatry" (Catalysis and Catalysts), Izd.Naukova Dumka, Kiev, 1971, No.8, p.81.
87. Ya.B.Gorokhovatskii, A.N.Surzhenko, E.A.Shamanskaya, and N.P.Evemenenko, Kinetia i Kataliz, **17**, 942 (1976).
88. Ya.B.Gorokhovatskii and N.P.Evmenenko, Dokl. Akad.Nauk SSSR, **227**, 133 (1976).
89. G.P.Kornienko, A.N.Surzhenko, Ya.B.Gorokhovatskii, Yu.E.Sinyak, and V.A.Uspenskaya, Kinetika i Kataliz, **13**, 977 (1972).
90. Ya.B.Gorokhovatskii, N.P.Evmenenko, and V.F. Gaevskii, Kinetika i Kataliz, **18**, 558 (1977).
91. Yu.K.Glotova and N.S.Enikolopyan, Kinetika i Kataliz, 11, 41 (1970).
92. Yu.K.Glotova, V.I.Irzhak, and N.S.Enikolopyan, Kinetika i Kataliz, **14**, 1419 (1973).
93. Yu.K.Glotova and V.I.Irzhak, Izv.Akad.Nauk SSSR, Ser.Khim., 1284 (1974).
94. Yu.K.Glotova and N.S.Enikolopyan, Izv.Akad.Nauk SSSR, Ser.Khim., 1159 (1969).
95. Yu.K.Glotova and V.I.Irzhak, Izv.Akad.Nauk SSSR, Ser.Khim., 2804 (1972).
96. Yu.K.Glotova and V.I.Irzhak, Izv.Akad.Nauk SSSR, Ser.Khim., 1134 (1973).
97. Yu.K.Glotova, Candidate's Thesis, Institute to Chemical Physics of the USSR Academy of Sciences, Chernogolovka, 1973.
98. T.Nakai, N.Tsujigado, and S.Sato, Nippon Nogei Kagaku Kaishi, **43**, 300 (1969).
99. T.Mizuno, Kagaku To Seibutsu, **10**, 314 (1972).
100. T.Mizuno, Kagaku No Ryoiki, **26**, 762 (1972).
101. T.Mizuno and M.Asai, Nippon Nogei Kagaku Kaishi, **45**, 344 (1971).
102. T.Mizuno and M.Asai, Nippon Nogei Kagaku Kaishi, **46**, 73 (1972).
103. T.Mizuno, Report of the Faculty of Agriculture, Shizucka University, **24**, 49 (1974).
104. Y.Shigemasa, M.Shimao, C.Sakazawa, and T.Matsuura, Bull.Chem.Soc.Japan, **48**, 2099 (1975).
105. Y.Shigemasa, T.Fujitani, C.Sakazawa, and T.Matsuura, Bull.Chem.Soc.Japan, **50**, 1527 (1977).
106. Y.Shigemasa, M.Shimao, C.Sakazawa, and T.Matsuura, Bull.Chem.Soc.Japan, **50**, 2138 (1977).
107. Y.Shigemasa, O.Nagae, C.Sakazawa, R.Nakashima, and T.Matsuura, J.Amer.Chem.Soc., **99**, 1309 (1977).
108. G.Harsch, W.Voelter, and H.Bauer, Z.Naturforsch., **32**, 826 (1977).
109. G.Guillot, I.Sadet, and P.Rumpf, Bull.Soc.chim. France, 2393 (1972).
110. R.Mayer and L.Jaschke, Annalen, **635**, 145 (1960).
111. T.I.Khomenko and O.V.Krylov, Kinetika i Kataliz, **15**, 625 (1971).
112. T.I.Chomenko, O.Z.Golovina, M.M.Sakharov, O.V. Krylov, R.D.Partridge, and A.H.Weiss, J.Catalysis, **45**, 356 (1976).
113. T.I.Khomenko, Candidate's Thesis, Institute of Chemical Physics of the USSR Academy of Sciences, Moscow, 1977.
114. R.D.Partridge, T.I.Khomenko, O.A.Golovina, M.M. Sakharov, A.H.Weiss, and o.V.Krylov, Kinetika i Kataliz, **18**, 557 (1977).
115. O.A.Golovina and T.I.Khomenko, Kinetika i Kataliz, **18**, 556 (1977).
116. O.A.Golovina, T.I.Khomenko, M.M.Sakharov, O.V. Krylov, A.A.Berlin, Yu.E.Sinyak, and V.P.Masenko, Izv.Akad.Nauk SSSR, Ser. Khim., 195 (1978).
117. M.Dixon and E.C.Webb, "Enzymes" (Translated into Russian), Inostr.Lit., Moscow, 1961, p.233.
118. T.I.Khomenko, O.Z.Golovina, M.M.Sakharov, O.V. Krylov, R.D.Partridge, and A.H.Weiss, "Tezisy Dokladov VI Vsesoyuznoi Konferentskii po Khimii i Biokhimii Uglevodov" (Abstracts of Reports at the VIth All-Union Conference on the Chemistry and Biochemistry of Carbohydrates), Izd.Nauka, Moscow, 1977, p.93.
119. A.H.Weiss, Kinetika i Kataliz, **18**, 539 (1977).
120. S.B.Ziemecki, R.B.LaPierre, A.H.Weiss, and M.M. Sakharov, J.Catalysis, **50**, 455 (1977).
121. N.Roy and A.K.Mitra, Carbohydr.Res., **24**, 175 (1972).
122. N.N.Maslovich, T.I.Khomenko, O.A.Golovina, A.L. Buchachenko, and M.M.Sakharov, Izv.Akad.Nauk SSSR, Ser.Khim., 1631 (1978).
123. R.Biebler and G.Trimpler, Helv.Chim.Acta, **30**, 1860 (1947).
124. C.K.Ingold, "Theoretical Principles of Organic Chemistry" ["Structure and Mechanism in Organic Chemistry"] (Translated into Russian), Izd.Mir, Moscow, 1973.
125. T.I.Khomenko, V.P.Lezina, A.U.Stepanyants, M.M. Sakharov, O.A.Golovina, and O.V.Krylov, Kinetika i Kataliz, **17**, 911 (1976).
126. V.A.Likholobov, A.H.Weiss, and M.M.Sakharov, React.Kinetics and Catalysis Letters, **8**, 155 (1978).
127. G.C.Akerlof and P.W.Mitchell, J.Spacecraft., **1**, 203 (1964).
128. V.Johnson, A.J.Carlson, and A.Johnson, Amer.J. Physiol., **103**, 517 (1933).
129. G.Freund, Arch.Inst.Med., **121**, 123 (1968).
130. N.A.Vasyunina, A.A.Balandin, and R.L.Slutskin, Dokl.Akad.Nauk SSSR, **169**, 1077 (1966).
131. K.Schoenemann, A.Apel, and E.Berger, German P. 725842 (1942); Chem.Abs., **37**, 5984 (1943).
132. W.E.Hanford, US P.2209055 (1940); Chem.Abs., **35**, 135 (1941).
133. A.F.Lean and A.L.Stautzenberger, US P. 2775621 (1956); Chem.Abs., **51**, 8781 (1957).
134. A.H.Weiss, R.D.Partridge, H.Tambawala, J.A. Shapira, DECHEMA Monogr., **68**, 239 (1971); Chem. Abs., **76**, 59923 (1972).
135. G.Van Ling, J.C.Buijterman, and J.C.Vlugter, Carbohydr.Res., **4**, 380 (1967).

136. G.Van Ling and J.C.Vlugter, J.Appl.Chem., **19**, 43 (1969).
137. T.Mizuno and A.H.Weiss, Adv.Carbohydr.Chem., **29**, 173 (1974).
138. J.Shapira, J.Agr.Food.Chemistry, **18**, 922 (1970).
139. H.B.Chermside, A.Gill, A.Furst, and J.Shapira, Proc.West.Pharmacol.Soc., **14**, 112 (1971).
140. V.M.Kaganov, "Belkovye Drozhzhi i Ikh Premenenie v Pishchu" (Protein Yeasts and Their Applications in Food), Medgiz, Moscow, 1944.
141. O.V.Krylov, Yu.E.Sinyak, A.A.Berlin, M.A.Lobanova, and I.L.Shul'gina, "Tezisy Dokladov VI Vsesoyuznoi Konferentskii po Khimii i Biokhimii Uglevodov" (Abstracts of Reports at the VIth All-Union Conference on the Chemistry and Biochemistry of Carbohydrates), Izd.Nauka, Moscow, 1977, p.65.

Institute of Chemical Physics,
USSR Academy of Sciences,
Moscow

Translated from *Uspekhi Khimii*, **49**, 1106-1135 (1980) U.D.C. 547.921

Photoageing of Aliphatic Polyamides

A.L.Margolin and L.M.Postnikov

The primary photophysical and photochemical processes in the amide group of polyamides and certain individual amides are examined. The mechanisms of the photolysis and photochemical oxidation of polyamides are analysed as a function of irradiation conditions. The problems of predicting the light stability of polyamides as well as the mechanisms of the stabilisation of polyamides with respect to the action of light and the sensitisation of their photochemical ageing are discussed. The bibliography includes 224 references.

CONTENTS

I. Introduction 585
II. Primary photoprocesses in aliphatic polyamides and model compounds 585
III. The formation of radicals in polyamides and in model compounds 588
IV. The mechanism of the photoageing of polyamides 588
V. Problems of controlled photoageing 595

I. INTRODUCTION

When used under natural conditions, polyamides (PA) decompose under the influence of sunlight over periods ranging from half a year to one year[1]. Since the annual manufacture of polyamides runs into millions of tons, the problem of their photochemical ageing is of practical importance. It includes a wide range of questions concerning the nature of the primary and secondary photochemical process responsible for the photochemical ageing, the mechanisms of chemical and structural changes in polyamides, their relation with the changes in the characteristics of their mechanical strength, and the mechanisms of the stabilisation of polyamides with respect to the action of light and the sensitisation of their photochemical ageing.

In the present review an attempt is made at a systematic account of the experimental data on the above questions. Reviews already exist on individual aspects of the problem of the ageing of polyamides[2-7].

II. PRIMARY PHOTOPROCESSES IN ALIPHATIC POLYAMIDES AND MODEL COMPOUNDS

1. Primary Photophysical Processes

In contrast to polymers (for example, polyolefins), in which photoageing can be induced solely by the absorption of light by the chromophoric groups of impurities or oxidation products[8] and in contrast to aromatic polyamides which exhibit an intense intrinsic ultraviolet absorption[9], aliphatic polyamides absorb extremely weakly[10-13] in the region where the absorption spectrum of the chromophoric amide group of the polyamide overlaps the spectrum of sunlight at the Earth's surface (Fig.1). In the study of light-induced transformations of polyamides, one must therefore take into account both the absorption of light by impurities and the intrinsic absorption of amides.

The amide group $-CO-N\langle$ in different compounds in liquid and solid solutions has two absorption bands corresponding to the $^1\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ and $^1\Gamma_{n\pi} \leftarrow {}^1\Gamma_1$ transitions[14-17]. The short-wavelength absorption band associated with the $^1\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ transition can be assigned to charge transfer from the nitrogen atom to the carbonyl group[18-20]. The introduction of electron-donating substituents at the nitrogen atom shifts the $\pi\pi^*$-absorption maximum towards longer wavelengths, while the introduction of electron-donating substituents at the carbon atom of the carbonyl group causes a hypsochromic shift. Thus, the energies of the $^1\Gamma_{\pi\pi^*}$ state for *N*-dimethylformamide $HCON(CH_3)_2$, formamide $HCONH_2$, and acetamide CH_3CONH_2 are 6.22, 7.16, and 7.48 eV respectively[20]. With increase of solvent polarity, the $\pi\pi^*$ absorption shifts towards longer wavelengths[21]. The polyamides PA-3, PA-4, PA-6, PA-6,6, PA-6,10† and polyglycine have a $\pi\pi^*$ absorption maximum at a wavelength $\lambda_{max} = 190$ nm in the solid state[22,23], while a solution of the copolymer PA-548 in methanol has an absorption maximum at 205 nm.

The long-wavelength absorption of the amide group ($^1L_{n\pi^*} \rightarrow {}^1\Gamma_1$ transition) has small extinction coefficients $\varepsilon < 100$ litre mol^{-1} cm^{-1}.[17] According to some estimates[24], $\varepsilon \cong 0.02$ litre mol^{-1} cm^{-1} at ~300 nm for specially pure amides. The $n\pi^*$ absorption maximum is in the range 210–240 nm; thus $\lambda_{max} =$ 208 nm for the $^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ transition of acetamide in water. A decrease of solvent polarity increases λ_{max} (Fig.1). The $n\pi^*$ absorption of the amide group in solid polyamides which are characterised by a low dielectric constant, should be similar to the absorption of solutions of *N*-alkylamides in hydrocarbons. Polyamides usually exhibit a more intense absorption in the long-wavelength region than in model compounds, which is evidently due to the absorption by impurities.

It has been shown that the isolated amide group does not fluoresce on excitation with light at wavelengths in the range $250 \leq \lambda \leq 300$ nm [24-26] in contrast to the amide group conjugated with an aromatic ring[27].

---

† The numerals indicate the numbers of carbon atoms between the NH groups in the repeating elements of the chain in the case of the homopolymer. For example, PA-6,6 and PA-6 are polyhexamethyleneadipamide $-(CH_2)_6NHCO(CH_2)_4.CONH-$~ and polycaproamide ~$-(CH_2)_5CONH-$~. The first of the two numerals separated by a comma characterises the amine component of the repeating unit, while the second numeral characterises the acid component. In naming mixed polyamides the numerals separated by an oblique stroke characterise components comprising the polymer. For example, PA-6,6/6,10/6 is the copolymer of ε-caprolactam ($\overline{(CH_2)_5CONH}$, the adipate of hexamethylenediamine $HOOC(CH_2)_4CONH(CH_2)_6.NH_2$, and the sebacate of hexamethylenediamine $HOOC(CH_2)_8.CONH(CH_2)_6NH_2$, known as PA-548.

The possibility of the phosphorescence of compounds with amide groups is controversial[24-26]. Larson et al.[25] investigated a large series of aliphatic amides and showed that the phosphorescence of these compounds (if it is observed after careful purification of the compounds) is very weak and is characterised by low quantum yields ($\Phi_p < 10^{-4}$–10^{-3}) and long lifetimes ($\tau_p > 0.1$ s); the phosphorescence spectrum depends on the excitation wavelength, which indicates the possibility of the phosphorescence of single crystals or of defects in vitrified solutions (the authors[25] used mainly EPA—mixtures of ether, pentane, and alcohol—as solvents). In another study[28] the phosphorescence of amides was not observed.

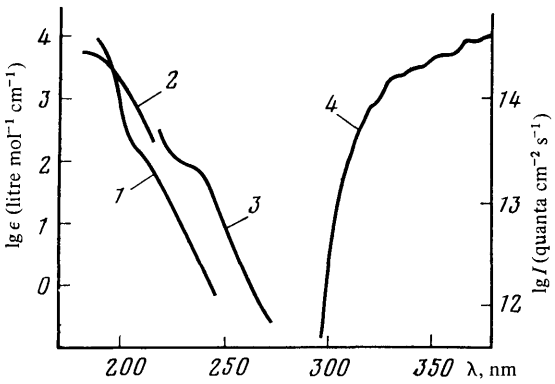


Figure 1. Ultraviolet absorption spectra[10-13] of acetamide solutions in water (curve *1*), of *N*-methylacetamide in cyclohexane (curve *2*), and of ε-caprolactam in n-heptane (curve *3*); curve *4* represents the spectrum of sunlight at the Earth's surface measured at 3 nm wavelength intervals (*I* represents the light intensity and ε is the extinction coefficient).

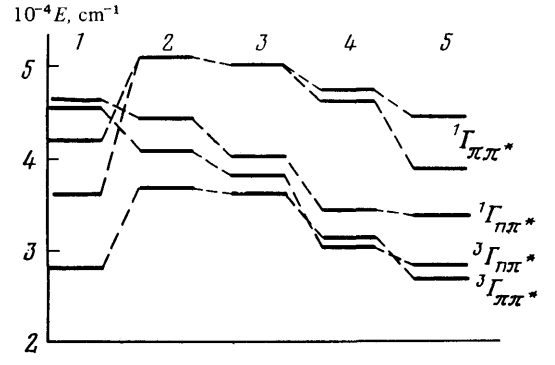


Figure 2. The energy levels (*E*) of the first electronically excited states of amides: 1) acetanilide ($\tau_p \approx 3$ s); 2) acetamide ($\tau_p > 0.1$ s, $\Phi_p < 10^{-4}$); 3) tetramethyloxamide ($\tau_p > 0.1$ s, $\Phi_p < 10^{-4}$); 4) dimethyloxamide ($\tau_p = 0.1$ s, $10^{-4} \leq \Phi_p < 10^{-3}$); 5) 1-isopropyl-5,5-dimethyl 2,3-dioxopiperazine ($\tau_p = 0.1$ s, $10^{-4} \leq \Phi_p < 10^{-3}$).

It has been concluded[24] that the amide group is responsible for the observed weak phosphorescence of vitrified alcoholic solutions of α,ω-polymethylenebishexaneamides having the general formula $C_5H_{11}CONH(CH_2)_nNHCOC_5H_{11}$, where $n = 3$, 4, 5, 6, 7, 8, or 12. The amides have been synthesised under special conditions in order to avoid contamination; subsequent purification of the substance did not affect the phosphorescence and the phosphorescence spectrum was independent of the excitation wavelength. Depending on the value of *n*, the maximum in the excitation spectra has been observed in the range from 280 to 294 nm, i.e. in the region where the amides hardly absorb. By analogy with the phosphorescence of an isolated –CO–O– group (in carboxylic acids and their salts, for example, in HCOONa), which also has no singlet–singlet absorption in the region corresponding to excitation[29], it has been suggested[24] that there is direct excitation of the amide group to the triplet as a result of the $^3\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ transition. Bellinger and Roberts[24] determined from the excitation and phosphorescence spectra the energy of the lowest triplet state of the amide group: $3.35 \leq E_{T_1} \leq 3.44$ eV.

Table 1. Characteristics of the phosphorescence observed in polyamides and model compounds (77 K).

Compound	Excitation λ, nm	Emission, λ_{max}, nm	$\lambda_{0,0}$, nm	τ_p, s	Refs.
N-Hexylhexanamide	300*	440	360	0.6	26
N,N-Bishexyladipamide	265*	415	360	0.2	26
1,6-Hexamethylenebishexanamide	285*	460	370	0.2	26
1,5-Pentamethylenebishexanamide	295*	440	360	0.4	24
1,3-Trimethylenebishexanamide	294*	443	360	0.6	24
Hexamethylenediamineadipate	280*	430	—	1.0	41
PA-6,6	280	410	—	2.2	41
PA-6,6	290*	410	—	2.0	42
PA-6,6	295*	400	~365	2.0	28
PA-6,6	280*	420	~370	2.1	37
PA-6	280*	435	—	1.4	37
PA-11	270*	445	—	0.9	37
PA-12	270	450	—	1.0	37

*The value of λ at the maximum in the excitation spectrum.

The changes in the ultraviolet absorption spectra and luminescence properties of molecules containing amide groups have been investigated[25,30,31] as a function of the nature of the conjugation of the amide group with another chromophore, particularly with one or two amide groups. As a result, it was possible to estimate approximately the sequence of the energy levels for an isolated amide group (in relation to acetamide) (Fig.2). It was found that the lowest excited state is the triplet $^3\Gamma_{\pi\pi^*}$. The $^3\Gamma_{\pi\pi^*}$ state is characterised by long lifetimes ($\tau_p > 0.01$ s) in relation to emission[32], which makes it possible to explain the low values of Φ_p. The phosphorescence of simple molecules can be observed if the vibrational levels of the $^3\Gamma_{\pi\pi^*}$ and $^3\Gamma_{n\pi^*}$ states are mixed, which leads to a decrease of τ_p (for example, in oxamides—Fig.2).

It has been concluded[22] that the luminescence of aromatic amides is caused by the influence of the aromatic ring, which reduces the probability of radiation-less transitions; the lowest triplet level of acetamide has been estimated[31] as $E_{T_1} = 4.6$ eV. As mentioned above[20], electron-donating substituents lower the energy of the $^1\Gamma_{\pi\pi^*}$ level by ~1 eV. Under conditions where the ST-splitting is retained, one may expect that the $^3\Gamma_{\pi\pi^*}$ level of N-alkylamides (modelling the PA chain) has an energy $E_{T_1} \cong 3.6$ eV, which agrees best with the estimate $E_{T_1} \cong 3.4$ eV.[24,30,33]. It is interesting to note that similar values $E_{T_1} = 3.2$–4.0 eV have been found for the lowest $^3\Gamma_{\pi\pi^*}$ level of the –CO–O– group, which has the same number of electrons as in the –CO–NH– group[30].

Table 1 presents for comparison the parameters of the phosphorescence spectra of polyamides[28,34–44] and model compounds[24,26]. The authors of all the investigations noted that the phosphorescence observed in polyamides can be induced by impurities. It has been suggested[41] that the phosphorescence in PA-6,6 is caused by the polymer oxidation products formed under the polymerisation conditions, because, with increase of the degree of polymerisation, the intensity of the phosphorescence rises and its maximum shifts towards shorter wavelengths with a simultaneous increase of the phosphorescence lifetime. However, on thermal oxidation of PA-6 at 180 °C, a bathochromic shift of the phosphorescence λ_{max} is observed with a simultaneous decrease of the phosphorescence intensity[43].

The change in the characteristics of the phosphorescence on passing from amides to polyamides can be accounted for by the intrinsic phosphorescence of polyamides. It is known[21] that the state of aggregation of a substance has almost no influence on the energy of the triplet level. Similar values of $\lambda_{0,0}$ for amides and polyamides therefore show that the energy of the luminescent state in PA is equal to the energy of the $^3\Gamma_{\pi\pi^*}$ level of the amide group. Polar solvents increase the phosphorescence intensity, because they decrease the degree of association of the aromatic amide molecules[27] or molecules containing the –CO–O– group[29], which reduces the probability of radiationless processes. With decreased probability of radiation less deactivation, the lifetime of the excited state τ_p approaches the limiting lifetime τ_p^0 corresponding to emission in the absence of radiation less deactivation. In the amorphous regions of the polyamide specimen the association of the amide groups in the macromolecular chain is less effective than in solutions of model amides. This is the reason for the appearance of non-associated amide groups, for which the lifetime of the excited state τ_p is close to τ_p^0. Indeed, in model compounds $\tau_p = 0.2$–0.6 s whereas in polyamides $\tau_p \cong 2$ s; the increase of phosphorescence intensity on passing from amides to polyamides is associated with this factor. Thus the available experimental data do not rule out the possibility of both an intrinsic phosphorescence of polyamides and the possibility of the "superposition" on the latter of the phosphorescence due to impurities and oxidation products.

Polyamides frequently exhibit a fluorescence[37,39,41,45], which is characterised by values of λ_{max} of 365 and 445 nm in excitation and fluorescence spectra respectively. Evidently, the fluorescence of polyamides is due to impurities. The most probable impurities can be the products of the oxidation of polyamides and the initial monomers[39].

2. Primary Photochemical Processes

In the early studies on the photochemistry of polyamides and model compounds a wide variety of reactions was proposed as the possible primary photochemical processes in amides:

$$\mathrm{R(CH_2)_3CONHCH_2CH_2R'} \xrightarrow{h\nu} \begin{cases} \rightarrow \mathrm{R(CH_2)_3\dot{C}O + \dot{N}HCH_2CH_2R'}, & (1) \\ \rightarrow \mathrm{R(CH_2)_3CONH\dot{C}HCH_2R' + \dot{H}}, & (2) \\ \rightarrow \mathrm{R(CH_2)_3C\dot{O}NH + \dot{C}H_2CH_2R'}, & (3) \\ \rightarrow \mathrm{R(CH_2)_3NHCH_2CH_2R' + CO}, & (4) \\ \rightarrow \mathrm{RCH{=}CH_2 + CH_2CONHCH_2CH_2R'}, & (5) \\ \rightarrow \mathrm{RCH_2CH{=}CH_2 + HCONHCH_2CH_2R'}, & (6) \\ \rightarrow \mathrm{R(CH_2)_3CONH_2 + CH_2{=}CHR'}, & (7) \\ \xrightarrow{\text{amide}} \mathrm{R(CH_2)_3\dot{C}(OH)NH(CH_2)_2R' + R(CH_2)_3CONH\dot{C}HCH_2R'} & (8) \end{cases}$$

($\dot{R}$ and $\dot{R}'$ are alkyl radicals or terminal alkyl macroradicals).

Reactions (5)–(8) have been suggested[46,47] by analogy with the Norrish type II and III reactions, i.e. reactions involving intramolecular and intermolecular abstraction of a hydrogen atom by the oxygen atom of the carbonyl group in ketones in an electronically excited state[10]. The data concerning the nature of the excited state of the amide group suggest that reactions (5)–(8) are unlikely owing to the differences in the nature of the excitation of the carbonyl and amide groups. Thus in formaldehyde the $n\pi^*$ excitation is accompanied by the transfer of a charge of 0.64e from the oxygen atom to the carbon atom[32]. The decrease of electron density at the oxygen atom promotes the abstraction of a hydrogen atom. The $\pi\pi^*$ excitation in formamide is accompanied by the transfer of a charge of 0.7e from the nitrogen atom to the carbon atom, while the electron density at the oxygen atom remains almost unchanged[17]. The oxygen atom of the amide group in the $^3\Gamma_{\pi\pi^*}$ state does not therefore exhibit an enhanced reactivity in respect of abstraction reactions. (There is evidence[48] that on $n\pi^*$ excitation, the main contribution to absorption comes from the transfer of a non-bonding electron from an atomic orbital of nitrogen to the π orbital of the amide.)

It has been shown experimentally[49] that Norrish type II and III processes do not occur in the photolysis of N-alkylpyrrolidinones and N-alkylamides[50]. The products of reactions (5)–(7) have been detected in extremely small amounts on irradiation of N-alkylamides[46], PA-6,6, and PA-6.[51]

Investigators of the photochemical oxidation of amides[11] and polyamides[3,51] put forward reactions (2) and (3) to account for the formation of products with terminal amide groups and hydrogen. Estimates have shown[52] that the quantum yield of hydrogen formed via reaction (2) is extremely low ($\Phi_2 < 7 \times 10^{-5}$). The large yields of hydrogen, usually observed in the photolysis of amides and polyamides, have been explained by the photolysis of the products, since, with increase of the degree of photochemical reaction, the rate of accumulation of H_2 also increases significantly[52,53]. It is difficult to determine the probability of reaction (3), since unsubstituted amides have not been detected in the photolysis of N-alkylamides[53] and, as will be shown below, the main pathway leading to the formation of unsubstituted amides in photochemical oxidation involves oxidation processes.

Since the excitation of the amide group entails a partial separation of electrons forming the amide bond, presumably the most probable reaction of the amide group in an electronically excited state is dissociation of the amide linkage [reaction (1)]. Reaction (4) can be regarded as a result of reaction (1), which is followed by the elimination of CO from the acyl group and recombination of the amino and alkyl radicals in the cage.

In aromatic amides the photodissociation of the amide bond is the main primary process, which proceeds with a high quantum yield ($\Phi_1 = 0.25$).[54,55] The reverse reactions of the

acyl and amine radicals reduce the quantum yield of the photochemical reaction to 0.13 when acetanilide is irradiated in cyclohexane. High values of Φ_1 have also been observed for aliphatic amides: when *N*-alkylpyrrolidinones are irradiated in alcoholic solutions, $\Phi_1 = 0.02-0.1$ depending on the substituent[49,50], while on photolysis of *N*,*N*-dialkylamides in cyclohexane and dioxan, $\Phi_1 = 0.1-0.15$.[56] In the photolysis of solid PA-6 [7] the quantum yield of the radicals which have emerged from the cage as a result of reaction (1) is 0.01.

The primary photochemical process in both aromatic and aliphatic amides is apparently the photodissociation of the peptide bond. This conclusion does not rule out the occurrence of a multiplicity of other reactions which proceed at a significantly lower rate and give rise to a set of a wide variety of secondary products. Thus analysis of the products of the photolysis of polyamides[46,51,57-61] indicates approximately identical probabilities for the dissociation of all the C–C bonds of the polyamide and the possibility of a non-radical decomposition via reaction (5). The evolution of small amounts (less than 1% of the main volatile products—H_2 and CO) of hydrocarbons (ethane, ehtylene, propane, and propene) has also been observed in the photolysis.

The formation of the photochemical oxidation products from polyamides[2,7,62-66] has been explained by the dark reactions of radicals and by secondary photochemical processes.

III. THE FORMATION OF RADICALS IN POLYAMIDES AND IN MODEL COMPOUNDS

The results of studies by Refikov and coworkers[58], who first observed the EPR spectrum of PA-6 irradiated by ultraviolet light, indicate a radical mechanism of the photoageing of polyamides. The EPR spectrum of a single radical $RCONH\dot{C}HR'$, which we shall designate by $\dot{P}_1$, has been observed for γ-irradiated PA-6.[67] However, the EPR spectra observed on ultraviolet irradiation of polyamides are very complex and are poorly resolved, which hinders their interpretation. The situation is complicated by possible photochemical reactions of free radicals[68], which absorb light very strongly. Thus the ultraviolet spectrum of the radical P_1 has two absorption maxima[69,70]—in the regions 245–248 and 350 to 380 nm with extinction coefficients of 7000 and 2000 litre mol^{-1} cm^{-1} respectively[71]. Under the influence of light at the above wavelengths, the radicals $\dot{P}_1$ readily undergo secondary photochemical reactions[72]. The radicals $\dot{P}_1$ are therefore most conveniently observed either in the presence of photoinitiating additives[73-76], which react under the influence of light with $\lambda > 380-400$ nm, or in the absence of light, when polyamides are acted upon by high-energy radiations[72,77-79], or under mechanical degradation[80,81]. Thus the concentration of $\dot{P}_1$ can reach 0.04 mol kg^{-1} on γ-irradiation of PA-6 at 30 °C.[82]

The photochemical reactions of the radicals in PA-6 films with added iron(III) chloride have been investigated[73-76]. The radicals were initiated by reactions (9) and (10) involving the abstraction of a hydrogen atom from the PA-6 molecule (P_1H) by a chlorine atom with formation of either the radical $\dot{P}_1$ or the radical $RCONHCH_2\dot{C}HR'$ ($\dot{P}_2$). Almost all the radicals detected were identified and the sequence of their formation was found:

$$Cl + P_1H \longrightarrow \dot{P}_1 + HCl \quad , \tag{9}$$

$$Cl + P_1H \longrightarrow \dot{P}_2 + HCl \quad , \tag{10}$$

$$\dot{P}_1 + h\nu \xrightarrow{\lambda \approx 365\ nm} R\dot{C}O + NH{=}CHCH_2R' \quad , \tag{11}$$

$$\dot{P}_1 + h\nu \xrightarrow{\lambda \approx 365\ nm} \dot{P}_2 + P_1H \quad , \tag{12}$$

$$R\dot{C}O + h\nu \xrightarrow{\lambda > 365\ nm} \dot{R} + CO \quad , \tag{13}$$

$$\dot{R} + P_1H \xrightarrow{T \approx 77K} RH + \dot{P}_1 \quad , \tag{14}$$

$$\dot{R} + P_1H \xrightarrow{T \approx 77K} RH + \dot{P}_2 \quad , \tag{15}$$

$$\dot{P}_2 + P_1H \xrightarrow{T > 150K} P_1H + \dot{P}_2 \quad , \tag{16}$$

$$R\dot{C}O + P_1H \xrightarrow{T \approx 273K} RCHO + \dot{P}_1 \quad . \tag{17}$$

The concentration of $\dot{P}_1$ is extremely low even under the conditions of sensitised photolysis owing to the important reactions (11) and (12); the accumulation of $\dot{P}_1$ becomes appreciable only on irradiation with light in the region of 313 nm, to which corresponds the minimum absorption. Measurements of the stabilities of the radicals $\dot{R}$, $\dot{P}_2$, $R\dot{C}O$, and $\dot{P}_1$ showed that they begin to disappear at appreciable rates at 117, 150, 273, and 300 K respectively. Thus the radical $\dot{P}_1$ shows the greatest thermal stability among the PA radicals identified; with increase of temperature, a quantitative conversion of various radicals into $\dot{P}_1$ via reactions (14)–(17) has been observed[73-76].

The EPR spectra of the radicals $R\dot{C}O$ or $\dot{R}$ have been observed in the non-sensitised photolysis of polyamides, which indicates the occurrence of reaction (1), involving the photolysis of the amide linkage, but the possibility of secondary photolysis hinders the interpretation of the EPR spectra[58,77,78,83-85].

In the presence of oxygen, the radicals $\dot{P}_1$, which accumulated during the mechanical degradation of polyamides are converted into the corresponding peroxy-radicals $P_1\dot{O}_2$.[80] An analogous reaction has not been observed in γ-irradiated PA-6 fibres following exposure to air[78]. The exposure of γ-irradiated thin (2–5 μm) PA-6 films to a O_2 atmosphere at room temperature leads to the rapid disappearance of $\dot{P}_1$, although peroxy-radicals are not then detected[86]. It has been suggested that the diffusion time of O_2 in the polyamide specimen is longer than the lifetime of the peroxy-radicals, so that the $P_1\dot{O}_2$ species are not formed in appreciable concentrations. On mechanical degradation, the radicals are formed on the surface of the specimen where diffusion-dependent limitations are insignificant.

Ultaviolet irradiation of PA-6 in air at room temperature led to the detection[87] of radicals of two types: $\dot{P}_1$ and the radical responsible for an unidentified singlet. Since films 80 μm were used for irradiation, one cannot rule out the possibility of the presence of $\dot{P}_1$ owing to the diffusion-dependent limitations to the photochemical oxidation.

The EPR spectra of the radicals in polyamides have also been discussed in other studies[88-90].

IV. THE MECHANISM OF THE PHOTOAGEING OF POLYAMIDES

1. The Mechanism of the Photolysis of Polyamides

When polyamides are irradiated with ultraviolet light at room temperature in the absence of O_2, the following reactions can take place[7]:

$$RCONHCH_2R' \xrightarrow{h\nu} \dot{R} + CO \quad (\Phi_{18} = 5 \cdot 10^{-4}) \quad , \tag{18}$$

$$RCONHCH_2R' \xrightarrow{h\nu} R\dot{C}O + \dot{N}HCH_2R' \quad (\Phi_1 = 5 \cdot 10^{-3}) \quad , \tag{1}$$

$$RCONHCH_2R' \xrightarrow{h\nu} \dot{P}_1 + \dot{H} \quad (\Phi_2 \leqslant 7 \cdot 10^{-6}) \quad , \tag{2}$$

$$\dot{R} + P_1H \rightarrow \dot{P}_1 + RH \quad , \tag{14}$$

$$R\dot{C}O + P_1H \rightarrow \dot{P}_1 + RCHO \quad , \tag{17}$$

$$R'CH_2\dot{N}H + P_1H \rightarrow \dot{P}_1 + R'CH_2NH_2 \quad , \tag{19}$$

$$\dot{H} + P_1H \rightarrow \dot{P}_1 + H_2 \quad , \tag{20}$$

$$\dot{P}_1 \xrightarrow{h\nu} \left\{ \begin{array}{l} \longrightarrow R\dot{C}O + NH{=}CHR' \\ \longrightarrow \dot{H} + RCON{=}CHR' \end{array} \right\} (\Phi_{11,21} \simeq 1) \quad , \qquad (11)$$

$$(21)$$

$$\dot{P}_1 + \dot{P}_1 \rightarrow P_1{-}P_1 \quad . \qquad (22)$$

Here $\dot{P}_1$ denotes the central macroradical RCONHĊHR′ and $\dot{R}$ and $\dot{R}'$ are the terminal alkyl macroradicals.

Reactions (1), (2), and (18) have already been discussed. Reactions (14), (17), (19), and (20) reflect the fact that different radicals are readily converted in polyamides into the more stable radical $\dot{P}_1$. Reaction (20) proceeds very efficiently (the minimum value of the rate constant is $k_{20} = 2 \times 10^{-3}$ litre mol^{-1} s^{-1}),[91] so that no other reactions of atomic hydrogen, for example, the recombination of H atoms, compete with it. Reaction (11) has been detected[76] by EPR. Reaction (21) cannot be detected by EPR, since the disappearance of the radicals $\dot{P}_1$ via reaction (21) leads to their regeneration via reaction (20). Nevertheless, evidence for the occurrence of reaction (21) has been obtained by comparing the photolysis products of deuterated and non-deuterated alanine peptides[92]. The rate of formation of H_2 in the photolysis of polyamides corresponds to a reaction order with respect to light intensity which is intermediate between the first and the second, which also indicates the formation of hydrogen in the photolysis of the radicals[52]. As a rule, the photolysis of the radicals proceeds with high quantum yields ($\Phi \simeq 1$).[68]

The cross-linking of polyamides on photolysis is explained by reaction (22), whose occurrence has been proposed by Zimmerman[70] on the grounds that the radical $\dot{P}_1$ is the most stable among all those present. The recombination of $\dot{P}_1$ with formation of a C–C bond is sterically impossible when there are free valences at the atoms of adjacent chains when the neighbouring amide groups are hydrogen-bonded[93]. The probability of cross-linking should therefore be greater in the amorphous regions of the polymer, where the hydrogen bonds are partly disrupted and where the radicals can migrate as a result of segmental diffusion or successive hydrogen atom abstraction reactions. Indeed polyamide copolymers with a degree of crystallinity lower than in PA-6,6 are cross-linked much more readily than the latter[93]. It has been noted that polyamides are cross-linked to a lesser extent than other polymers, for example, polyethylene[94–96]. Direct evidence for the occurrence of reaction (22) has been obtained in a study[97] where the formation of a C–C bond between the α-methylene groups adjoining the nitrogen atom was observed. We may note that cross-linking via the formation of C–N bonds has been observed by NMR in the thermal degradation of polyamides[98].

2. Model Polyamide Photochemical Oxidation Reactions

In the presence of oxygen, the composition of the products of the photochemical reactions of polyamides and low-molecular-weight *N*-alkylamides, which provide the most effective models of the polyamide chain, differ from the products characteristic of photolysis. Analysis of the composition of the photochemical oxidation products (as well as thermal oxidation products[99]) indicates the important role of the oxidative reactions of a single free radical, namely $\dot{P}_1$.

In the first study on the photochemical oxidation of model compounds[47] the products of prolonged (285 h) non-sensitised photochemical oxidation of *N*-pentylcaproamide at 38 °C were investigated and measurements were made of the absorption of oxygen; the different positions in the amide $C_4H_9{-}\overset{a}{C}H_2{-}\overset{b}{C}O{-}\underset{c}{N}H{-}CH_2{-}C_4H_9$ were labelled with ^{14}C. It was noted that CO is evolved from the α-methylene group adjoining the nitrogen atom (position *c*). When position *a* was labelled with ^{14}C, the only radioactive product was caproic acid, labelling of position *b* gave caproic acid and CO_2, while labelling of positions *c* gave valeraldehyde, valeric acid, CO, and CO_2. Substitution of the hydrogen atoms of the α-methylene group adjoining the nitrogen atom by methyl groups suppressed the photochemical oxidation. These findings led to the conclusion that amides are oxidised via a stage in which a hydrogen atom is abstracted from the α-methylene group with formation of the radical $\dot{P}_1$. In order to account for the composition of the final products, Sharkey and Mochel[47] postulated (by analogy with the oxidation of hydrocarbons) a mechanism in which the following reactions involving the radical $\dot{P}_1$ take place after reaction (1) and the exchange of primary radicals in dark processes:

$$\dot{P}_1 + O_2 \rightarrow P_1\dot{O}_2 \quad , \qquad (23)$$

$$P_1\dot{O}_2 + P_1H \rightarrow P_1OOH + \dot{P}_1 \quad , \qquad (24)$$

$$P_1OOH \rightarrow P_1\dot{O} + \dot{O}H \quad . \qquad (25)$$

The radicals $P_1\dot{O}$ and ȮH formed in the radical decomposition of the hydroperoxide [reaction (25)] lead to the reformation of the radical $\dot{P}_1$, giving rise at the same time to N_1-(1-hydroxyalkyl)amide (P_1OH), which is a precursor of the products detected—the unsubstituted amide, aldehydes, and acids.

It was found subsequently that the probability of the radical decomposition of P_1OOH is low. The amide hydroperoxide was isolated for the first time[100] in the oxidation of fused ε-caprolactam. The formation of the products of the decomposition of ε-hydroperoxycaprolactam, adipimide, and water indicated the occurrence of the non-radical decomposition $\overbrace{(CH_2)_4CONHC}(OOH)H \rightarrow \overbrace{(CH_2)_4CONHCO} + H_2O$. The addition of ε-hydroperoxycaprolactam did not accelerate the oxidation of caprolactam[101,102]. The polymerisation of diallyl phthalate cannot be initiated by the hydroperoxides of *N*-alkylamides at 131 °C over a period of 6 h, while the addition of di-t-butyl peroxide or dibenzoyl peroxide under the same conditions causes the formation of a polymer after 40 and 5 min respectively[103]. It has been shown by the inhibitor method that more than 97% of P_1OOH decomposes via a non-radical mechanism at 131 °C.[104]

Analysis of the products of the thermo- and photo-sensitised oxidation of 89 different *N*-alkylamides led to a mechanism[103–106] of the model oxidation of polyamides in which the $\dot{P}_1$ initiation stage and reactions (23) and (24) are followed by the processes

$$P_1OOH \rightarrow \delta\,(P_1\dot{O} + \dot{O}H) \xrightarrow{2P_1H} \delta\,(P_1OH + H_2O + 2\dot{P}_1) \quad , \qquad (25')$$

$$P_1\dot{O}_2 + P_1\dot{O}_2 \left\{ \begin{array}{l} \longrightarrow 2RCONHCOR' + H_2O_2 \quad , \\ \longrightarrow P_1OOP_1 + O_2 \quad , \\ \longrightarrow P_1OH + RCONHCOR' + O_2 \quad , \end{array} \right. \qquad (26)\ (27)\ (28)$$

$$P_1OH \rightarrow RCONH_2 + R'CHO \quad , \qquad (29)$$

$$P_1OOH \left\{ \begin{array}{l} \longrightarrow RCONHCOR' + H_2O \quad , \\ \longrightarrow RCONHCHO + R'OH \quad , \\ \longrightarrow RCONHCH{=}CHR' + H_2O_2 \quad , \\ \longrightarrow RCONH_2 + R'CHO \quad . \end{array} \right. \qquad (30)\ (31)\ (32)\ (33)$$

At low temperatures (below 100 °C) the chain propagation reaction (24) is insignificant: the main products are formed in reactions (26)–(28) involving the destruction of peroxy-radicals. In photochemical oxidation at 0 °C the hydroperoxide P_1OOH was not detected. The high activation energies for reaction (24) $E_D > 13$ kcal mol^{-1} also shows that the chain

propagation reaction is difficult at low temperatures. In thermal oxidation the chain length increases under the experimental conditions from three units at 70 °C to 20–30 at 130 °C, where the main product becomes the hydroperoxide; its decomposition via reactions (30)–(33) gives rise to the final set of stable products. The probability δ of the liberation of radicals from the cage in the decomposition of P_1OOH is extremely low ($\delta < 0.015$ at 130 °C). When the temperature is reduced and after passing from solutions to a solid polymer, a considerable decrease of δ is to be expected as a result of the decrease of the mobility of molecules.

A similar mechanism of the photosensitised non-chain oxidation of *N*-alkylamides at 30 °C has been proposed by other workers[107], who wanted to explain the formation of the main products by the recombination reactions of the peroxy-radicals $P_1\dot{O}_2$.

Having determined all the products of prolonged (685 h) non-sensitised photochemical oxidation of *N*-butylcaproamide and their proportion relative to the amount of oxygen absorbed, Lánska and Šebenda[11] showed that the principal products are the imide, unsubstituted amides, water, CO, CO_2, hydrocarbons, and carboxylic acids. Peroxides, aldehydes, butylamine, and H_2 are formed in significantly smaller amounts. Pyrrole derivatives were present in trace amounts; other products were not detected.

3. The Influence of Experimental Conditions on the Photochemical Oxidation

The differences in the conditions of the photochemical experiments lead to differences in the composition of the products of the photochemical oxidation of *N*-alkylamides and polyamides. Thus, the main products in the non-sensitised photochemical oxidation are acids, the unsubstituted amides $RCONH_2$ and $R'CONH_2$, and the volatile products CO, CO_2, etc., but *N*-formylamide RCONHCHO was not detected. In the sensitised photochemical oxidation *N*-formylamide was detected together with the main products—imides and unsubstituted amides, but acids and volatile products were not found. It is not possible to account for the above differences by the inadequacy of the analytical methods[11].

We believe that the dependence of the composition of the products on the method of photoinitiation can be explained by differences between the primary photochemical reactions, by the competition between photochemical and dark processes, and also by the competition between primary and secondary photochemical reactions. Whereas photoinitiation as a result of the rupture of the amide bond, leading to the formation of an acyl radical whose oxidation gives rise to acids, is more probable in the non-sensitised process, in the sensitised photochemical oxidation reactions involving the abstraction of a hydrogen atom from the α-methylene group adjoining the nitrogen atom and leading to the formation of $\dot{P}_1$ are more likely. In the absence of oxidation chains, the composition of the products is determined by the photoinitiation mechanism.

The oxidation products formed can be extremely unstable. Thus the slow formation of acetone has been observed[105] on storage in the dark of preirradiated *N*-isopropylamides even at 0 °C; the liberation of acetone ceased only after 26 h. One can therefore postulate that, after very prolonged irradiation (in non-sensitised photochemical oxidation the duration of irradiation amounts to hundred of hours, while in sensitised photochemical oxidation its duration is only 1–3 h), the dark processes in certain cases compete with the photochemical processes, which alters the proportions of the products.

Finally, competition between the absorption of light by the initiating chromophoric group and the oxidation products can play an extremely important role, because in the wavelength range of the light incident on the amide usually employed ($\lambda > 250$–260 nm) amides absorb extremely weakly ($\varepsilon_{PA} < 1$–3 litre mol^{-1} cm^{-1}), while the products have extinction coefficients ε_P greater by three–four orders of magnitude than the amides. By irradiating thick layers of the amide (as a rule >1 cm), it is possible to increase the role of the secondary photolysis, since by shielding the amide from light, the products formed decrease the amount of light which it absorbs. The use of photoinitiating additives makes it possible to reduce the role of secondary photolytic reactions.

In order to assess the role of secondary photolytic reactions in the nonsensitised photochemical oxidation of polyamides, one can use[7] the equation

$$[P]_{min} = \Phi_{form} K_{PA}/\varepsilon_P, \qquad (34)$$

where $[P]_{min}$ is the minimum concentration of the product for which the rates of its formation and consumption via secondary photolysis are equal, Φ_{form} is the quantum yield in the formation of the product, ε_P the extinction coefficient of the product, and $K_{PA} = \varepsilon_{PA}[PA]$ is the absorption coefficient of PA. At 254 nm we have $K_{PA} = 32$ cm^{-1} [108] and the quantum yield in the formation of radicals is $\Phi_{form} = 0.01$. Assuming that the extinction coefficient of the radicals $\dot{P}_1$ and $P_1\dot{O}_2$ is $\varepsilon_P \cong 7 \times 10^3$ litre mol^{-1} cm^{-1},[68,71] we find from Eqn.(34) that the photolysis of radicals under the influence of light at $\lambda = 254$ nm can be come appreciable at radical concentrations of $\sim 4 \times 10^{-5}$ mol kg^{-1}. Such radical concentrations are indeed observed, for example, in the irradiation of PA-6.[109] It is possible to determine similarly the concentrations at which the photolysis of peroxides, aldehydes, etc. becomes significant.

For the photoageing of polyamides sensitised by an additive D, Eqn.(34) can be written in the form

$$[P(sens)]_{min} = \Phi_{form}\varepsilon_D [D]/\varepsilon_P. \qquad (35)$$

Compounds whose extinction coefficients $\varepsilon_D \cong 10^4$ litre mol^{-1} cm^{-1}, and whose quantum yields for the formation of radicals are extremely high ($\Phi_{form} \cong 0.1$–1), are usually employed as the initiating additives. Evidently, by selecting a suitable sensitiser and its concentration, it is possible to reduce to zero the role of secondary photolytic reactions. In this case photoageing is determined solely by initiation and dark reactions.

An additional factor influencing the photochemical oxidation—diffusion-dependent limitations—appears in the photochemical oxidation of polyamides. Even in the liquid-phase oxidation diffusion-dependent limitations can play a significant role[110]. In solid polymers the diffusion coefficients of O_2 are several orders of magnitude smaller than in the liquid phase. The range of the permissible rates of oxidation of the polymer, where the diffusion of O_2 does not limit the reaction, is therefore restricted to more severe conditions. It has been found[7] that the oxidation must proceed in the kinetic region when

$$w < 10^{11}(P/L^2)p_{O_2}, \qquad (36)$$

where w is the rate of absorption of oxygen (mol litre^{-1} h^{-1}), P the constant of the permeability of the polymer to O_2#, L

The permeability constant P is expressed[111] in cubic centimetres, adjusted to the standard temperature and pressure, of the gas which has passed in 1 s through 1 cm^2 of the area of a membrane 1 mm thick when the pressure drop is 1 cmHg.

the thickness of the film or the diameter of the fibre (μm), and p_{O_2} is the partial pressure of oxygen (atm). The values of P for different polymers have been published[111]; $P = 3.8 \times 10^{-11}$ for PA-6 at 30 °C.

Examples of the influence of diffusion-dependent limitations on the photochemical oxidation of polyamides have been published in a number of communications[112-114] and discussed by Margolin et al.[7]

4. The Sequence of the Formation of Photochemical Oxidation Products

In the liquid-phase oxidation of hydrocarbons, the primary product is as a rule the hydroperoxide whose reactions determine both the initiation and the composition of the main products[110]. As shown above, the same situation obtains also in the oxidation of *N*-alkylamides at temperatures above 100 °C, but, when the temperature is reduced, the oxidation of *N*-alkylamides proceeds via a non-chain mechanism and the primary products arise from the recombination of peroxy-radicals. In polymers, the peroxy-radical recombination reaction is difficult owing to the restricted molecular ability; the radicals can therefore participate in other reactions leading to an increased chain length for oxidation[115]. The problem of the sequence of the polyamide photochemical oxidation products therefore requires special consideration.

The first study on the accumulation of peroxides in the photochemical oxidation of polyamides was carried out by Anton[64]. When PA-6,6 fibres are irradiated in air by light at $\lambda > 270$ nm, the concentration of peroxides increases from 1.7×10^{-3} to 4.2×10^{-3} mol kg^{-1} over a period of 60 h; the polymer is then almost completely decomposed long before the attainment of a steady-state concentration of peroxides. Under the influence of light at $\lambda > 300$ nm and also $\lambda > 340$ nm, the decrease in stability takes place at lower rates but peroxides accumulate almost as much as under the influence of light at $\lambda > 270$ nm. On illumination with light at $\lambda > 415$ nm, the decrease in the stability of the polyamide is not accompanied by an appreciable change in the concentration of peroxides. We believe that the results obtained show that the main pathway in the photochemical decomposition of polyamides is unrelated to the peroxide formation reaction under the given experimental conditions.

It is of interest to note that, in the radiation-induced oxidation of PA-6 [65,116] and model *N*-alkylamides[82], peroxy-radicals are converted via parallel pathways into peroxide, carbonyl, and carboxy-compounds, which has been explained by the non-chain oxidation of PA-6 at temperatures below 100 °C.

The results of studies[108,112-114,117-120] on the kinetics of the accumulation of the non-sensitised photoageing of polyamides under the influence of light at $\lambda = 254$ nm are presented in Fig. 3 and in Table 2. Table 2 shows that the main contribution to the photodecomposition of polyamides comes from oxidation processes. Thus the increase in the quantum yield for the chain dissociation process following an increase of the O_2 partial pressure indicates that, apart from the primary ruptures S_{prim} caused by the photolysis of the amide linkage [reaction (1)], secondary ruptures S_{sec}, due to oxidative processes, also arise. The formation of peroxides does not then constitute the only pathway in the photochemical oxidation. Separate experiments have shown[121] that, for concentrations in the range 0–0.02 mol kg^{-1}, peroxides do not initiate the photochemical oxidation of polyamides. The quantum

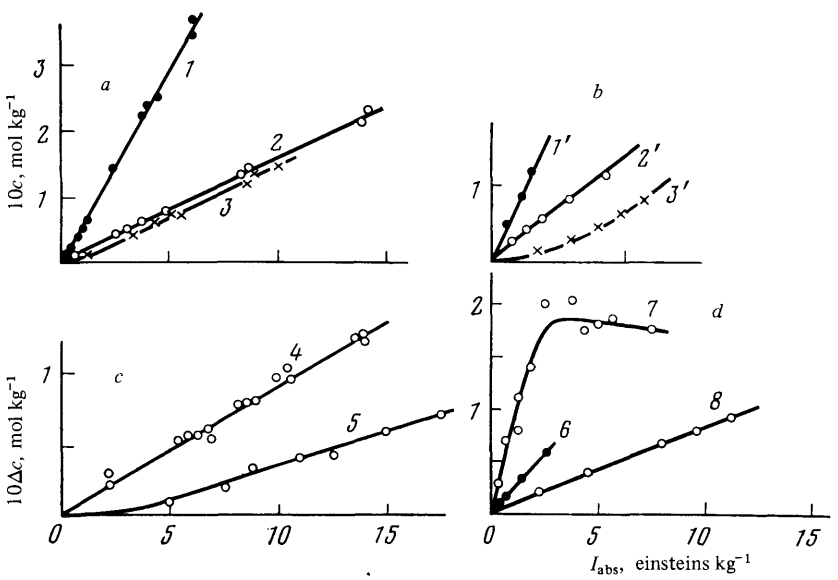


Figure 3. Photochemical oxidation of PA-6 and PA-548 films 3–6 μm thick under the influence of light at $\lambda = 254$ nm as a function of the irradiation dose I_{abs} at 25–30 °C: *a*) kinetic curves for the absorption of oxygen (curve *1*), the accumulation of breaks (curve *2*), and the evolution of CO (curve *3*) on irradiation of PA-6 (curves *1*–*3*) and PA-548 (curve *1*) in air; *b*) kinetic curves for the absorption of oxygen (curve *1'*), the accumulation of breaks (curve *2'*), and the evolution of CO (curve *3'*) on irradiation of PA-6 (curve *1'*) and PA-548 (curves *1'*–*3'*) in an O_2 atmosphere; *c*) kinetic curves for the accumulation of aldehydes (curves *4*) and carboxylic acids (curve *5*) on irradiation of PA-6 and PA-548 in air; *d*) kinetic curves for the accumulation of peroxy-compounds in air (curve *6*) and in an oxygen atmosphere (curve *7*) on irradiation of PA-548 and for the accumulation of pyrrole derivatives (curve *8*) on irradiation of PA-6 in air.

yields of a number of processes in PA-6 are identical with the yields of the corresponding processes in PA-548, which is explained by the fact that in both PA-6 and PA-548 the photoageing is caused by the absorption of light by the amide group.

A schematic sequence of the formation of products (the numbers over the arrows indicate the quantum yields of the corresponding processes in the photochemical oxidation of polyamides in air) has been proposed[7] on the basis of a comparison of the kinetic curves in Fig. 3:

Scheme I

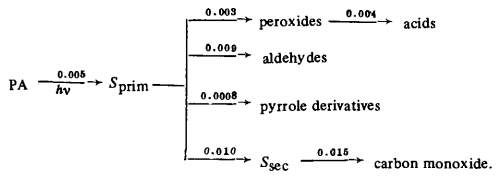


Table 2. The quantum yields of the photolysis and photochemical oxidation processes in the kinetic region on irradiation of PA-6 ($\lambda = 254$ nm; 25–30 °C).

Chemical process	Quantum yield of process (Ref.7)		
	photolysis	photochemical oxidation	
		air	oxygen
Formation of radicals	0,01[a]	—	—
Formation of carbon monoxide	$5\cdot10^{-4}$	0.015	0.030[c]
Formation of hydrogen	$7\cdot10^{-5}$	0.000[c]	0.000[c]
Ruptures in main PA chain	$5\cdot10^{-3}$[b]	0.015[c]	0.030[c]
Absorption of oxygen	—	0.060[c]	0.090[c]
Formation of carboxylic acids	$1.5\cdot10^{-4}$	0.004[c]	—
Formation of aldehydes	—	0.009[c]	—
Consumption of amino-groups	$1.5\cdot10^{-4}$	0.001[d]	—
Accumulation of peroxides	—	0.003[e]	0,007[e]
Accumulation of pyrrole derivatives	$2\cdot10^{-4}$[a]	0.0008	—

Note. [a]Estimate. [b]Estimated on the assumption that the primary process involves the dissociation of the amide bond. [c]The same value, within the limits of experimental error (10%), was obtained on irradiation of PA-548. [d]Determined from the initial rate of consumption of amino-groups. [e]Determined on irradiation of PA-548.

5. The Mechanisms of the Formation of the Products of the Photochemical Oxidation of Polyamides

The photoageing of polyamides is characterised by a large number of reactions, the relative rates of which depend on the experimental conditions. Since the same product can be formed in different reactions in the photoageing of polyamides, it is necessary to examine the possible mechanisms of the formation of the most important products: carboxylic acids, aldehydes, pyrrole and pyridine derivatives, peroxides, and carbon monoxide. Aparte from the composition of the products, in the study of the photoageing of polyamides one determines the number of breaks in the macromolecules and the decrease of stability, which, like the chemical products, characterise the process. Such processes, leading to the rupture of polyamide macromolecules and a decrease of the stability of polyamides, are examined below.

The formation of carboxylic acids. The formation of acids is attributed either to the oxidation of the acyl radical $R\dot{C}O$, which arises when the amide bond is ruptured[62], or to the oxidation (at advanced stages of the process) of aldehydes (Scheme II):[47]

Scheme II

$$R\dot{C}O + O_2 \rightarrow RC(O)O\dot{O} \quad , \tag{37}$$

$$RC(O)O\dot{O} + P_1H \rightarrow RC(O)OOH + \dot{P}_1 \quad , \tag{38}$$

$$RC(O)OOH \rightarrow RC(O)\dot{O} + \dot{O}H \quad , \tag{39}$$

$$RC(O)\dot{O} + P_1H \rightarrow RCOOH + \dot{P}_1 \quad , \tag{40}$$

$$RC(O)\dot{O} \rightarrow \dot{R} + CO_2 \quad , \tag{41}$$

$$2RC(O)OOH \rightarrow 2RCOOH + O_2 \quad , \tag{42}$$

$$R'CHO + RC(O)OOH \rightarrow R'COOH + RCOOH \quad , \tag{43}$$

$$RCHO + O_2 \rightarrow RCOOH \quad . \tag{44}$$

As in the oxidation of hydrocarbons[122], the radical decomposition of the peracid via reaction (39) hardly leads to the formation of acids owing to the rapid decomposition of the radical $RC(O)\dot{O}$ [reaction (41)], with which reaction (40) cannot compete ($k_{41}/k_{40} \cong 100$ at 85 °C). Therefore reactions (42) and (43), involving a non-radical transformation of the peracid, make the main contribution to the formation of acids and explain the low quantum yields in the formation of peroxides and acids in Scheme I. Reaction (39) should occur particularly effectively under the influence of light, resulting in the evolution of CO_2, as has been observed, for example, on irradiation of *N*-alkylamides by light at $\lambda > 300$ nm. However, in conformity with Eqn. (34) and the data in Fig. 3, the photolysis of the peracid at $\lambda = 254$ nm cannot compete with the dark reactions of the peracid, which agrees with the absence of CO_2 from the products and with the induction period with respect to the absorption of oxygen (Fig. 3, line *1*). At advanced stages of the photochemical oxidation the additional pathways leading to the formation of acids consist of photochemical and dark reactions of aldehydes and other oxidation products[11].

The formation of aldehydes. It has been suggested[7,11,123,124] that there is a possibility of the formation of aldehydes in parallel processes, which include the dark reactions of the radicals $R\dot{C}O$, $P_1\dot{O}_2$, and $P_1\dot{O}$ as well as the photochemical reaction of $P_1\dot{O}_2$ (Scheme III)

Scheme III

$$R\dot{C}O + P_1H \rightarrow RCHO + \dot{P}_1 \quad , \tag{17}$$

$$P_1\dot{O}_2 + P_1\dot{O}_2 \rightarrow P_1OH + RCONHCOR' + O_2 \tag{28}$$

$$\rightarrow RCONH_2 + R'CHO \quad , \tag{29}$$

$$P_1OOH \rightarrow P_1\dot{O} + \dot{O}H \quad , \tag{25}$$

$$P_1OOP_1 \rightarrow P_1\dot{O} + P_1\dot{O} \quad , \tag{45}$$

$$P_1\dot{O} + P_1H \rightarrow P_1OH + \dot{P}_1 \quad , \tag{46}$$

$$P_1\dot{O}_2 \rightarrow RCONHCHO + CH_2O + \dot{R}' \quad , \tag{47}$$

$$P_1\dot{O}_2 \xrightarrow{h\nu} RCONHCHO + R'\dot{C}HOH \quad , \tag{48}$$

$$P_1\dot{O}_2 + R'\dot{C}HOH \rightarrow RCONHCOR' + R'CHO + H_2O \quad . \tag{49}$$

The $P_1\dot{O}_2$ isomerisation reaction [reaction (47)] is significant only at high temperatures[123]. It has been suggested[7] that the photolysis of radicals via reaction (48) can lead to the formation of aldehydes in reaction (49).[124] The fact that, under the influence of light at $\lambda = 254$ nm, aldehydes are formed independently of peroxy-compounds makes it possible to rule out a significant contribution of reactions (25), (45), and (46) to the formation of aldehydes under the experimental conditions of Margolin et al.[7] However, under other irradiation conditions, these reactions may prove to be highly important.

The formation of pyrrole and pyridine derivatives. It has been suggested[65] that pyrroles are formed in the photochemical oxidation of PA-6,6 as a result of the condensation of dicarbonyl compounds with primary amines. Peebles and Hoffman[66] explained the formation of pyridine derivatives in the ageing of PA-6,6 and PA-10.6 by the condensation reactions of carbonyl compounds with the terminal amide groups and subsequent cyclisation. Owing to the structural characteristics of the molecule, in PA-6 the analogous reactions lead to pyrrole derivatives. The suggested derivatives explained to some extent the extremely low quantum yields in their formation (Scheme I).

The formation of peroxy-compounds. It is believed[2,7,11,47,100,101,103-107] that there is a possibility of the formation of five peroxy-compounds. There are peracids [reaction (38)], the hydroperoxide P_1OOH [reaction (24)], hydrogen peroxide [reactions (26) and (32)], the peroxide P_1OOP_1 [reaction (27)], and the terminal alkyl hydroperoxide of the type RCH_2OOH, which is formed on oxidation of the terminal alkyl radical. The above reactions result from processes involving different radicals and functional groups, which explains the dependence of the composition of the peroxy-products on the method of photoinitiation and temperature.

Breaks in the main polyamide chain and the formation of carbon monoxide. These can occur in the following reactions (Scheme IV):[7,11]

Scheme IV

$$P_1H \xrightarrow{h\nu} R'CH_2\dot{N}H + R\dot{C}O \quad , \qquad (1)$$

$$RCONHCOR' \xrightarrow{h\nu} \begin{cases} \longrightarrow RCO\dot{N}H + R'\dot{C}O \quad , & (50) \\ \longrightarrow R'CO\dot{N}H + R\dot{C}O \quad , & (51) \end{cases}$$

$$\dot{P}_1 \xrightarrow{h\nu} \begin{cases} \longrightarrow R'CH{=}NH + R\dot{C}O \quad , & (11) \\ \longrightarrow RCON{=}CHCH_2R'' + \dot{H} \quad , & (21) \end{cases}$$

$$P_1OOH \rightarrow RCONHCH{=}CHR'' + H_2O_2 \quad , \qquad (32)$$

$$RCON{=}\overset{\uparrow}{C}HCH_2R'' \xrightarrow{H_2O} \underset{RCONHCH=CHR''}{RCONH_2} + R'CHO \quad , \qquad (52)$$

$$P_1OOH \rightarrow RCONH_2 + R'CHO \quad , \qquad (33)$$

$$P_1\dot{O}_2 \rightarrow RCONHCHO + R''\dot{C}HOH \quad , \qquad (48)$$

$$P_1\dot{O}_2 + P_1\dot{O}_2 \rightarrow RCONH_2 + R'CHO + RCONHCOR' + O_2 \quad , \qquad (28)$$

$$P_1\dot{O} \rightarrow RCONHCHO + \dot{R}' \quad , \qquad (53)$$

$$P_1OOH \rightarrow RCONHCHO + R'OH \quad , \qquad (31)$$

$$P_1OOP_1 \rightarrow RCONHCHO + RCONHCOR' + R''CH_3 \quad , \qquad (54)$$

$$RCONHCHO \rightarrow RCONH_2 + CO \quad , \qquad (55)$$

$$RCHO \xrightarrow{h\nu} RH + CO \quad , \qquad (56)$$

$$R\dot{C}O \rightarrow \dot{R} + CO \quad . \qquad (18)$$

The secondary breaks can occur in the photolysis of imides [reactions (50) and (51)], alkyl radicals [reactions (11) and (21)], and peroxy-radicals [reaction (48)], as a result of the decomposition of peroxy-compounds [reactions (31)–(33) and (54)] and the radicals $P_1\dot{O}$ [reaction (53)], and the recombination of peroxy-radicals [reaction (28)]. The breaks in the polyamide macromolecules are accompanied by the evolution of CO either in the decomposition of acyl radicals [reaction (18)], or in the photolysis of aldehydes [reaction (56)], or in the decomposition of the unstable *N*-formylamide [reaction (55)][107,123]. At reduced temperatures the occurrence of reaction (55) under the influence of light is more likely. In this case it is analogous to the photolysis of aldehydes[10].

Scheme IV shows clearly that in the oxidation process all the reactions involving the rupture of the main polyamide chain lead ultimately to the formation of unsubstituted amides; the latter are obtained either directly in the dissociation reaction or on further reactions of the radicals and the unstable products formed when the chain is broken. In the oxidation process the number of breaks in the polyamide should therefore be close to the number of terminal amide groups obtained. The second product of the majority of dissociation reactions is an aldehyde or the oxidation product of the acyl radical—a peracid and an acid.

The photolysis of imides, which is significant at advanced stages of the oxidation process, leads to the rupture of the polyamide chain with formation of an unsubstituted amide and an aldehyde or acid in subsequent reactions. The unstable products of reactions (21) and (32) (enamides or their tautomers) lead to breaks via the formation of the intermediate P_1OH, the decomposition of which also gives rise to an unsubstituted amide and an aldehyde [reaction (52)]. The most probable product of the oxidation of the amino-radical, formed in reaction (1), is a primary amide.

The mechanism of reaction (53), involving the decomposition of the radical $P_1\dot{O}$, has been formulated by analogy with the decomposition reaction of secondary alkoxy-radicals, which usually constitutes the main pathway in their transformation on oxidation of hydrocarbons[110]. There is no reason to believe that the radicals $P_1\dot{O}$ are less reactive in the decomposition reactions. On the other hand, the reactivity of the radicals $P_1\dot{O}$ in the reactions involving the abstraction of a hydrogen atom should be lower than for alkoxy-radicals owing to the influence of the nitrogen atom, which increases the electron density around the oxygen atom. The analogous influence of the nitrogen atom leads to an appreciable diminution of the reactivity of the radical $\dot{P}_1$ compared with alkyl radicals. The formation of $P_1\dot{O}$ is most probable in the photolysis of peroxides.

The wide variety of alternative reactions leading to the formation of the same products via different pathways provides an idea of the complexity of the mechanism of the photochemical oxidation of polyamides in which particular reactions occur depending on the experimental conditions and the ratios of the final products differ very widely. In photochemical oxidation, where virtually all the alkyl radicals are converted into peroxy-radicals, reactions (11) and (21) are insignificant. At reduced temperatures, where the photochemical oxidation of polyamides is a non-chain process, one can neglect the contribution of the hydroperoxide decomposition reactions (31)–(33) to the chain dissociation processes. However, there remains the possibility of the formation of the peroxides P_1OOP_1, whose pohotolysis can lead to chain breaks either via the formation of the radicals $P_1\dot{O}$ or via reaction (54).

In the sensitised photochemical oxidation it is possible to neglect the photolysis of the peroxy-radicals $P_1\dot{O}_2$ via reaction (48), since the principal breaks at reduced temperatures occur on recombination of $P_1\dot{O}_2$, according to the observations of Lock and Sagar[105]. In the non-sensitised photochemical oxidation of PA-6 under the influence of light at $\lambda = 254$ nm, for small extents of oxidation (Fig.3 and Table 2) when it is possible to neglect the photolysis of aldehydes but not the photolysis of peroxy-radicals, the quantum yields of the secondary dissociation processes and the formation of aldehydes and CO have similar values. Considering the possible dissociation reactions, these relative amounts of the products can be accounted for by the photolysis of the peroxy-radicals [reaction (18)], this being followed by the evolution of CO in the decomposition of *N*-formylamide via reaction (55) and the formation of an aldehyde on recombination of the radicals [reaction (49)].

In the non-sensitised photochemical oxidation under the influence of the total light of the PRK-2 lamp aldehydes undergo vigorous photolysis at advanced stages of the oxidation process, so that their yield is extremely low and that of CO is somewhat lower than the yield of unsubstituted amides[11]. Under these conditions, the imides are photolysed via reactions (50) and (51), which makes an additional contribution to the number of breaks, and the oxidation of acyl radicals to peracids and the subsequent photolysis of the latter lead to the evolution of CO_2. In the sensitised photochemical oxidation at reduced temperatures there is no evolution of CO, despite the formation of breaks, *N*-formylamide, and aldehydes, owing to the shielding effect of the sensitiser on the photolytic reactions of *N*-formylamide and the aldehyde [reactions (55) and (56)].

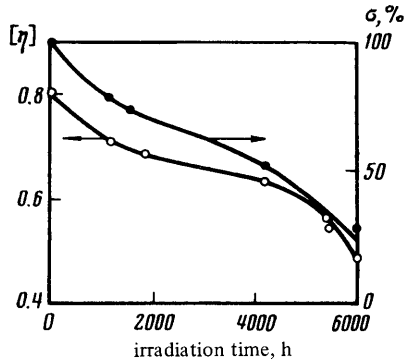


Figure 4. Photochemical ageing of PA-6.6 fibres under natural conditions {variation of the intrinsic viscosity (η) and of the loss of strength σ as a function of the duration of irradiation by sunlight with $\lambda > 300$ nm}.

6. The Decrease of the Strength of Polyamides

The impairment of the mechanical strength characteristics of polyamides on photoageing is associated with chemical processes[46]. For example, the simultaneous decrease of the tensile strength of the polymer and of its molecular weight are observed in the photoageing of PA-6,6 [46] (Fig.4).

In order to elucidate the nature of the strength of polyamides, the dependence of their lifetime τ on the applied load σ, described by Zhurkov's equation[126]

$$\tau=\tau_0 \exp[(U_0-\gamma\sigma)/kT], \qquad (57)$$

was investigated. For polyamides, the empirical parameters are $\tau_0 = 10^{-12}$ s and $U_0 = 45$ kcal mol^{-1}. The influence of the change of the molecular weight of the polyamide on the parameters τ_0, U_0, and γ has been investigated[127]. By irradiating PA-6 with different doses of ultraviolet light, the authors obtained specimens with different molecular weights; subsequently, the lifetimes of the specimens were measured in the dark. Preliminary irradiation affected only the parameter γ. A linear relation was observed[127] between $1/\gamma$ and the molecular weight and its theoretical validity was demonstrated[128]. Thus one may conclude that the breaks in the main polyamide chain lead to an increase of γ and hence to a decrease in the strength of the polymer.

The strength of the polyamide is influenced not only by the molecular weight of the polymer but also by the nature of the supermolecular structure. For example, the tensile strength of the highly oriented PA-6 is twelve times greater than that of the non-oriented material[129]. It follows from the theory[130–133] and has been confirmed by experiment[134], that $1/\gamma$ is directly proportional to the degree of extrusion. The structural changes in the photoageing of polyamides are observed as an increase in the density, the degree of crystallinity, and the surface microrelief; they are explained by the fact that the breaks in the main polyamide chain facilitate the movement of the macromolecules, which leads to more ordered structures[135–139]. Thus in this case too the breaks in the main polyamide chain lead ultimately to an alteration of the mechanical and stength characteristics of the polymer.

During use, polyamide articles can be subjected to different loads. The joint influence of the light intensity I and of the load σ, resulting in a decrease of the lifetime τ_I of the polyamide, has been investigated[140–143]. It has been shown that, for a certain load σ_{lim}, a characteristic break is observed in the experimental lg τ–σ linear plots:

$$\tau_I=\tau_0 \exp[(U_0-\gamma\sigma)/kT] \text{ for } \sigma>\sigma_{lim}; \qquad (58)$$

$$\tau_I=B(T)/IK\Phi_{0,s} \exp(m\gamma\sigma) \text{ for } \sigma<\sigma_{lim}, \qquad (59)$$

where K is the light absorption coefficient of the polyamide, m a constant coefficient, $\Phi_{0,S}$ the quantum yield of the dissociations in the main polyamide chain in the specimen not subjected to a load, and $B(T)$ a function which only slightly depends on temperature.

For $\sigma > \sigma_{lim}$, the action of light is weak compared with that of the load and can be neglected, so that the lifetime of the specimen is described by Zhurkov's equation (57). The quantity $\Phi_{0,S} \exp(m\gamma\sigma)$ is regarded as the quantum yield for dissociation in the molecules subjected to a load. It is believed that the increase of the quantum yield of the dissociation under the influence of the load occurs mainly as a result of the suppression of the cage recombination of the radicals formed on rupture of the macromolecule subjected to extending forces[144–150]. It is readily seen that the expression $IK\Phi_{0,S} \exp(m\gamma\sigma)$ in Eqn.(59) represents the number of breaks in the main polyamide chain. Thus for $\sigma < \sigma_{lim}$, the lifetime of the polyamide on irradiation in the loaded state is inversely proportional to the number of breaks.

The influence of ultraviolet irradiation and oxygen[142,143] and of nitrogen dioxide[151] on the lifetime of polyamide specimens subjected to a load has been investigated. In all the investigations a relation has been observed between the number of breaks in the main polyamide chain and the decrease of their strength. This relation makes it possible to regard the changes in the mechanical and strength characteristics as a result of chemical changes determined by the mechanism of the photoageing of the polyamide.

7. Kinetics of the Photochemical Oxidation of Polyamides

The kinetics of the destruction of macroradicals in polyamides of different structure have been studied[70,77,152,153]. It has been established that the destruction of macroradicals $\dot{P}_1$ is of second order with respect to concentration. The quadratic termination of macroradicals, including peroxy-radicals, has been observed in various polymers[154]. Presumably, peroxy-radicals $P_1\dot{O}_2$ in polyamides are also destroyed via a second-order reaction, as happens in the oxidation of model *N*-alkylamides[155,159].

The rate of photochemical oxidation of polyamides with quadratic termination can be represented by the expression

$$w = \frac{1}{2} w_{in} + (k_p/\sqrt{k_t})[P_1H]\sqrt{w_{in}}, \quad (60)$$

where $w_{in} \cong I$ is the rate of photoinitiation and k_p and k_t are the chain propagation and termination rate constants respectively.

Experiment shows[7] that the rates of absorption of O_2 and of accumulation of polyamide photochemical oxidation products under the influence of light at $\lambda = 254$ nm are proportional to the light intensity I at 20–30 °C and that with increase of temperature the order of the reaction based on the rate of initiation diminishes. Thus at 100 °C the rate of photochemical oxidation of PA-6 is proportional to $I^{1/2}$. These results can be accounted for by the absence of oxidation chains in the low-temperature oxidation owing to the unduly high rates of photoinitiation under the experimental conditions where it is possible to neglect the second term of the sum on the right-hand side of Eqn.(60). With increase of temperature, the photochemical oxidation at the same rates of photoinitiation acquires a chain mechanism as a result of the increase of $k_p/\sqrt{k_t}$.

It might have been supposed that the reaction is first order with respect to light intensity because it is a chain oxidation process with linear termination and that the decrease of the reaction order with increase of temperature is caused by a change in the termination mechanism. For long oxidation chains, the rate of absorption of O_2 determines the concentration of the radicals. It is known[70] that the efficiency of the destruction of macroradicals in polyamides depends very markedly on the supermolecular structure of the polymer. The dependence of the destruction of radicals on the supermolecular structure should influence also the rate of oxidation, as has been observed, for example, in the thermal oxidation of different polyamides[160] and other polymers[161]. However, it has been found that the rate of photochemical oxidation of PA-6 is independent of the degree of orientation and the degree of crystallinity of the specimen[162,163], which conflicts with the hypothesis of chain oxidation with linear termination.

At the same time, in the low-temperature non-sensitised photochemical oxidation of polyamides the rate of photochemical oxidation exceeds by a factor of nine the rate of the primary photoinitiation (Table 2). Under the experimental conditions, there is apparently additional initiation as a result of secondary photolysis. Indeed, a different relation between the rates of photochemical oxidation and photoinitiation is observed in the photochemical oxidation of polyamides sensitised by benzophenone under conditions where, according to Eqn.(35), secondary photolysis can be neglected[7]:

$$w \simeq w_{in} \simeq 0.11 \text{ mol kg}^{-1} \text{ h}^{-1}. \quad (61)$$

The parameter $k_p/\sqrt{k_t} = 2.7 \times 10^{-4}$ litre mol^{-1} s$^{-1/2}$ at 30 °C can be estimated from Eqns.(60) and (61); it is of interest to compare it with the kinetic parameters of the oxidation of model N-alkylamides and other compounds (Table 3).

The values of $k_n\sqrt{k_t}$ for different amides recalculated per reactive α-C–H, bond are similar and equal to $(0.2–0.3)\times10^{-4}$. On passing from low-molecular-weight amides to solid polyamides, the parameter $k_n\sqrt{k_t}$ increases by a factor of approximately 6. An analogous situation has been observed also for polypropylene and its low-molecular-weight analogue 2,4-dimethylpentane, mainly owing to the appreciable decrease of the termination rate constants k_t as a result of the limitation of molecular mobility on passing from the liquid phase to the solid polymer.

V. PROBLEMS OF CONTROLLED PHOTOAGEING

1. Prediction of the Resistance to the Action of Light

Prediction of the resistance to the action of light makes possible a fairly well-founded approach to the selection of the material for use under specific conditions. A direct prediction procedure is based on natural tests, which make it possible to estimate the time during which the useful properties of the polymer are retained when it is employed under natural conditions. The main operational property of polyamides is their strength. Therefore in tests of the resistance of polyamides to the action of light under natural conditions one investigates the changes in the mechanical strength characteristics. Fig.5 presents data[1] concerning the changes in relative elongation on rupture and of the ultimate tensile strength under conditions of natural photoageing of specimens of different polymers. Fig.5 shows that polyamides exhibit a low resistance to the action of light: all aliphatic polyamides lose their useful operational properties in all climatic zones during less than one year. A significant impairment of properties occurs after only one–two months[4,164–166].

Table 3. Kinetic parameters of the oxidation of a series of compounds at 30 °C*.

Compound	k_p, litre mol^{-1} s^{-1}	$10^{-7}k_t$ litre mol^{-1} s^{-1}	$10^4(k_p/\sqrt{k_t})$, litre$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$	Refs.
N,N-Dimethylacetamide	1.44	14	1.2	155
N-Isopropylacetamide	0.05	0.9	0.16	155
N-Isopropylacetamide	—	—	0.38	104
N-n-Butylacetamide	0.22	2.3	0.47	155
N-n-Propylpropionamide	—	—	0.62	104
PA-548**	—	—	2.7	—
Polypropylene (60°)	0.015	$5.7\cdot10^{-5}$	6.3	154
2,4-Dimethylpentane (60°)	0.014	$2.2\cdot10^{-3}$	0.9	154

*Determined by extrapolation of the temperature variations of k_p and k_t to 30 °C.
**Estimated from Eqns.(60) and (61).

The photoageing of polymers during their use (and in tests under natural conditions) takes place under conditions characterised by significant changes in operating factors: the intensity and spectral composition of light, temperature, humidity, and level of corrosive impurities in the atmosphere, etc. Fig.5 shows that humidity has a significant influence on certain polymers. It has been found that humidity retards somewhat the evolution of CO in the photolysis of PA-669 [167] but has almost no influence on strength when polyamide fibres are irradiated by light at $\lambda > 340$ nm and retards slightly the loss of strength by polyamides after irradiation by light at shorter wavelengths at room temperature; however, one should note that at higher temperatures (100 °C) and in the presence of titanium dioxide humidity accelerates appreciably the photoageing processes of polyamides[4,46,168,169]. The decrease of the strength of polyamides on photoageing in the vicinity of cities proceeds at higher rates than in the country[4], which indicates the possible influence of corrosive impurities in the atmosphere. Nitrogen dioxide and ozone also accelerate the photoageing of PA-6,6.[170] However, the most significant factor influencing the photoageing of polyamides is evidently the intensity and spectra composition of sunlight.

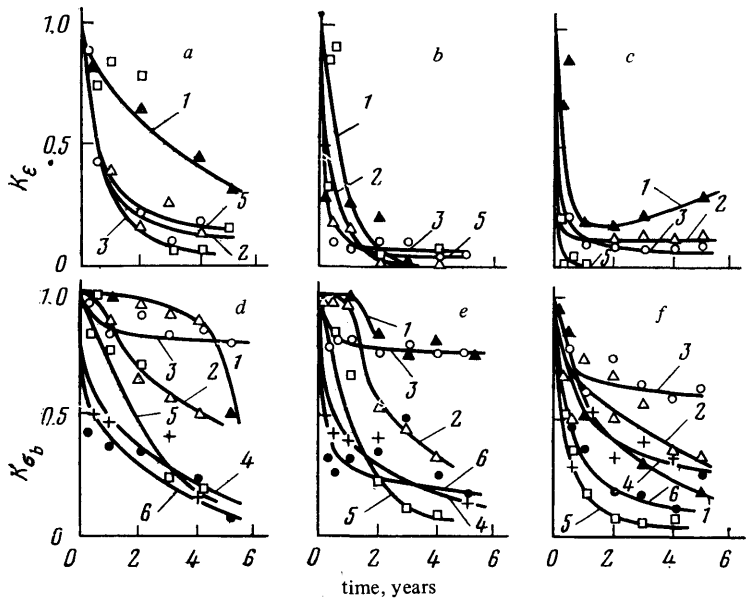


Figure 5. Dependence of the relative elongation (K_ε) on rupture (*a*, *b*, and *c*) and of the ultimate tensile strength (K_{σ_b}) (*d*, *e*, and *f*) as a function of the ageing time in moderately cold (*a* and *d*), warm and humid (*b* and *e*), and hot and dry (*c* and *f*) climatic zones for specimens of the trioxan-dioxolan copolymer (curves *1*), the formaldehyde–dioxolan copolymer (curves *2*), polycarbonate (curves *3*), PA-6 (curves *4*), PA-12 (curves *5*), and PA-6,10 (curves *6*).

A second way of predicting photoageing involves prediction based on the rsults of accelerated tests. Empirical relations, which describe with a greater or lesser degree of approximation the result of both natural and accelerated tests, are of great assistance in such tests[1,171]. In order to be able to extrapolate the results of accelerated tests to conditions corresponding to the photoageing of polyamides under natural conditions, one takes into account during the accelerated tests the factors which are significant in natural tests. Allowance for the influence of temperature, atmospheric humidity, and the content of ozone in air is achieved by a modelling procedure. An essential condition for a correlation between the results of natural and accelerated tests is also believed to be complete identity of the spectral composition of sunlight and artificial light[139,172–176]. It has been found[176] that photochemical activity is not shown by light over the entire spectral range but only by the short-wavelength part of the spectrum with $\lambda < 315$ nm; the nature of the spectra composition of light at $\lambda < 315$ nm is therefore most significant.

The intensity of sunlight in the region corresponding to absorption by polyamides, i.e. at $\lambda < 290$–300 nm, is extremely low ($I < 3.6 \times 10^{12}$ quanta cm^{-2} s^{-1}).[12] This suggests that secondary photolysis makes a major contribution to the initiated photoageing of polyamides under natural conditions. A wide variety of photochemical oxidation products—aldehydes, peroxy-compounds, and nitrogen-containing compounds (for example, imides or pyrrole derivatives, the absorption spectra of which differ)—can be involved in secondary photolytic reactions. This explains in its turn the necessity for maintaining the identity of the spectral composition of light as a condition for a correlation between the results of natural and accelerated tests.

At the same time one should note that the use of a high light intensity in accelerated tests with the remaining operating factors unchanged affects the form of chemical process occurring and alters the relative roles of different reactions. Thus, for fairly high light intensities I, the polyamide oxidation reaction has a non-chain mechanism and is determined solely by the initiation and radical destruction reactions. For very low values of I, the chain propagation stage may prove to be significant. The study of the influence of light intensity on the photoageing of polyamides therefore constitutes a more valid approach to the solution of the problem of a correlation between accelerated and natural tests.

Quantitative allowance of the factors already examined makes it possible to approach on a sounder basis the search for a correlation between the reults of natural and accelerated tests. The accuracy of such correlation is however inevitably limited by the uncertainty in the weather conditions (cloud cover, humidity, etc.). The study of the resistance of polyamides to the action of light in the presence of a wide variety of additives is of greatest interest. However, additives can influence the mechanism of the photoageing of polyamides, which also limits the scope of the correlation and of the theoretical predictions.

2. The Influence of Additives on the Photoageing of Polyamides

Titanium dioxide[46,51,62,65,177,178], which is used to etch fibres, is an active photosensitiser of the oxidation of polyamides. It has been shown[42] that the action spectrum of light on PA-6,6 in the presence of titanium dioxide is identical with the absorption spectrum of the latter and a number of possible mechanisms for the photosensitised oxidation of polyamides by titanium dioxide have been discussed.

Anthraquinone derivatives are believed to be the most powerful photosensitisers of the oxidation of polyamides[179]. Sodium anthraquinone-2-sulphonate at concentrations of 0.02 to 0.04 mol kg^{-1} increases the rate of photochemical oxidation of *N*-alkylamides by three orders of magnitude[107]. Initiation

in *N*-alkylamides takes place as a result of the abstraction of a hydrogen atom from the amide molecule by the excited sensitiser molecule and subsequent oxidation of the semiquinone radical by molecular oxygen.

Dyes such as β-Hydroxyethylsulphonium Red and Yellow and Monochlorotriazine Red and Yellow increase the rate of formation of radicals when PA-6 is irradiated by light at $\lambda = 254$ nm in air[87], the increase in the yield of radicals being directly proportional to the increase in the yield of carboxy-groups[109,180,181]. The impurities present in the initial monomers and formed in the synthesis of polyamides can also accelerate photoageing[182]. For a controlled acceleration of photoageing of polyamides, one can employ a wide variety of radical initiators, for example, iron(III) chloride, peroxides, etc.

The extensive experimental data accumulated hitherto on the stabilisation of PA with respect to the action of light have been published in reviews[3,4,6,183]. There exist literally thousands of substances and compositions which retard by factors of 2–5 the photoageing of polyamides. Apart from the large class of u.v. shields and u.v. absorbers, the action of which consists in the simple shielding of the polymer from light, among the most widely used light-stabilisers of polyamide mention may be made of copper and manganese compounds[3]. There is evidence for the efficiency of the protective action of chromium[2,6], nickel, and cobalt[184] salts, sodium and potassium halides[185], and phosphorus-containing compounds[3]. In recent years much attention has been devoted to manganese and phosphorus compounds[186–190], which prevent the photosensitising action of titanium dioxide, as well as copper and iodine compounds[191–195].

One should note that many of the compounds indicated also function as thermostabilisers of polyamides. For example, sodium bromide is effective both in thermal oxidation and in the photochemical oxidation of polyamides[196]. A qualitative correlation has been observed between the thermal and photochemical efficiencies of a number of copper-containing complexes of cyclo-1,3-phenylenethioisoindolenines used as stabilisers of PA-6.[197,198] There is also the opposite evidence: copper naphthenate, which is a powerful inhibitor of thermal oxidation of polyamides[199], does not influence the photochemical oxidation of *N*-alkylamides in an oxygen atmosphere[107], which is probably associated with the absence of oxidation chains in this instance.

Attempts have been made in a number of studies to elucidate the mechanism of the reaction of the most effective light stabilisers for polyamides—copper compounds. The changes in the supermolecular structure of PA-6 as a function of the introduction of copper-containing stabilisers (stabilines) have been studied[200]. It has been found that the introduction of stabilines tends to strengthen cord fibres, which can reduce the diffusion of oxygen into polyamides. This effect in the diffusion region of the photochemical oxidation leads to retardation of the oxidation process. However, in natural photoageing of polyamides, which lasts for months, one can hardly expect limiting by diffusion-dependent processes. Furthermore, the stabilising action of copper salts with respect to light has been observed also in the photochemical oxidation of PA-6 in the kinetic region[112].

The study of the gas evolution on irradiation of PA-6 by the total light of a moderate-pressure mercury lamp *in vacuo* has shown[201] that copper, chromium, zinc, and cadmium chlorides do not affect the gas evolution and that, on irradiation by light at $\lambda > 300$ nm, copper chloride accelerates the evolution of H_2. Under these conditions, the above stabilisers retard the decrease of the mechanical strength characteristics of PA-6. It has been suggested[201] that the action of the test compounds is due to their shielding properties. This explanation is apparently inadequate, because the shielding effect should lead solely to a decrease of the rate of gas evolution. It was shown subsequently, taking into account the shielding effects, that the protective action of copper and certain other metal salts cannot be reduced wholly to the shielding effect[112].

When PA-6 films are irradiated *in vacuo*, the addition of copper acetylacetonate (0.001–0.01 mol kg^{-1}) does not affect the evolution of CO and increase slightly the rate of evolution of H_2, which has been explained by the absence of an effect by copper acetylacetonate and the primary photochemical processes in polyamides[202]. However, at the same concentrations copper acetylacetonate reduces severalfold the quantum yields of the degradation processes, of the absorption of oxygen, and other PA-6 photochemical oxidation processes. Copper acetylacetonate retarded the benzophenone-sensitised photochemical oxidation of polyamides but did not influence the luminescence and kinetics of the consumption of benzophenone. This permits the conclusion that copper compounds are capable of inhibiting dark polyamide photoageing processes.

Since hydroperoxides were not detected in PA-6 fibres stabilised by copper salts, it was suggested that the additives suppress oxidation as a result of the formation of an inactive complex with the peroxy-radicals or as a result of the decomposition or binding of hydroperoxides with formation of inactive compounds[197,200]. An analogous effect—the absence of hydroperoxides—had been observed earlier in a study[65] of the photochemical oxidation of model amides with the addition of manganese salts, which enabled the authors to reach the same conclusion concerning manganese salts. Strictly speaking, the decreased content of peroxy-compounds may be a consequence also of other processes preventing the formation of peroxides.

A qualitative analogy between the action of copper salts and an acceptor of alkyl radicals (the 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yloxy-radical) has been observed[120,202]; the efficiency of the alkyl radical acceptor increases, like that of copper acetylacetonate, with decrease of the partial pressure of oxygen in accordance with the increase of the relative role of the alkyl radical participating in the photochemical oxidation of polyamides. Thus copper compounds can compete with oxygen in the alkyl radical oxidation reaction. The ability of copper(II) compounds to oxidise alkyl radicals has been demonstrated[203,204]. We believe that the protective action of copper(II) salts as a result of their interaction with alkyl radicals is most likely, although other protective mechanisms cannot be ruled out.

---o0o---

In conclusion we may note that the mechanism of the photoageing of polyamides continues to be the subject of numerous investigations.

A number of recent studies[205–214] are of interest for the elucidation of the mechanisms of the primary photochemical processes responsible for the initiation of the photoageing of polyamides. The nature of the luminescence in polyamides continues to be controversial[205,213]. Additional data[216], showing that the main primary reaction in the direct photolysis of amides is the breakdown of the amide linkage, have been obtained. It has been shown[214,215] that, in the sensitisation of the photoageing of polyamides by compounds of different classes, the principal primary initiation reaction involves the abstraction of a hydrogen atom with formation of the macroradical $RCONH\dot{C}HCH_2R'$ (P_1). Therefore the possibility of the involvement of singlet oxygen $^1O_2$ in initiation steps appear unlikely. An analogous conclusion was reached in other investigations[209,210] of the photochemical oxidation of

PA-6,6 and in a study[217] of the photochemical oxidation of low-molecular-weight amides.

A number of studies have been made on the mechanism of the photochemical oxidation of polyamides[218,219]. It has been shown experimentally for the first time[218] that the photochemical oxidation of PA-6 and PA-548 proceeds with participation of peroxy-radicals P_1O_2; measurements have been made of the rate of destruction of peroxy-macroradicals and of the corresponding rate constants [$k_d = 2.4\times10^{15}\exp(-16000/RT)$] kg mol^{-1} s^{-1} in both PA-6 and PA-548. $k_p/k_d^{1/2} = 1.4\times10^{-4}$ kg$^{1/2}$ (mol s)$^{-1/2}$ for the photochemical oxidation of PA-548 at 25 °C has been measured[219]. It was shown in the same study[219] that the chain oxidation becomes significant at extremely low rates of oxidation, comparable to the rates of photochemical oxidation of PA-6 under natural conditions.

The ideas concerning the role of secondary photolytic reactions in polyamides, discussed above, have found further confirmation in a number of investigations[212,218,220]. The possibility of the photochemical reaction of the amino-radicals has been demonstrated[212] and the photorecombination of PA peroxy-radicals, which proceeds at extremely high rates, has been observed[218].

New studies have been made on the mechanism of the stabilisation of polyamides with respect to the action of light[207, 221,222]. It has been shown[221] that the grafting of an inhibitor of radical processes (vinylhydroquinone) to PA-6 protects the polyamide against the action of light. It has been shown by EPR [222] that copper salts react with the macroradicals $\dot{P}_1$ and the rate constant for this reaction has been measured.

It can be regarded as established that the photoageing of polyamides is a radical-chain process with quadratic oxidation chain termination and that the oxidative degradation processes make the main contribution to the photochemical decomposition. Thus the photoageing of polyamides resembles the photoageing of certain carbochain polymers (for example, polyolefins, in relation to which an analogous conclusion has been reached[8]).

Whereas the photochemical oxidation of carbochain polymers is known to be initiated by hydroperoxy- and carbonyl groups, the nature of the photoinitiating groups in polyamides on irradiation by long-wavelength light continues to be controversial. The mechanism of the photoinitiated oxidation of polyamides can differ from the mechanism of the photoinitiated oxidation of other polymers. The cause of this difference may be related to the greater number of nitrogen-containing products (pyrroles, imides, and imines) which exhibit an intense ultraviolet absorption.

Although the nature of the chromophoric group responsible for the initiation of the photoageing of polyamides remains controversial, studies have shown that effective stabilisation of polyamides (as well as other polymers) with respect to the action of light can be achieved by introducing radical process inhibitors into the polyamide.

The photoageing of polyamides is characterised by a complex composition of products and a large number of reactions, the relative rates of which depend on experimental conditions. Secondary photolytic processes make a significant contribution to the photoageing process and studies of the photochemical reactions of polyamide macroradicals merit particular attention.

REFERENCES

1. N.I.Pavlov and A.I.Krotova, Plast.Massy, No.2, 56 (1976).
2. S.R.Rafikov and I.A.Arkhipova, Trudy.Inst.Khim.Nauk Akad.Nauk Kazakh.SSR, **29**, 3 (1970).
3. I.A.Arkhipova and S.R.Rafikov, Trudy.Inst.Khim.Nauk Akad.Nauk Kazakh.SSR, **31**, 208 (1971).
4. B.S.Stove, R.E.Fornes, and R.D.Gilbert, Polymer Plast.Technol.Eng., **3**, 159 (1974).
5. I.I.Levantovskaya, Symposium, "Starenie i Stabilizatsiya Polimerov" (The Ageing and Stabilisation of Polymers) (Edited by M.B.Neiman), Izd.Nauka, Moscow, 1964, p.197.
6. Yu.A.Voitelev and N.D.Katorzhnov, Khim.Voloknaa, No.3, 3 (1960).
7. A.L.Margolin, L.M.Postnikov, and V.Ya.Shlyapintokh, Vysokomol.Soed., **19A**, 1954 (1977).
8. O.N.Karpukhin and E.M.Slobodetskaya, Uspekhi Khim., **42**, 391 (1973) [Russ.Chem.Rev., No.3 (1973)].
9. D.J.Carlsson, R.D.Parnell, and D.M.Wiles, J.Polymer Sci., B, **11**, 149 (1973).
10. J.G.Calvert and J.N.Pitts, "Photochemistry" (Translated into Russian), Izd.Mir, Moscow, 1968.
11. B.Lànska and J.Šebenda, Coll.Czech.Chem.Comm., **34**, 1911 (1969).
12. M.R.Kamal and R.Saxon, Appl.Polymer Symp., **4**, 1 (1967).
13. R.C.Hirt and N.Z.Searle, Appl.Polymer Symp., **4**, 61 (1967).
14. W.B.Gratzer, "Poly-α-amino Acids" (Edited by G.Fasman), Marcel Dekker, New York, 1969.
15. R.M.Silverstein, G.C.Bassler, and T.C.Morril, "Spectrometric Identification of Organic Compounds", Wiley, New York, 1970.
16. E.B.Nielsen and J.A.Schellman, J.Phys.Chem., **71**, 2297 (1967).
17. J.Zabicky (Editor), "The Chemistry of Amides", Wiley, New York, 1970.
18. D.I.Peterson and W.T.Sympson, J.Amer.Chem.Soc., **79**, 2375 (1957).
19. S.Nagakura, Molec.Phys., **3**, 105 (1960).
20. K.Kaya and S.Nagakura, Theor.Chim.Acta, **7**, 117 (1967).
21. N.J.Turro, "Molecular Photochemistry" (Translated into Russian), Izd.Mir, Moscow, 1967, p.114.
22. S.Onari, Japan.J.Appl.Phys., **9**, 227 (1970).
23. S.Onari, J.Phys.Soc.Japan, **27**, 269 (1969).
24. J.A.Dellinger and C.W.Roberts, J.Polymer Sci., Polymer Letters Ed., **14**, 167 (1976).
25. D.B.Larson, J.F.Arnett, C.J.Seliskar, and S.P.McGlynn, J.Amer.Chem.Soc., **96**, 3370 (1974).
26. H.S.Koenig and C.W.Roberts, J.Appl.Polymer Sci., **19**, 1847 (1975).
27. H.Shizuka, Bull.Chem.Soc.Japan, **42**, 52 (1969).
28. H.H.Dearman, F.T.Long, and W.C.Neely, J.Polymer Sci., **A2**, 7, 497 (1969).
29. L.W.Johnson, H.J.Maria, and S.P.McGlynn, J.Chem. Phys., **54**, 3823 (1971).
30. H.J.Maria, D.B.Larson, M.E.McCarville, and S.P.McGlynn, Acc.Chem.Res., **3**, 369 (1970).
31. D.B.Larson and S.P.McGlynn, J.Molec.Spectrosc., **47**, 496 (1973).
32. S.P.McGlynn, T.Azumi, and M.Kinoshita, "Molecular Spectroscopy of the Triplet State" (Translated into Russian), Izd.Mir, Moscow, 1972.
33. M.A.J.Rogers, H.A.Sokol, and W.M.Garrison, Biochem. Biophys.Res.Comm., **40**, 622 (1970).
34. N.S.Allen, J.E.McKellar, G.O.Phillips, and D.G.M.Wood, J.Polymer Sci., **B12**, 241 (1974).
35. N.S.Allen, J.F.McKellar, and G.O.Phillips, J.Polymer Sci., Polymer Letters Ed., **12**, 477 (1974).
36. N.S.Allen, J.F.McKellar, G.O.Phillips, and C.B.Chapman, J.Polymer Sci., Polymer Letters Ed., **12**, 727 (1974).

37. N.S.Allen, J.F.McKellar, and G.O.Phillips, J.Polymer Sci., Polymer Letters Ed., **12**, 1233 (1974).
38. N.S.Allen, J.F.McKellar, and G.O.Phillips, J.Polymer Sci., Polymer Letters Ed., **12**, 2623 (1974).
39. N.S.Allen, J.Homer, J.F.McKellar, and J.O.Phillips, Brit.Polymer J., **7**, 11 (1975).
40. N.S.Allen, J.F.McKellar, and D.Wilson, J.Photochem., **6**, 73 (1976).
41. N.S.Allen, J.F.McKellar, and C.B.Chapman, J.Appl. Polymer Sci., **20**, 1717 (1976).
42. H.A.Taylor, W.C.Tincher, and W.E.Hammer, J.Appl. Polymer Sci., **14**, 141 (1970).
43. L.P.Bondareva, G.D.Litovchenko, and N.V.Mikhailov, Vysokomol.Soed., **15B**, 96 (1973).
44. N.S.Allen, J.F.McKellar, and D.Wilson, J.Photochem., **6**, 337 (1976/1977).
45. T.S.Mel'nik, I.I.Petrosyuk, and Yu.P.Tret'yakov, Khim.Volokna, No.3, 8 (1968).
46. R.F.Moor, Polymer, **4**, 493 (1963).
47. W.H.Sharkey and W.E.Mochel, J.Amer.Chem.Soc., **89**, 3000 (1959).
48. J.A.Schellman and E.B.Nielsen, J.Phys.Chem., **71**, 3914 (1967).
49. P.H.Mazzocchi, F.Danisi, and J.J.Thomas, J.Polymer Sci., Polymer Letters Ed., **13**, 737 (1975).
50. P.H.Mazzocchi and F.Bowen, J.Org.Chem., **47**, 1279 (1976).
51. E.H.Boasson, B.Kamerbeck, and A.Algera, Rec.trav. chim., **81**, 624 (1962).
52. A.L.Margolin and L.M.Postnikov, Vysokomol.Soed., **17B**, 59 (1975).
53. J.S.Guzman, "Dissertation", The Catholic University of America, Washington, 1971.
54. H.Shizuka, Bull.Chem.Soc.Japan, **42**, 57 (1969).
55. H.Shizuka and I.Tanaka, Bull.Chem.Soc.Japan, **41**, 2243 (1968).
56. C.H.Nicolls and P.A.Leermakers, J.Org.Chem., **35**, 2754 (1961).
57. C.V.Stephenson, J.C.Lacay, and W.C.Wilox, J.Polymer Sci., **55**, 451 (1961).
58. S.R.Rafikov and Chi-P'ing Hsü, Vysokomol.Soed., **3**, 56 (1961).
59. A.Visokinskas and A.Paulauskas, Vysokomol.Soed., **9B**, 604 (1967).
60. B.M.Kowarskaja, W.W.Gurjanowa, E.E.Said-Galiew, and W.W.Korschak, "Die Natürliche und Künstliche Alterung von Kunststoffen", Fakultas-Verlag, Vienna, 1975, p.94.
61. B.G.Achhammer, R.W.Reinhart, and G.M.Kline, J.Res. Nat.Bur.Stand.USA, **46**, 391 (1951).
62. C.N.Kroes, Rec.Trav.chim., **82**, 391 (1963).
63. V.V.Gur'yanova, A.B.Blyumenfel'd, E.B.Said-Galiev, T.A.Pertsova, and B.M.Kovarskaya, Vysokomol.Soed., **16A**, 909 (1974).
64. A.Anton, J.Appl.Polymer Sci., **9**, 1631 (1965).
65. B.Marek and E.Lerch, J.Soc.Dyers Colour, **81**, 481 (1965).
66. I.H.Peebles and M.W.Hoffman, J.Polymer Sci., A1, 9, 1807 (1971).
67. A.I.Brodskii, A.S.Fomenko, and T.M.Abramova, Vysokomol.Soed., **7**, 116 (1965).
68. E.R.Klinshpont and V.K.Milinchuk, "Obzory po Otdel'nym Proizvodstvam Khimicheskoi Promyshlennosti" (Reviews of Individual Manufacturing Processes in Chemical Industry), Izd.NIITEKhIM, 1976, No.5, p.46.
69. M.Nakashima and E.Hayon, J.Phys.Chem., **75**, 1910 (1971).
70. J.Zimmerman, J.Appl.Polymer Sci., **2**, 181 (1959).
71. E.Hayon, T.Ibata, N.N.Lichtin, and M.Simic, J.Amer.Chem.Soc., **92**, 3898 (1970).
72. V.P.Kiryukhin and V.K.Milinchuk, Khim.Vys.Energii, **3**, 451 (1969).
73. G.B.Pariiskii, E.Ya.Davydov, and D.Ya.Toptygin, Izv.Akad.Nauk SSSR, Ser.Khim., 1054 (1973).
74. G.B.Pariiskii, L.M.Postnikov, D.Ya.Toptygin, and E.Ya.Davydov, "IUPAC Int.Symp.on Macromolecules (Helsinki, 1972)", 1972, Vol.5, p.233.
75. G.B.Pariiskii, L.M.Postnikov, D.Ya.Toptygin, E.Ya.Davydov, J.Polymer Sci., Polymer Sym., C42, 1287 (1973).
76. G.B.Pariiskii, L.M.Postnikov, E.Ya.Davydov, and D.Ya.Toptygin, Vysokomol.Soed., A16, 482 (1974).
77. F.Szöcs, J.Becht, and H.Fischer, Europ.Polymer J., 7, 173 (1971).
78. G.S.Verma and A.Peterlin, Kolloid.Z., **236**, 111 (1970).
79. M.Kashivagi, J.Polymer Sci., A1, 189 (1963).
80. P.Yu.Butyagin, A.M.Dubinskaya, and V.A.Radtsig, Uspekhi Khim., **38**, 593 (1969) [Russ.Chem.Rev., No.4 (1969)].
81. V.A.Zakrevskii, V.V.Baptizmanskii, and E.E.Tomashevskii, Fiz.Tverd.Tela, **10**, 1699 (1968).
82. E.G.Furman, A.S.Fomenko, T.M.Abramova, E.P.Dar'eva, and I.A.Spirina, Vysokomol.Soed., **11A**, 836 (1969).
83. F.G.Golemba and J.E.Guillet, J.Paint Technol., **41**, 315 (1969).
84. H.M.Heuvel and K.C.J.Lind, J.Polymer Sci., **A2**, 8, 401 (1970).
85. V.K.Milinchuk and E.R.Klinshpont, Khim.Vys.Energii, **1**, 352 (1967).
86. A.S.Fomenko, T.M.Abramova, E.P.Dar'eva, A.A.Beloded, E.G.Furman, and A.I.Brodskii, Vysokomol Soed., **10A**, 507 (1968).
87. V.A.Roginskii, E.V.Dovbii, and Yu.A.Ershov, Dokl. Akad.Nauk SSSR, **205**, 130 (1972).
88. D.Campbell, J.Polymer Sci., **D4**, 91 (1970).
89. H.Hefter and H.Fischer, Ber.Bunsenges.Phys.Chem., **74**, 493 (1970).
90. Y.Nazawa, Bull.Chem.Soc.Japan, **43**, 657 (1970).
91. A.M.Dubinskaya and N.N.Yusubov, Izv.Akad.Nauk SSSR, Ser.Khim., 2095 (1975).
92. R.B.Johns and M.G.Seuret, Photochem.Photobiol., **16**, 413 (1972).
93. J.Zimmerman, J.Polymer Sci., **46**, 151 (1960).
94. C.W.Deeley, A.E.Woodward, and J.A.Sayer, J.Appl. Phys., **28**, 1124 (1957).
95. V.L.Karpov, V.G.Yurkevich, L.M.Kavalerova, N.L.Petrova, Yu.V.Glazkovskii, and E.L.Egorova, Khim.Volokna, No.1, 30 (1969).
96. T.G.Majury and S.H.Pinner, J.Appl.Chem.(London), **8**, 168 (1958).
97. G.Reinisch, W.Jaeger, and K.Ulbert, J.Polymer Sci., C16, 4453 (1969).
98. Y.Yoshizawa, H.Saito, and K.Nukada, J.Polymer Sci., B10, 145 (1972).
99. G.Valk, G.Heidemann, S.Dugal, and H.Kruessmann, Angew.Makromol.Chem., **10**, 135 (1970).
100. A.Rieche, Kunststoffe, **54**, 429 (1964).
101. A.Rieche and W.Schön, Chem.Ber., **99**, 3238 (1966).
102. A.Rieche and W.Schön, Kunststoffe, **57**, 49 (1967).
103. B.F.Sagar, J.Chem.Soc.B, 428 (1967).
104. B.F.Sagar, J.Chem.Soc.B, 1047 (1967).
105. M.V.Lock and B.F.Sagar, J.Chem.Soc.B, 690 (1966).
106. M.V.Lock and B.F.Sagar, Proc.Chem.Soc., 358 (1960).
107. G.M.Burnett and K.M.Riches, J.Chem.Soc.B, 1229 (1966).

108. A.L.Margolin, L.M.Postnikov, and L.M.Pipan, Vysokomol.Soed., **A17**, 617 (1975).
109. Yu.A.Jerschow and Je.W.Dowbii, "Die Natürliche und Künstliche Alterung von Kunststoffen", Facultas-Verlag, Vienna, 1975, p.110.
110. N.M.Emanuel', E.T.Denisov, and Z.K.Maizus, "Tsepnye Reaktsii Okisleniya Uglevodorodov v Zhidkoi Faze" (Liquid-Phase Chain Oxidation Reactions of Hydrocarbons), Izd.Nauka, Moscow, 1965.
111. K.Rogers, Symposium, "Problemy Fiziki i Khimii Tverdogo Sostoyaniya Organicheskikh Soedinenii" (Problems of the Physics and Chemistry of the Solid State of Organic Compounds)(Translated into Russian), Izd.Mir, Moscow, 1968, p.245.
112. A.L.Margolin, L.M.Postnikov, and I.V.Semenova, Vysokomol.Soed., **16A**, 1037 (1974).
113. A.L.Margolin, L.M.Postnikov, and E.V.Vichutinskaya, Vysokomol.Soed., **14B**, 57 (1972).
114. A.L.Margolin, L.M.Postnikov, V.S.Bordakov, and E.V.Vichutinskaya, Vysokomol.Soed., **14A**, 1586 (1972).
115. C.Thomassin and J.Marchal, Makromol.Chem., **178**, 1313 (1977).
116. E.G.Furman, Candidate's Thesis, Institute of Physical Chemistry, Academy of Sciences of Ukrainian SSR, Kiev, 1972.
117. A.L.Margolin, L.M.Postnikov, V.S.Bordakov, E.K.Vichutinskaya, "IUPAC Int.Conf.Chemical Transformations of Polymers (Bratislava)", 1971, Vol.2, p.31.
118. L.M.Postnikov, A.L.Margolin, V.Ya.Shlyapintokh, and E.V.Vichutinskaya, J.Polymer Sci., Polymer Symp., **C42(3)**, 1275 (1973).
119. A.L.Margolin, L.M.Postnikov, and V.Ya.Shlyapintoch, "Die Natürliche und Künstliche Alterung von Kunststoffen", Fakultas-Verlag, Vienna, 1975, p.100.
120. A.L.Margolin, I.A.Kabanova, L.M.Postnikov, and V.Ya.Shlyapintokh, Vysokomol.Soed., **18A**, 1094 (1976).
121. E.V.Vichutinskaya, G.G.Makarov, A.L.Margolin, and L.M.Postnikova, Vysokomol.Soed., **19B**, 441 (1977).
122. I.V.Berezin, E.T.Denisov, and N.M.Emanuel', "Okislenie Tsiklogeksana" (Oxidation of Cyclohexane), Izd.Moskov.Gos.Univ., Moscow, 1962.
123. I.I.Levantovskaya, B.M.Kovarskaya, and M.B.Neiman, Vysokomol.Soed., **6**, 1885 (1964).
124. N.A.Bakh and N.I.Popov, "Sbornik Rabot po Radiatsionnoi Khimii" (Collected Papers on Radiation Chemistry), Izd.Akad.Nauk SSSR, Moscow, 1955, p.145.
125. H.Howard, Canad.J.Chem., **51**, 870 (1973).
126. S.N.Zhurkov and E.E.Tomashevskii, Symposium, "Nekotorye Problemy Prochonosti Tverdogo Tela" (Some Problems of the Strength of Solids), Izd.Akad. Nauk SSSR, Moscow, 1959.
127. S.N.Zhurkov and S.A.Abasov, Fiz.Tverd.Tela, **4**, 928 (1962).
128. A.I.Gubanov and A.D.Chevychekov, Fiz.Tverd.Tela, **4**, 928 (1962).
129. R.G.Treloar, "Introduction to Polymer Science" (Translated into Russian), Izd.Mir, Moscow, 1973, p.177.
130. A.D.Chevychelov, Mekhanika Polimerov, No.1, 8 (1967).
131. A.D.Chevychelov, Candidate's Thesis, Physicotechnical Institute, Leningrad, 1966.
132. A.I.Gubanov, Vysokomol.Soed., **7**, 1192 (1965).
133. V.A.Berestenev, R.V.Torner, and V.A.Kargin, Mekhanika Polimerov, No.5, 848 (1970).
134. B.A.Levin, A.V.Savitskii, and V.P.Demicheva, Mekhanika Polimerov, No.4, 591 (1967).
135. B.S.Stove, V.S.Salvin, R.E.Fornes, and R.D.Gilbert, Text.Res.J., **43**, 704 (1973).
136. R.D.Fornes, R.D.Gilbert, B.S.Stove, and G.P.Cheek, Text.Res.J., **43**, 714 (1973).
137. G.Fujiwara and T.Yasuda, Sen-i-Gakkashi, **29**, 274 (1973).
138. G.Fujiwara and T.Yasuda, Sen-i-Gakkashi, **30**, 434 (1974).
139. L.M.Lock and G.C.Frank, Text.Res.J., **43**, 502 (1973).
140. V.R.Regel' and N.N.Chernyi, Khim.Volokana, No.6, 50 (1969).
141. V.R.Regel' and N.N.Chernyi, Mekhanika Polimerov, No.4, 636 (1969).
142. T.B.Boboev, V.R.Regel', T.P.Sanfirova, and N.N.Chernyi, Mekhanika Polimer, No.4, 661 (1968).
143. T.B.Boboev, V.R.Regel', and N.N.Chernyi, Mekhanika Polimer, No.3, 559 (1969).
144. V.R.Regel', A.I.Slutsker, and E.E.Tomashevskii, "Kineticheskaya Priroda Prochnosti Tverdykh Tel" (Kinetic Nature of the Strength of Solids), Izd.Nauka, Moscow, 1974.
145. G.G.Samoilov and E.E.Tomashevskii, Fiz.Tverd.Tela, 10, 1729 (1968).
146. G.A.Samoilov, Candidate's Thesis, Tajik State University, Dushanbe, 1970,
147. T.B.Boboev, G.G.Samoilov, and S.Tabirov, Mekhanika Polimerov, No.2, 348 (1975).
148. M.Kh.Kholov and G.G.Samoilov, Dokl.Akad.Nauk Tadzh.SSR, **17**, No.8, 27 (1974).
149. M.Kh.Kholov, G.G.Samoilov, and B.N.Narzullaev, "Prochnost' i Razrushenie Tverdykh Tel" (The Strength and Breakdown of Solids), Tajik State University, Dushanbe, 1975, No.1, p.15.
150. G.G.Samoilov and E.E.Tomashevskii, Fiz.Tverd.Tela, 10, 1094 (1968).
151. V.R.Regel', T.B.Boboev, and M.P.Vershinina, Fiz.-Khim.Mekh.Materialov, 6, 70 (1970).
152. J.Tiňo, J.Plaček, and F.Szöcs, Europ.Polymer J., 13, 19 (1977).
153. J.Tiňo, J.Plaček, and F.Szöcz, Europ.Polymer J., 11, 609 (1975).
154. E.L.Shanina, V.A.Roginskii, and M.B.Miller, Vysokomol.Soed., **18A**, 1160 (1976).
155. N.N.Pozdeeva, T.I.Sapacheva, and A.L.Aleksandrov, Izv.Akad.Nauk SSSR, Ser.Khim., 1738 (1976).
156. T.I.Sapacheva, G.G.Agliullina, and A.L.Aleksandrov, Neftekhimiya, **14**, 450 (1974).
157. T.I.Sapacheva, G.G.Agliullina, A.A.Aleksandrov, and E.T.Denisov, Neftekhimiya, **14**, 623 (1974).
158. T.I.Sapacheva, E.A.Dzhavadyan, and A.L.Aleksandrov, Zhur.Fiz.Khim., **49**, 331 (1975) [Russ.J.Phys.Chem., No.2 (1975)].
159. J.Šebenda, L.M.Postnikov, and B.Lànská, Coll.Czech. Chem.Comm., **40**, 1877 (1975).
160. A.Machulis and E.Tornau, "Diffuzionnaya Stabilizatsiya Polimerov" (Diffusional Stabilisation of Polymers), Izd.Mintis, Vilna, 1974.
161. N.Ya.Rapoport and V.B.Miller, Dokl.Akad.Nauk SSSR, **227**, 911 (1976).
162. E.V.Vichutinskaya, L.M.Postnikov, and N.Ya.Kushnerev, Vysokomol.Soed., 17A, 621 (1975).
163. E.V.Vichutinskaya and L.M.Postnikov, Vysokomol.Soed., **18B**, 279 (1976).
164. R.V.R.Subramanian and T.V.Talele, Text.Res.J., **42**, 207 (1972).
165. L.N.Smirnov, T.I.Tekhonova, and V.M.Kharitonov, Zhur.Vses.Khim.Obshch.im.Mendeleeva, **17**, 669 (1972).
166. L.N.Smirnov, E.V.Merkur'eva, and V.M.Kharitonov, Collected Preprints of the International Symposium on Chemical Fibres, Section 5, Kalinin, 1974. p.173.

167. S.R.Rafikov and Chi-P'ing Hsü, Vysokomol.Soed., **4**, 851 (1962).
168. G.S.Egerton and K.M.Shah, Text.Res.J., **38**, 130 (1968).
169. G.S.Egerton, Faserforsch.Textiltechnik, **22**, 86 (1971).
170. H.H.G.Jellinek and A.K.Chaudhuri, J.Polymer Sci., **A1**, 10, 1773 (1972).
171. A.V.Provornikov and L.N.Smirnov, Khim.Volokna, No.5, 60 (1976).
172. R.W.Singleton and P.A.C.Cook, Text.Res.J., **39**, 43 (1969).
173. R.W.Singleton, R.K.Kunkel, and R.S.Sprague, Text. Res.J., **35**, 228 (1965).
174. M.J.Wall and G.C.Frank, Text.Res.J., **41**, 32 (1971).
175. M.J.Wall and G.C.Frank, Text.Res.J., **41**, 38 (1971).
176. L.M.Lock, G.C.Frank, and J.R.Stevens, Text.Res.J., **43**, 483 (1973).
177. G.Klare, E.Fritzche, and F.Grebe, "Synthetic Polyamide Fibres" (Translated into Russian), Izd.Mir, Moscow, 1966.
178. G.S.Egerton and A.G.Morgan, J.Soc.Dyers Colour, **87**, 268 (1971).
179. M.R.Benedict and H.L.Needles, Canad.Text J., 91 (1972).
180. E.V.Dovbii, G.E.Krichevskii, and Yu.A.Ershov, Izv. Vys.Ucheb.Zaved., Tekhnol.Tekstil'n.Prom., No.6, 87 (1971).
181. E.V.Dovbij and Yu.A.Ershov, J.Appl.Polymer Sci., **21**, 1511 (1976).
182. L.E.Nikulina, V.R.Koroleva, and L.N.Mizerovskii, Izv. Vys.Ucheb.Zaved., Khim.i Khim.Tekhnol., **17**, 778 (1974).
183. E.Martens, Plaste und Kautschuk, No.12, 26 (1965).
184. Japanese P.9747 (1972); Ref.Zhur.Khim., 7S622 (1973).
185. V.N.Kochetkov, N.V.Morozova, and V.A.Ponomarev, Plast.Massy, No.9, 15 (1963).
186. Japanese P.10 533 (1972); Ref.Zhur.Khim., 13S1048 (1973).
187. Japanese P.29 382 (1972); Ref.Zhur.Khim., 21S515 (1973).
188. Japanese P.28 088 (1972); Ref.Zhur.Khim., 13S1050 (1973).
189. Japanese P.39 573 (1972); Ref.Zhur.Khim., 17S1034 (1973).
190. Japanese P.39 211 (1972); Ref.Zhur.Khim., 18S916 (1973).
191. Japanese P.19 612 (1972); Ref.Zhur.Khim., 12S240 (1973).
192. Japanese P.48-7698 (1973); Ref.Zhur.Khim., 4S1128 (1973).
193. Japanese P.48-7697 (1973); Ref.Zhur.Khim., 4S1127 (1973).
194. L.N.Smirnov, V.M.Kharitonov, G.P.Smirnov, E.V.Merkur'eva, R.P.Smirnov, V.A.Gnedina, and I.S.Tikhomirova, USSR P.352 917 (1972); Byul. Izobret., No.29 (1972).
195. Japanese P.45 585 (1972); Ref.Zhur.Khim., 21S654 (1973).
196. V.N.Kochetkov, Plast.Massy, No.3, 12 (1965).
197. V.N.Klyuev, L.N.Smirnov, F.P.Snegireva, E.V.Merkur'eva, I.S.Tikhomirova, and V.M.Kharitonov, Izv. Vys.Ucheb.Zaved., Khim.i Khim.Tekhnol., 17, 1209 (1974).
198. L.N.Smirnov, V.M.Kharitonov, and R.P.Smirnov, Collected Preprints of the International Symposium on Chemical Fibres, Section 5, Kalinin, 1974, p.180.
199. I.I.Levantovskaya, M.P.Yazvikova, B.M.Kovarskaya, and K.N.Vlasova, Plast.Massy, No.3, 19 (1963).
200. L.N.Smirnov, V.M.Kharitonov, and V.V.Korshak, Symposium, "Sinteticheskie Volokna" (Synthetic Fibres), Izd.Khimiya, Moscow, 1969, p.77.
201. S.R.Rafikov and Chi-P'ing Hsü. Symposium, "Khimicheskie Svoistva i Modifikatsiya Polimerov" (Chemical Properties and Modification of Polymers), Izd.Nauka, Moscow, 1964, p.131.
202. A.L.Margolin, I.A.Kabanova, L.M.Postnikov, and V.Ya.Shlyapintokh, Vysokomol.Soed., **18B**, 378 (1976).
203. C.L.Jenkins and J.K.Kochi, J.Org.Chem., **36**, 3095 (1971).
204. C.I.Jenkins and J.K.Kochi, J.Org.Chem., **36**, 3103 (1971).
205. N.S.Allen, J.F.McKellar, and D.Wilson, J.Polymer Sci., Polymer Chem.Ed., **15**, 2793 (1977).
206. N.S.Allen, J.F.McKellar, and D.Wilson, J.Photochem., 7, 405 (1977).
207. N.S.Allen, J.F.McKellar, and D.Wilson, J.Photochem., **7**, 319 (1977).
208. M.Terashima, K.Seki, K.Ito, and Y.Kanaoka, Heterocycles, **8**, 421 (1977).
209. N.S.Allen and J.F.McKellar, Macromol.Chem., **179** (1), 269 (1978).
210. N.S.Allen and J.F.McKellar, J.Appl.Chem.Biotechnol., **27**, 269 (1977).
211. H.Aoyama, T.Hasewaga, M.Watabe, H.Shiraishi, and Y.Omote, J.Org.Chem., **43**, 419 (1978).
212. H.Neubacher and G.H.Schnepel, Radiation Res., **72**, 48 (1977).
213. J.A.Dellinger and C.W.Roberts, J.Polymer Sci., Polymer Letters Ed., **16**, 357 (1978).
214. E.V.Vychutinskaya, A.L.Margolin, L.M.Postnikov, and V.Ya.Shlyapintokh, Vysokomol.Soed., **21A**, 1284 (1979).
215. A.V.Sorokina, E.V.Vichutinskaya, A.L.Margolin, L.M.Postnikov, and N.M.Nosalevich, "Tezisy Dokladov I Vsesoyuznoi Konferentsii 'Svetostabilizatsiya Okrashennykh Volokon i Plenok'" (Abstracts of Reports at the Ist All-Union Conference on 'The Stabilisation of Coloured Fibres and Films with Respect to the Action of Light'), Rotaprint at Moscow Textile Institute, Moscow, 1979, p.39.
216. P.H.Mazzocchi and F.Bowen, J.Org.Chem., **44**, 50 (1979).
217. J.C.Gramain, R.Renusen, and Y.Troin, Chem.Comm., 194 (1976).
218. E.Ya.Davydov, A.L.Margolin, G.B.Pariiskii, L.M.Postnikov, and D.Ya.Toptygin, Dokl.Akad.Nauk SSSR, **243**, 1475 (1978).
219. A.L.Margolin, A.V.Sorokina, and L.M.Postnikov, Vysokomol.Soed., **21B**, 472 (1979).
220. T.S.Popravko, G.G.Makarov, Yu.A.Mikheev, G.B.Pariiskii, L.M.Postnikov, and D.Ya.Toptygin, Vysokomol.Soed., **19A**, 2690 (1977).
221. T.A.Matusevich and L.Yu.Brazhnikova, Vestsi Akad. Nauk Beloruss.SSR, Ser.Khim.Nav., No.5, 62 (1977).
222. E.Ya.Davydov, G.B.Pariiskii, and D.Ya.Toptygin, Vysokomol.Soed., **19B**, 853 (1977).
223. N.S.Allen and J.F.McKellar, J.Polymer Sci., Macromolec.Rev., **13**, 241 (1978).
224. V.Ya.Shlyapintokh, "Fotokhimicheskie Prevrashcheniya i Stabilizatsiya Polimerov" (Photochemical Transformations and Stabilisation of Polymers), Izd.Khimiya, Moscow, 1979.

Institute of Chemical Physics,
USSR Academy of Sciences,
Moscow

RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

July 1980

Translated from *Uspekhi Khimii*, **49**, 1137-1173 (1980)

U.D.C. 541.11

Thermochemistry of Organic Derivatives of Non-transition Elements

V.I.Tel'noi and I.B.Rabinovich

Studies of the enthalpies of formation (ΔH_f°) of a wide variety of organic derivatives of non-transition Group I-VI elements (450 substances), described in the literature, are discussed. The recommended values of ΔH_f° are tabulated and different versions of the enthalpy of combustion method and reaction calorimetry, used to determine the enthalpies of formation, are examined; the characteristic features, advantages, and disadvantages of specific experimental techniques are noted. All the thermochemical quantities quoted have been recalculated taking into account up to date initial data. The average dissociation energies ($\bar{D}$) of 115 chemical bonds, formed by non-transition elements (E^{nt}) in their organic compounds, have been calculated from the enthalpies of formation. The regular variation of the quantity $\bar{D}(E^{ent}-R)$, where R is an organic group, with the atomic number of the element E^{nt} down the corresponding Group in the Periodic System is demonstrated. The influence of the nature of the organic group on $\bar{D}(E^{nt}-R)$ is described.

The bibliography includes 260 references.

CONTENTS

I.	Introduction	603
II.	Compounds of Group I non-transition elements	605
III.	Compounds of Group II non-transition elements	606
IV.	Compounds of Group III non-transition elements	607
V.	Compounds of Group IV non-transition elements	609
VI.	Compounds of Group V non-transition elements	614
VII.	Compounds of Group VI non-transition elements	616
VIII.	The average dissociation energies of the chemical bonds formed by non-transition elements in their organic compounds	616

I. INTRODUCTION

In the last 20 years many organic derivatives of non-transition elements have found extensive applications in the national economy. For example, the use of organomagnesium halides (Grignard reagents) as intermediates in the industrial synthesis of a large number of organic substances and the use of alkyl and alkyl halide compounds of aluminium as well as lithium alkyls as components of catalytic mixtures for polymerisation processes are well known. Organosilicon compounds are used to prepare lubricating agents, rubber-like polymers with a wide temperature range of high elasticity, and polymeric films with selective gas permeability, and for other purposes. In recent years methods have been developed for the use of alkyl derivatives of a number of Group II–VI non-transition elements in the industrial synthesis of semiconductor compounds of the type $A^{III}-B^{V}$,

$A^{II}-B^{VI}$, and $A^{II}-B^{IV}$. There are also other important possibilities for the applications of the compounds under consideration.

On the other hand the thermodynamic parameters of the syntheses and reactions of many industrially important organic derivatives of non-transition elements have still not been determined or have been merely estimated. This hinders the development and improvement of the technology of the processes involved in their manufacture and their applications. Calculations of the thermodynamic parameters of the above reactions are in many instances impossible owing to the lack of literature data on the thermodynamic properties of the initial compounds. On the other hand, in other cases such data are available, but they are scattered among different literature sources and the most reliable results have not been selected. This applies in the first place to the enthalpies of formation.

The present review considers critically the enthalpies of formation of all 450 organic derivatives of non-transition elements, relevant information about which has been published in 250 papers in scientific journals of different countries up to 1977† and reliable standard enthalpies of formation of the substances indicated are recommended.

The standard enthalpy of formation of a compound $\Delta H^{\circ}_{f,298}$ is the term given to the enthalpy of its synthesis under standard conditions (298 K; 101325 Pa), in the stable physical state under the given conditions, from the elements in their stable state under standard conditions. In many instances such reactions do not really occur, since their enthalpies cannot be measured, but the above quantities can be calculated on the basis of Hess's law from the enthalpies of other (real) reactions involving the relevant compounds.

The standard enthalpies of formation of the compounds have in fact been selected as the fundamental thermochemical quantities for the calculation of the enthalpies of a wide variety of other reactions under standard conditions on the basis of Hess's law by means of the equation

$$\Delta H^{0}_{r,298} = \sum_{i} \nu_i \Delta H^{0}_{f,298}(i) - \sum_{j} \nu_j \Delta H^{0}_{f,298}(j), \qquad (1)$$

where ν is the stoichiometric coefficient of the reactant in the reaction equation and the indices i and j denote the reaction products and the starting materials respectively#. The enthalpies of reaction at 298 K can be adjusted to any temperature T by means of the Kirchhoff formula:

$$\Delta H^{0}_{r,T} = \Delta H^{0}_{r,298} + \int_{298}^{T} \Delta(\nu C_p)\,dT, \qquad (2)$$

where $\Delta(\nu C_p) = \sum_i \nu_i C_p(i) - \sum_j \nu_j C_p(j)$ and $C_p = f(T)$ is the heat capacity of the reactant at constant pressure. Here one usually employs polynomials of the type $C_p = a + bT + cT^2$, which are fitted to the experimental data. In Eqn.(2) it is assumed that in the range 298–T (K) the reactants do not undergo phase transformations. Otherwise it would be necessary to take into account also the enthalpies of these transitions.

The enthalpies of formation of organic compounds (OC) are as a rule calculated from their experimental enthalpies of combustion (ΔH°_{c}) in oxygen§ (the enthalpy of combustion method) by means of Eqn.(3) which follows from Eqn.(1):

$$\Delta H^{0}_{f,298}(\mathrm{OC}) = \sum_{i} \nu_i \Delta H^{0}_{f,298}(i) - \Delta H^{0}_{c,298}(\mathrm{OC}), \qquad (3)$$

where the index i denotes the combustion product (CO_2, H_2O, and other oxides). In many instances the quantities ΔH°_{f}(OC) are calculated from the enthalpies of other reactions involving the given organic compound (reaction calorimetry). In calculations by Eqn.(1) and (3) the values of $\Delta H^{\circ}_{f,298}$ for all the reactants except for the test substance are tabulated quantities[1,2].

The combustion of organoelemental compounds in order to determine their enthalpies of combustion is carried out in stationary or rotating bomb calorimeters. Combustion of such substances in a stationary bomb was carried out in early investigation by Berthelot[3] (1899) in a study of the thermochemistry of dimethyl- and diethyl-mercury. The specific difficulties arising in the study of organoelemental compounds in a stationary bomb calorimeter were first discovered much later when Long and Norrish[4] (1949) made a detailed study of the combustion products of a number of alkyl derivatives of zinc, cadmium, boron, and aluminium formed in the bomb. These investigators established two factors which reduce the accuracy of the measurement of enthalpies of combustion: incomplete oxidation of the initial substances and the possibility of additional reactions between the combustion products.

However, despite the experimental complications which are frequently encountered, the method of combustion in a stationary bomb calorimeter has been widely used and is at present the principal procedure for the study of the thermochemistry of organoelemental compounds. In particular it is used successfully in the investigation of organic derivatives of mercury, tin, germanium, and certain other metals, whose oxidation products in the bomb calorimeter are not difficult to identify.

In order to overcome difficulties characteristic of the combustion of substances in a stationary bomb calorimeter, Good and coworkers[5-9] developed a method for the determination of the enthalpies of combustion of organoelemental compounds of certain classes by combusting them in a rotating bomb calorimeter. This method provides for the dissolution of the combustion products in a specially selected solvent in order to obtain a thermodynamically unambiguous final state of the reaction system. This combustion method has been applied successfully to organic derivatives of boron, silicon, germanium, lead, phosphorus, arsenic, bismuth, and selenium. Nevertheless, the need to choose an appropriate solvent in each specific instance, the appearance of new sources of error, and the difficulty of many operations prevent the wide-scale employment of the rotating bomb calorimeter method.

Among the different versions of reaction calorimetry, the determinations of the enthalpies of hydrolytic and halogenation reactions have been most widely used. During the fairly rapid course of the selected reactions close to room temperature and in the absence of side reactions, these methods lead to more accurate results than the combustion of a test compound in a bomb calorimeter. However, they are difficult to apply to new relatively little investigated classes of compounds, for which it is difficult to select reactions suitable for calorimetric measurements.

†The properties of ~200 such compounds are quoted in a monograph[1] published in England in 1970 (there is no Russian translation).

#If useful work is not performed in the given process (for example, electrical work) and the process takes place at constant pressure, then its enthalpy is equal to the evolved heat or the heat absorbed from outside, corresponding to a specific mass of the substances which have reacted.

§The enthalpy of formation of molecular oxygen is zero at any temperature, like that of any other elements.

Tables 1–5 present the enthalpies of formation of organic derivatives of non-transition elements, which we selected as the most reliable as a result of the analysis of the corresponding literature sources. In choosing these quantities, we turned attention to the method of their determination, the purities of the initial preparations, the unambiguity of the analytical results for the reaction products, and the precision of the calorimetric experiment (allowance for the necessary corrections and errors of the measurements and calculations). In cases where the given substance has been investigated more than once Tables 1–5 present all the references (in chronological order) and those from which the most reliable value of ΔH_f° has been selected are printed bold. After the references to the original literature, the method of determination of the given quantity is indicated in brackets and the following notation is used: SB—combustion in a stationary bomb; RB—combustion in a rotating bomb; R—reaction calorimetry. The enthalpies of vaporisation or sublimation, required for the calculation of ΔH_f° in the gaseous monomeric state, are in most cases quoted in the reports in which the experimental enthalpies of formation in the condensed state are given. In the remaining cases they were taken from other literature sources[1,10,11].

Analysis of the literature data showed that the real accuracy of the determination of the ΔH_f° for the compounds under consideration is usually not better than to within 1 kcal mol^{-1} and only in the most favourable conditions (mainly when reaction calorimetry is used) is it approximately to within 0.5 kcal mol^{-1}. The attainment of a higher accuracy is restricted, on the one hand, by the specific features of the given calorimetric experiment, and, on the other hand, by the need to use in the calculations a number of auxiliary thermochemical quantities. The values of the latter, quoted in modern handbooks[10,11], are frequently insufficiently accurate and their agreement with one another is inadequate. The authors of the present review therefore thought it desirable to round off appropriately the selected experimental values of ΔH_f°.

All the enthalpies of formation and the average bond dissociation energies taken from the original reports were recalculated taking into account the new enthalpies of formation of the compounds and atoms quoted in Ref. 11. In the absence of the necessary information in the given handbook[11], the latter was taken from other publications[2,10,12–14].

Together with compounds containing element–carbon bonds, we examined also certain compounds without such bonds but with compositions and physicochemical properties close to those of organoelemental compounds. The review does not include organic derivatives containing, apart from C–H and C–C bonds, only bonds formed by carbon with oxygen, the halogens, nitrogen, or sulphur. For these substances, there are very many thermochemical data[1,2] and it is desirable to consider them separately.

In each of Tables 1–5 the substances are arranged in order of increasing atomic number of their non-transition elements in the given Group of the Periodic System. For the same element, related compounds are grouped together. Compounds containing, apart from the given element, only carbon and hydrogen are indicated first; next follow compounds containing also oxygen, the halogens, nitrogen, or sulphur. Heterocyclic compounds have been isolated in individual groups and have been arranged in an analogous sequence. The physical states of the substances, to which the values of ΔH_f° refer, are denoted by the following symbols: (c) = crystal; (l) = liquid (appended to the formulae of the compounds), and (g) = gas [appended in brackets to the symbol of the enthalpy of formation: $\Delta H_{f\,(g)}$].

The enthalpies of formation (ΔH_f°) examined in this review are expressed in thermochemical kilocalories (1 kcal = 4.1840 kJ) and are referred to the standard pressure of 101325 Pa (this is indicated by superscript 0) and the standard temperature of 298.15 K.

II. COMPOUNDS OF GROUP I NON-TRANSITION ELEMENTS

The recommended enthalpies of formation of these substances are listed in Table 1.

Table 1. Standard enthalpies of formation of organic derivatives of Group I non-transition elements (kcal mol^{-1}).*

Compound	ΔH_f^0	References	Compound	ΔH_f^0	Refs.
CH_3Li (c)	−17.9±0.5	15 (R)	p-$CH_3C_6H_4Li$ (c)	+0.9±0.5	15 (R)
C_2H_5Li (c)	−13.5±0.5	16 (SB), 15 (R)	p-ClC_6H_4Li (c)	+1.3±0.5	15 (R)
C_3H_5Li (l)	−1.4±0.5	15 (R)	CH_3NHLi (c)	−22.5±0.5	18 (R)
$(CH_3)_2CHLi$ (l)	−13.8±0.5	15 (R)	C_2H_5OLi (c)	−109±1	19 (R)
n-C_4H_9Li (l)	−31.6±0.5	17 (R), 16 (SB) 15 (R)	C_2H_5ONa (c)	−98±1	19 (R)
s-C_4H_9Li (l)	−21.0±0.5	15 (R)	C_2H_5OK (c)	−98±1	19 (R)
t-C_4H_9Li (l)	−22.0±0.5	15 (R)	C_2H_5ORb (c)	−97±1	20 (R)
C_6H_5Li (c)	+11.8±0.5	15 (R)	C_2H_5OCs (c)	−97±1	20 (R)
$C_6H_5CH_2Li$ (c)	+3.7±0.5	15 (R)			

*For the explanation of the Table, see the introduction.

Lebedev et al.[16] determined the enthalpies of formation of ethyl-lithium and n-butyl-lithium by the enthalpy of combustion method. The above compounds were oxidised under the conditions of a stationary bomb calorimeter to LiO_2(c), CO_2(g), and H_2O(l). Chemical analysis of the solid combustion products showed that significant amounts of Li_2O_2 and Li_2CO_3 were absent.

A number of workers[15,17–20] believe that different versions of reaction calorimetry constitute a more reliable method for the determination of the enthalpies of formation of organolithium compounds. Thus the enthalpy of formation of n-butyl-lithium has been calculated[17] from the enthalpy of its hydrolysis measured calorimetrically: ΔH_f°[n-C_4H_9Li(l)] = −31.4 ± 0.7 kcal mol^{-1}. However, this value is close to that found by the enthalpy of combustion method[16] (−31.8 ± 1.7 kcal mol^{-1}). Table 1 lists the average of the above values[16,17] as the enthalpy of formation of n-butyl-lithium. The interactions of organolithium compounds with gaseous HBr are also suitable for calorimetric measurements. The study of the thermochemistry of these processes, occurring in petroleum ether at room temperature, made it possible[15] to calculate the enthalpies of formation of 11 organic derivatives of lithium.

The enthalpies of formation of alkali metal ethoxides have been found[19,20] from the enthalpies of their reactions with aqueous sulphuric acid solution determined calorimetrically. The calculation of the ΔH_f° for the compounds under consideration in the gaseous state requires, apart from the data in Table 1, the corresponding enthalpies of sublimation (vaporisation), which are not available in the literature. The temperature variation of the vapour pressures of ethyl-lithium and n-butyl-lithium has been studied[16,21]. However, the calculation of the enthalpies of sublimation (vaporisation) from these data is complicated by the fact that the above

compounds vaporise in the form of associated species. Thus ethyl-lithium sublimes in the form of tetrameric and hexameric molecules[22,23]. The association of gaseous n-C_4H_9Li has not been studied, but it is known[24] that gaseous t-butyllithium is tetrameric.

III. COMPOUNDS OF GROUP II NON-TRANSITION ELEMENTS

The recommended enthalpies of formation of the above substances are listed in Table 2.

The application of the enthalpy of combustion methods to organozinc compounds involves serious experimental difficulties. Firstly, the degree of oxidation of these compounds in the bomb calorimeter never reaches 100%. Thus, in a study of diethylzinc, Long and Norrish carried out 50 combustions of this substance, but complete combustion was never achieved, as shown both by visual inspection of the contents of the bomb calorimeter after the experiments and by chemical analysis of the combustion products. Secondly, there is a possibility of reactions between the combustion products which are difficult to take into account. For example, in the combustion of dimethylzinc the zinc oxide formed was partly hydrated and partly (to the extent of ~8%) reacted with carbon dioxide to form zinc carbonate. The interpretation of the experimental results[4] therefore involved the calculation of corrections due to both the incomplete combustion of the zinc compounds investigated and to the occurrence of side reactions between their combustion products.

In order to find the ΔH_f° for the methyl and ethyl compounds of zinc and cadmium, Skinner and coworkers[30,34] measured the enthalpies of their hydrolysis, iodination, and reaction with aqueous sulphuric acid solution. The hydrolytic reactions led to the formation of the metal hydroxides and the modifications of the $Zn(OH)_2$ and $Cd(OH)_2$ formed were not established, which introduced an error into the calculation of the ΔH_f° for the test compounds.

The study of iodination processes[30,34] was complicated by side reactions. For example, in the case of ethyl compounds the main process

$$(C_2H_5)_2M + 2I_2 \rightarrow MI_2 + 2C_2H_5I,$$

where M = Zn or Cd, was accompanied by the reactions

$$(C_2H_5)_2M + I_2 \rightarrow MI_2 + C_4H_{10},$$

$$(C_2H_5)_2M + 2I_2 \rightarrow MI_2 + C_2H_4I_2 + C_2H_6.$$

The thermal corrections caused by the above side reactions were taken into account by the authors[30,34] in their calculations of the enthalpies of formation of the test substances. The interaction of zinc and cadmium alkyls with aqueous sulphuric acid proved to be more convenient for the calorimetric study than hydrolysis and iodination of the same compounds in view of its high rate and the lack of uncertainty as to the products.

The application of these versions of reaction calorimetry to each of the above compounds yielded satisfactorily concordant results. Thus the authors[30] obtained +4.7 ± 0.3 kcal mol^{-1} (by the hydrolytic reaction), +4.0 ± 1.0 kcal mol^{-1} (by the iodination reaction), and + 2.8 ± 0.5 kcal mol^{-1} (by the reaction with sulphuric acid) for $\Delta H_f^\circ[(C_2H_5)_2Zn(l)]$, while the corresponding values found in the same way[30,34] for $\Delta H_f^\circ[(CH_3)_2Cd(l)]$ were respectively +15.2 ± 0.2, +17.0 ± 0.1, and +15.7 ± 0.3 kcal mol^{-1}.

For organozinc compounds, a satisfactory agreement has been observed in addition between the values of ΔH_f° found by reaction calorimetry[30] and by the enthalpy of combustion method[4]. We therefore based the choice of the ΔH_f° for the above compounds on the results obtained by both methods.

In the case of organocadmium compounds there are significant differences between the values of ΔH_f° obtained by different calorimetric methods. Thus the enthalpies of formation of liquid $(CH_3)_2Cd$ and $(C_2H_5)_2Cd$ by the combustion method were found to be[4,31–33] +20.5 ± 2.8 and +20.9 ± 0.8 kcal mol^{-1}, while the values obtained by reaction

Table 2. Standard enthalpies of formation of organic derivatives of Group II non-transition elements (kcal mol^{-1}).*

Compound	ΔH_f^0	ΔH_f^0 (g)	References	Compound	ΔH_f^0	ΔH_f^0 (g)	References
$(C_6H_5)_2Be$ (c)	+37±1	+73±5	25(R)	$(n\text{-}C_4H_9)_2Hg$ (l)	−23±2	−7±2	38(SB)
$(C_5H_7O_2)_2Be$ (c)	−298±1	−276±1	26(R)	$(iso\text{-}C_4H_9)_2Hg$ (l)	−24±2	−9±2	38(SB)
$(C_{10}H_{16}O_2)_2Be$ (c)	−386±2	−362±2	26(R)	$(iso\text{-}C_5H_{11})_2Hg$ (l)	−37±2	−20±3	38(SB)
$(C_5H_4F_3O_2)_2Be$ (c)	−597±2	−574±2	26(R)	$(C_6H_5)_2Hg$ (c)	+67.3±0.5	+94.3±0.5	36(SB), 40(R), 41(SB), 42(SB)
$(cyclo\text{-}C_7H_5O_2)_2Be$ (c)	−208±1	−184±5	26(R)				
$(C_5H_5)_2Mg$ (c)	+16±1	+32±1	27(R(	$(C_2H_5Hg)_2O$ (c)	−23±2	—	43(R)
$n\text{-}C_4H_9MgCl$ (c)**	−107.7±0.5	—	28(R)	$C_2H_5HgO_2C(CH_3)_2C_6H_5$ (c)	−18±2	—	43(R)
$(C_5H_7O_2)_2Ca$ (c)	−313±1	−300±4	29(R)	$(CN)_2Hg$ (c)	+63±2	+89±2	44(R)
$(CH_3)_2Zn$ (l)	+5.7±0.5	+12.8±0.5	4(SB), 30(R)	CH_3HgCl (c)	−28.6±0.5	−13.1±0.5	35(R)
$(C_2H_5)_2Zn$ (l)	+3.9±0.5	+13.4±0.5	4(SB), 30(R) 31—33(SB)	CH_3HgBr (c)	−21±1	−5±1	35(R)
				CH_3HgI (c)	−10.6±0.5	+5±1	35(R)
$(n\text{-}C_3H_7)_2Zn$ (l)	−14±6	−3±6	4(SB)	C_2H_5HgCl (c)	−34±1	−16±1	37(R)
$(n\text{-}C_4H_9)_2Zn$ (l)	−25±6	−12±6	4(SB)	C_2H_5HgBr (c)	−26±1	−8±1	37(R)
$(C_5H_7O_2)_2Zn$ (c)	−223±1	−208±4	29(R)	C_2H_5HgI (c)	−16±1	+3±1	37(R)
$(C_{10}H_9O_2)_2Zn$ (c)	−179±1	−166±4	29(R)	$n\text{-}C_3H_7HgCl$ (c)	−40.8±0.5	−21±2	39(R)
$(CH_3)_2Cd$ (l)	+16±1	+25±1	4(SB), 34(R)	$n\text{-}C_3H_7HgBr$ (c)	−32.3±0.5	−12±2	39(R)
$(C_2H_5)_2Cd$ (l)	+13±1	+24±1	30(R), 31—33(SB)	$n\text{-}C_3H_7HgI$ (c)	−21.9±0.5	−1±2	39(R)
$(CH_3)_2Hg$ (l)	+13±1	+21±1	35(R), 36(SB)	$iso\text{-}C_3H_7HgCl$ (c)	−40.5±0.5	−20±2	39(R)
$(C_2H_5)_2Hg$ (l)	+7.3±0.5	+18±1	37(R), 38(SB) 31—33(SB)	$iso\text{-}C_3H_7HgBr$ (c)	−32.8±0.5	−13±2	39(R)
				$iso\text{-}C_3H_7HgI$ (c)	−22.4±0.5	−1±2	39(R)
$(n\text{-}C_3H_7)_2Hg$ (l)	−5.6±0.5	+7.4±0.5	38(SB), 39(R)	C_6H_5HgCl (c)	+0.1±0.5	+25±2	40(R)
$(iso\text{-}C_3H_7)_2Hg$ (l)	−4±1	+9±1	38(SB), 39(R)	C_6H_5HgBr (c)	+8±1	+33±2	40(R)
				C_6H_5HgI (c)	+18±1	+43±2	40(R)

*For the explanation of the Table, see the introduction.

**The enthalpies of formation of etheral solutions of a series of halogen-containing organomagnesium compounds are quoted by Carson and Skinner[55] and Holm[46].

calorimetry[30,32] were +16 ± 1 and +13 ± 1 kcal mol^{-1} respectively. The authors[4] note that, when organocadmium compounds are combusted in a bomb calorimeter, the solid combustion products always contain appreciable amounts of metallic cadmium and unoxidised carbon in addition to the oxide CdO. The exact calculation of the relevant corrections is difficult, which might have been the reason for the erroneous results in a number of studies[4,31–33]. Therefore, in choosing the values of ΔH_f° for cadmium compounds, we took into account only the results[30,34] obtained by reaction calorimetry.

The study of organomercury compounds has attracted much attention by thermochemists. When these substances are combusted in a bomb calorimeter, they are converted into carbon dioxide, water, and liquid mercury. A small amount of mercury (up to 10%) is then oxidised to HgO and $HgNO_3$, which requires allowance for the corresponding heat corrections. When the latter are applied correctly, it is possible to obtain fairly reliable results, as shown by the agreement, to within 1 kcal mol^{-1}, between the values of ΔH_f° for dimethyl-, diethyl-, and diphenyl-mercury found, on the one hand, by the combustion method[36,41,42], and, on the other hand, by reaction calorimetry[35,37,40].

The enthalpies of formation of the compounds R_2Hg, where $R = CH_3$, C_2H_5, C_3H_7, or C_6H_5, were obtained by Skinner and coworkers[35,37,39,40] by studying the enthalpies of bromination and iodination of the above substances.

The same workers investigated the thermochemistry of processes

$$R_2Hg + HgX_2 \rightarrow 2RHgX,$$

where X = Cl, Br or I, which made it possible to calculate the ΔH_f° for the products RHgX from the enthalpies of formation of the compounds R_2Hg found beforehand (Table 2).

IV. COMPOUNDS OF GROUP III NON-TRANSITION ELEMENTS

The recommended enthalpies of formation of the above substances are listed in Table 3.

The thermochemistry of organoboron compounds has been studied comparatively thoroughly. In the first studies in this field[4,47,48,54] the enthalpies of combustion of a number of alkylboron compounds were measured using a stationary bomb calorimeter. A number of methodological difficulties, characteristic of these substances were discovered. However, the above studies did not lead to the creation of a thoroughly developed method for the determination of the enthalpies of combustion of these compounds. Furthermore, some of the above workers expressed doubts concerning the possibility of the successful combustion of such substances in a stationary bomb calorimeter.

Gal'chenko[128], who developed a reliable method for the combustion of organoboron compounds in a stationary bomb calorimeter and applied it to a large number of organic substances containing 5–75 wt.% of boron (Table 3), made a major contribution to the development of the thermochemistry of such compounds. He established[128] that the products of their incomplete combustion include boron carbide, free carbon, and boron, and, in the case of nitrogen-containing compounds, also boron nitride. Furthermore, the combustion of the initial substance is accompanied by secondary reactions between the combustion products: the hydration of the boron oxide formed and the dissolution of part of boric acid in the water present in the bomb. However, for a high degree of combustion of the test compounds, which constitutes a necessary condition for the application of this method and is readily achieved by varying the oxygen pressure in the bomb, the mass of the specimen, the size of the crucible, and other conditions, the calculation of corrections for the incomplete combustion and secondary processes does not present special difficulty.

The correction for incomplete combustion, calculated from the determinations of carbon dioxide and boric acid in the combustion products, did not exceed 1% of the total amount of energy evolved during the experiment in most instances. It was also shown that the hydration of boron oxide and dissolution of the boric acid thus formed proceed comparatively rapidly and do not distort the variation of the temperature in the final period of the experiment. This method was used by Gal'chenko and coworkers for both liquid[50,52,53,56,60,61,63–65,74–80,85,90,103] and solid[91–102] boron compounds, the accuracy of the determination of their enthalpies of combustion being to within 0.05–0.10%.

The difficulties in the combustion of boron-containing compounds in a stationary bomb calorimeter led Good and coworkers[8,9] to develop a method involving their combustion in a rotating bomb calorimeter. By this procedure, the authors[8,9] measured the enthalpies of combustion of trimethyl- and tirethyl-amineborane. Specimens of the test substances mixed with vinylidine fluoride $(CH_2CF_2)_n$ were placed in polyester tubes. The combustion was carried out in a platinised bomb calorimeter containing an excess of aqueous HF solution. On rotation of the bomb, the combustion products interacted with the hydrogen fluoride solution and a solution of $HBF_4.14.67HF.58.72H_2O$, preliminary values of the enthalpy of which had been found in other experiments, was obtained. No solid combustion products were detected after the experiments.

The use of this combustion method involves certain difficulties as regards the assignment of the experimental results to a standard state. For example, there are not data for the solubility and enthalpy of solution of the resulting carbon dioxide in aqueous HBF_4 and HF solutions. In order to take into account the corresponding corrections, the authors[8,9] performed the so called "comparison experiments" in addition to the main experiments. In the "comparison experiment" a substance (benzoic acid or paraffin) with an accurately established enthalpy of combustion was used instead of the test compound. The amount of this substance as well as the concentration and volume of the aqueous HBF_4 and HF solution introduced into the bomb calorimeter were selected so that the final states of the reaction systems in both the comparison experiments and in the experiments designed to combust the boron compound were as far as possible similar.

The methods of reaction calorimetry have come to be widely used in the thermochemical studies of organoboron compounds. This is due to the high reactivity of the above compounds and the availability for many of them of reactions suitable for thermochemical measurements. The enthalpies of hydrolysis of the compounds have been measured most frequently. In many cases such reactions rapidly reach completion at room temperature and give rise to products whose properties have been studied in detail and which can be easily identified. Thus, in order to find the enthalpies of formation of alkoxyboron compounds, Skinner and coworkers[59] measured the enthalpies of the reactions

$$(C_nH_{2n+1}O)_3B\ (l) + 3H_2O\ (l) \rightarrow H_3BO_3\ (c) + 3C_nH_{2n+1}OH\ (l).$$

Table 3. Standard enthalpies of formation of organic derivatives of Group III non-transition elements (kcal mol^{-1}).*

Compound	ΔH_f^0	ΔH_f^0 (g)	References
$(CH_3)_3B$ (l)	−34±6	−30±6	4(SB), 47(SB),
$(C_2H_5)_3B$ (l)	−45±2	−36±2	48(SB), 47(SB), 49(R)
$(n\text{-}C_3H_7)_3B$ (l)	−66±3	−56±3	48(SB), 50(SB),
$(iso\text{-}C_3H_7)_3B$ (l)	−70±3	−60±3	50(SB)
$(n\text{-}C_4H_9)_3B$ (l)	−83±1	−68±1	51(SB), 47(SB), 52(SB), 53(SB)
$(iso\text{-}C_4H_9)_3B$ (l)	−81±2	−67±2	49(R), 50(SB)
$(s\text{-}C_4H_9)_3B$ (l)	−73±6	−58±6	54(SB)
$(iso\text{-}C_5H_{11})_3B$ (l)	−108±2	−91±2	50(SB)
$(n\text{-}C_6H_{13})_3B$ (l)	−116±1	−95±1	55(R), 56(SB)
$(cyclo\text{-}C_6H_{11})_3B$ (c)	−115±2	−95±3	57(R)
$(n\text{-}C_7H_{15})_3B$ (l)	−133±2	−109±2	55(R)
$(n\text{-}C_8H_{17})_3B$ (l)	−152±2	−124±2	55(R)
$(s\text{-}C_8H_{17})_3B$ (l)	−148±2	−121±2	55(R)
$(C_6H_5)_3B$ (c)	+12±2	+31±2	57(R)
$(CH_3O)_2BH$ (l)	−144.5±0.5	−138.4±0.5	58(R)
$(CH_3O)_3B$ (l)	−222.9±0.5	−214.6±0.5	59(R)
$(CH_3O)B(n\text{-}C_4H_9)_2$ (l)	−132±1	—	60(SB), 61(SB)
$(C_2H_5O)_3B$ (l)	−250.4±0.5	−239.8±0.5	59(R)
$(iso\text{-}C_3H_7O)_2BH$ (l)	−183.0±0.5	—	62(R)
$(n\text{-}C_3H_7O)_3B$ (l)	−269.4±0.5	−258±1	59(R)
$(n\text{-}C_4H_9O)B(n\text{-}C_4H_9)_2$ (l)	−155±1	—	63(SB)
$(n\text{-}C_4H_9O)_2B(n\text{-}C_4H_9)$ (l)	−224±2	—	65(SB)
$(n\text{-}C_4H_9O)_3B$ (l)	−286±1	−273±1	59(R), 64(SB), 43(R)
$(C_6H_5O)_3B$ (c)	−159.9±0.5	−140±1	66(R)
$(m\text{-}CH_3C_6H_4O)_3B$ (l)	−183±1	−163±1	67(R)
$(p\text{-}CH_3C_6H_4O)_3B$ (l)	−181±1	−160±1	67(R)
$(n\text{-}C_4H_9)_2BOH$ (l)	−146±1	−131±2	68(R)
$C_6H_5B(OH)_2$ (c)	−172.0±0.5	—	69(R)
$[(n\text{-}C_4H_9)_2B]_2O$ (l)	−213±1	—	64(SB)
$[(C_6H_5)_2B]_2O$ (c)	−84±2	—	69(R)
$s\text{-}C_4H_9O_2B(O\text{-}n\text{-}C_4H_9)_2$ (l)	−276±2	−264±2	43(R)
$(s\text{-}C_4H_9O_2)_2BO\text{-}n\text{-}C_4H_9$ (l)	−265±2	−254±2	43(R)
$(CH_3)_4NB_3H_8$ (c)	−38±1	—	84(SB)
$(C_2H_5)_4NB_3H_8$ (c)	−63±2	—	84(SB)
$(n\text{-}C_4H_9)_4NB_3H_8$ (c)	−106±3	—	84(SB)
$(n\text{-}C_4H_9)B(OCH_3)N(C_2H_5)_2$ (l)	−146±1	−132±1	85(SB)
$[(CH_3)_2N]_2BCl_2$ (l)	−107±2	−98±2	86(R)
$[(CH_3)_2N]_2BCl$ (l)	−94±1	−84±1	86(R)
$B(SCH_3)_3$ (l)	−50±1	−37±1	87(R)
$B(SC_2H_5)_3$ (l)	−81±1	−67±1	88(R)
$B(S\text{-}n\text{-}C_3H_7)_3$ (l)	−100±1	−79±1	87(R)
$B(S\text{-}n\text{-}C_4H_9)_3$ (l)	−117±1	−94±1	87(R)
$B(S\text{-}n\text{-}C_5H_{11})_3$ (l)	−135±1	−110±1	87(R)
$B(SC_6H_5)_3$ (c)	+16±1	+46±2	87(R)
$CH_2(CH_2)_3B(n\text{-}C_4H_9)$ (l)	−46±1	—	52(SB), 61(SB)
$CH_2(CH_2)_3B(n\text{-}C_6H_{13})$ (l)	−67±1	—	61(SB)
$CH_2(CH_2)_3B(OCH_3)$ (l)	−93±1	—	60(SB), 61(SB)
$O(CH_2)_3B(n\text{-}C_4H_9)$ (l)	−108±1	−97±1	80(SB)
$cyclo\text{-}(C_6H_5BO)_3$ (c)	−301±2	—	69(R)
$O(CH_2)_2OBCl$ (l)	−186±1	—	89(R)
$O(CH_2)_3OBCl$ (l)	−183±3	—	89(R)
$OCH(CH_3)CH_2OBCl$ (l)	−191±1	—	89(R)
$O[CH(CH_3)]_2OBCl$ (l)	−200±1	—	89(R)
$N(C_2H_5)(CH_2)_3B(n\text{-}C_4H_9)$ (l)	−71±2	−57±2	80(SB), 90(SB)
$N(n\text{-}C_3H_7)(CH_2)_3B(n\text{-}C_3H_7)$ (l)	−73±2	—	80(SB), 90(SB)
$S(CH_2)_2SBC_6H_5$ (l)	−32±1	—	88(R)
$S(CH_2)_3SBC_6H_5$ (l)	−37±1	—	88(R)
$S(CH_2)_2SBCl$ (l)	−66±1	—	88(R)
$S(CH_2)_3SBCl$ (l)	−73±1	—	88(R)
$SCH_2CH(CH_3)SBCl$ (l)	−72±1	—	88(R)
$o\text{-}B_{10}C_2H_{12}$ (c)	−42±4	−27±4	91—94(SB)
$m\text{-}B_{10}C_2H_{12}$ (c)	−59±3	−45±3	94—98(SB), 93(SB)
$p\text{-}B_{10}C_2H_{12}$ (c)	−76±4	−61±4	96(SB), 99(SB),
$(C_7H_5O_2)_3Al$ (c)	−317±1	−287±5	116(R)
$(C_7H_4CH_3O_2)_3Al$ (c)	−330±2	−300±6	116(R)
$(C_{10}H_{17}O_2)_3Al$ (c)	−572±3	−543±3	118(R)
$(C_5H_4F_3O_2)_3Al$ (c)	−893±3	−867±3	118(R)
$(C_2H_5)_2AlCl$ (l)	−97±1	—	119(R), 120(R)
$(iso\text{-}C_4H_9)_2AlCl$ (l)	−118±1	—	119(R)
$(C_2H_5)AlCl_2$ (l)	−133±4	—	120(R)
$(C_2H_5)_3Al_2Cl_3$ (l)	−230±4	—	120(R)
$(C_2H_5)_2AlBr$ (l)	−83±2	—	120(R)
$(C_2H_5)AlBr_2$ (l)	−104±4	—	120(R)
$(C_2H_5)_3Al_2Br_3$ (l)	−188±4	—	120(R)
$(t\text{-}C_4H_9O_2)_3B$ (l)	−254±2	−243±2	43(R)
$(n\text{-}C_4H_9)_2BCl$ (l)	−99±2	−88±2	68(R)
$(C_6H_5)BCl_2$ (l)	−72±1	−64±1	57(R), 70(R)
$(C_6H_5)_2BCl$ (l)	−32±2	−22±2	57(R), 70(R)
$o\text{-}CH_3C_6H_4BCl_2$ (l)	−71.9±0.5	−60.7±0.5	71(R)
$p\text{-}CH_3C_6H_4BCl_2$ (c)	−81±1	−70±1	71(R)
$(CH_3O)_2BCl$ (l)	−186.2±0.5	−178.0±0.5	1(R)
$C_2H_5OBCl_2$ (l)	−157±1	−149±1	72(R)
$(C_2H_5O)_2BCl$ (l)	−205±1	−196±1	72(R)
$(m\text{-}ClC_6H_4O)_3B$ (l)	−180±6	−166±6	67(R)
$(p\text{-}ClC_6H_4O)_3B$ (l)	−177±6	−168±6	67(R)
$(n\text{-}C_4H_9)_2BBr$ (l)	−84±1	−72±1	68(R)
$C_6H_5BBr_2$ (l)	−41±1	−31±0.8	57(R), 70(R)
$(C_6H_5)_2BBr$ (l)	−17±2	−3±2	57(R), 70(R)
$(n\text{-}C_4H_9)_2BI$ (l)	−67±1	−54±1	68(R)
$[(CH_3)_2N]_3B$ (l)	−77±1	−66±1	73(R)
$[(C_2H_5)_2N]_3B$ (l)	−111±2	—	74(SB)
$(n\text{-}C_4H_9)_2BNH_2$ (l)	−88±1	—	75(SB), 76(SB)
$(iso\text{-}C_4H_9)_2BNH_2$ (l)	−90±1	—	75(SB)
$(n\text{-}C_4H_9)_2BNH(n\text{-}C_4H_9)$ (l)	−108±1	—	76(SB)
$(n\text{-}C_4H_9)B[NH(n\text{-}C_4H_9)]_2$ (l)	−120±3	—	77(SB), 78(SB)
$(n\text{-}C_4H_9NH)_3B$ (l)	−142±2	—	77(SB), 78(SB)
$(n\text{-}C_3H_7)_2B(CH_2)_3NH_2$ (l)	−75±2	—	77(SB)
$(n\text{-}C_3H_7)_2B(CH_2)_3N(CH_3)_2$ (l)	−78±2	−60±2	80(SB)
$(n\text{-}C_4H_9)_2B(CH_2)_3NH_2$ (l)	−94±2	—	79(SB), 80(SB)
$(n\text{-}C_3H_7)_2BN(n\text{-}C_3H_7)_2$ (l)	−104±1	−89±2	80(SB)
$(n\text{-}C_4H_9)_2BN(n\text{-}C_4H_9)_2$ (l)	−127±2	−107±2	80(SB)
$CH_3H_2NBH_3$ (c)	−31.6±0.5	−13±1	81(R)
$(CH_3)_2HNBH_3$ (c)	−32.5±0.5	−14±1	81(R)
$(CH_3)_2NBH_3$ (c)	−34±1	−20±1	8(RB), 81(R)
$(C_2H_5)_3NBH_3$ (l)	−47.4±0.5	−32.9±0.5	9(RB)
$(CH_3)_4NBH_4$ (c)	−17±1	—	82(SB)
$(C_2H_5)_4NBH_4$ (c)	−34±2	—	83(SB)
$(n\text{-}C_4H_9)_4NBH_4$ (c)	−63±4	—	83(SB)
$(CH_3)_2NB_2H_5$ (l)	−35±1	−28±1	1(R)
$o\text{-}B_{10}C_2H_{11}CH_3$ (c)	−60±4	−45±4	98(SB), 94(SB) 98(SB), 100(SB), 94(SB)
$m\text{-}B_{10}C_2H_{11}CH_3$ (c)	−74±3	−59±3	100(SB), 94(SB)
$p\text{-}B_{10}C_2H_{11}CH_3$ (c)	−66±4	−54±4	100(SB), 94(SB)
$o\text{-}B_{10}C_2H_{10}\text{-}1.2\text{-}(CH_3)_2$ (c)	−68±4	−52±4	98(SB), 94(SB)
$m\text{-}B_{10}C_2H_{10}\text{-}1.7\text{-}(CH_3)_2$ (c)	−75±4	−61±4	98(SB), 94(SB)
$p\text{-}B_{10}C_2H_{10}\text{-}1.12\text{-}(CH_3)_2$ (c)	−88±4	−72±4	98(SB), 94(SB)
$o\text{-}B_{10}C_2H_{11}CH_2OH$ (c)	−83±4	−65±4	98(SB), 101(SB), 94(SB)
$m\text{-}B_{10}C_2H_{11}CH_2OH$ (c)	−108±3	−89±3	98(SB), 101(SB), 94(SB)
$p\text{-}B_{10}C_2H_{11}CH_2OH$ (c)	−110±3	−90±3	98(SB), 101(SB), 94(SB)
$o\text{-}B_{10}C_2H_{11}COOH$ (c)	−131±3	−108±3	98(SB), 102(SB), 94(SB)
$m\text{-}B_{10}C_2H_{11}COOH$ (c)	−159±3	−136±3	98(SB), 102(SB), 94(SB)
$p\text{-}B_{10}C_2H_{11}COOH$ (c)	−151±4	−128±4	98(SB), 102(SB), 94(SB)
$o\text{-}B_{10}C_2H_{11}C_6H_{13}$ (l)	−108±4	−88±4	94(SB), 103(SB),
$cyclo\text{-}[HBN(CH_3)]_3$ (l)	−227±1	−217±1	104(R)
$cyclo\text{-}[ClBN(CH_3)]_3$ (c)	−262±1	—	104(R)
$cyclo\text{-}[BrBN(CH_3)]_3$ (c)	−245±1	—	105(R)
$(CH_3)_3Al$ (l)	−36±1	−21±1	4(SB), 106(R), 107(SB)
$(C_2H_5)_2AlH$ (l)	−74±4	—	108(SB)
$(C_2H_5)_3Al$ (l)	−52±2	−35±2	44(R), 108(SB), 109(SB), 107(SB)
$(n\text{-}C_3H_7)_3Al$ (l)	−69±3	−48±3	110(R, SB)
$(iso\text{-}C_4H_9)_2AlH$ (l)	−96±4	—	108(SB)
$(iso\text{-}C_4H_9)_3Al$ (l)	−70±7	—	111(SB)
$(C_2H_5)_2Al(OC_2H_5)$ (l)	−125±1	−110±2	112(SB)
$(C_2H_5)_2Al(O\text{-}n\text{-}C_3H_7)$ (l)	−156±3	−141±4	112(SB)
$(C_2H_5)_2Al(O\text{-}t\text{-}C_4H_9)$ (l)	−185±4	—	112(SB)
$[(iso\text{-}C_3H_7O)_3Al]_3$ (l)	−692.5±0.5	—	113(R)
$[(iso\text{-}C_3H_7O)_3Al]_4$ (l)	−1230.8±0.5	—	113(R)
$(CH_3COO)_3Al$ (c)	−452±1	—	106(R)
$(C_5H_7O_2)_3Al$ (c)	−428±1	−399±1	114(SB); 115(R), 116(R) 117(SB)
$(C_2H_5)_2All$ (l)	−65±2	—	120(R)
$(C_2H_5)All_2$ (l)	−69±4	—	120(R)
$(CH_3)_3Ga$ (l)	−19±1	−11±1	121(SB), 122(R)
$(C_2H_5)_3Ga$ (l)	−24±2	−14±1	123(SB), 124(SB)
$(n\text{-}C_4H_9)_3Ga$ (l)	−68±1	−54±1	124(SB)
$(iso\text{-}C_4H_9)_3Ga$ (l)	−70±1	−57±1	124(SB)
$(C_5H_7O_2)_3Ga$ (c)	−354±2	−325±3	125(R), 117(SB)
CH_3GaI_2 (c)	−51±1	—	122(R)
$(CH_3)_3In$ (c)	+34±2	+48±2	126(R)
$(C_5H_7O_2)_3In$ (c)	−336±1	−307±2	117(SB)
C_5H_5Tl (c)	+26±1	—	127(R)

*For the explanation of the Table, see the introduction.

The reactions were carried out by breaking under water a glass bulb containing a specific amount of the test compound. The water also served as the calorimetric liquid. The process reaches completion rapidly and unambiguously at room temperature. From the results of the measured enthalpies of hydrolysis, Skinner and coworkers[59,68,72,73,86] as well as

Finch, Gardner, and coworkers[57,70,87-89], calculated the enthalpies of formation of a large number of organoboron compounds of different classes: alkoxy- and alkylthio-compounds, substances containing halogens, etc.

The enthalpies of formation of a series of trialkylboron compounds were calculated by Skinner and coworkers[49,55] from the enthalpies of hydroboration of olefins measured by a calorimetric method[49,55]:

$$B_2H_6\,(g) + 6C_nH_{2n}\,(g) \rightarrow 2\,(C_nH_{2n+1})_3B\,(l)$$

This process was carried out by passing diborane through a saturated solution of the olefin in diglyme. Owing to the possible occurrence of side reactions, the hydroboration reactions are less convenient for the determination of the enthalpies of formation of boron compounds than the hydrolytic reactions. For example, when $n = 6$, 7, 8, the main olefin hydroboration product is accompanied by the formation of ~6% of its isomers in which the boron atom is attached to the second and not the first carbon atom, which requires the calculation of the appropriate corrections in the interpretation of the experimental results.

The thermochemistry of organoaluminium compounds has been less thoroughly investigated than that of boron-containing substances. Furthermore, the results obtained by different workers for the same compound differ markedly. Thus the literature values of the enthalpy of formation of liquid $(CH_3)_3Al$ include -28.7 ± 2.3 and -21.4 ± 3 kcal mol^{-1} found by the method of combustion in a stationary bomb calorimeter[4,107] and -36.1 ± 1.3 kcal mol^{-1} obtained[106] by reaction calorimetry. Bearing in mind the difficulty of attaining the complete combustion of organoaluminium compounds, we gave preference to the value[106] calculated from the measurements of the enthalpy of reaction of trimethylaluminium with acetic acid.

Even more contradictory data are available for triethylaluminium, the enthalpy of formation of which has been found to be -32.4 ± 3, -51.9 ± 2.2, -41.4 ± 1.1, and -56.6 ± 0.8 kcal mol^{-1} by the combustion method in Refs. 107–109 and 129 respectively and -36.5 ± 5 kcal mol^{-1} by reaction calorimetry[44]. The last value, calculated from the experimental enthalpy of hydrolysis of $(C_2H_5)_3Al$, cannot be regarded as reliable owing to the lack in the relevant report[44] of a detailed analysis of the gaseous products of the above reactions and the inaccuracy of the value of ΔH_f° of the amorphous product $Al(OH)_3$ formed in the hydrolysis.

The most accurate value $\Delta H_f^\circ[(C_2H_5)_3Al(l)] = -52 \pm 2$ kcal mol^{-1} has been obtained by the combustion method in a study[108] where the combustion products were analysed quantitatively and in the interpretation of the experimental results account was taken of the corresponding corrections for the incomplete combustion of the initial compound.

Measurements of the enthalpies of combustion of 30 aluminium-containing substances, including alkylaluminium hydrides and alkylaluminium chloride have been reported[129,130]. However, the above studies were carried out using insufficiently accurate calorimetric measurements. For example, the chlorine-containing substances were combusted without the use of reducing agents (hydrazine or arsenic oxide), which ensure unambiguously the state of chlorine in the combustion products; the internal surface of the bomb was not protected from the action of chlorine-containing products formed in the oxidation of the initial compound, etc. Furthermore, insufficiently purified specimens of the test compounds were used in the combustion experiments. Thus the purity of aluminium trialkyl and dialkylaluminium hydrides studied by Pawlenko[129] was between 94 and 99.5%, while that of alkylaluminium chlorides investigated in another study by Pawlenko[130] ranged from 93 to 97%.

Owing to the above deficiencies, Pawlenko[129] obtained $\Delta H_f^\circ[(\text{iso-}C_4H_9)_3Al(l)] = -92.8 \pm 2$ kcal mol^{-1}, while more careful measurements[111] lead to -69.9 ± 7.2 kcal mole^{-1}; he obtained[129] $\Delta H_f^\circ[(C_2H_5)_2AlH(l)] = -48.7 \pm 1$ kcal mol^{-1}, which does not agree with the more reliable value -73.5 ± 4.5 kcal mol^{-1} found by Shaulov et al.[108]; he quotes[130] $\Delta H_f^\circ[(C_2H_5)_2.AlCl(l)] = -56.9 \pm 1.0$ kcal mol^{-1}, while the values found in other investigations[119,120] are respectively -99.2 ± 1.3 and -96.0 ± 1.5 kcal mol^{-1}, etc. For these reasons, Pawlenko's results[129,130] have not been included in Table 3.

Smith[120] believes that calorimetric study of reactions of the type

$$^2/_3R_3Al + {}^1/_3AlX_3 \rightarrow R_2AlX,$$

where R = alkyl group and X = Cl, Br, or I, constitutes a convenient method for the determination of the enthalpies of formation of alkylaluminium halides. To reduce the rate, these processes were carried out[120] in hexadecane, where they reached completion in the course of several minutes at room temperature. The ΔH_f° for halogen-containing aluminium compounds, calculated from the experimental enthalpies of the above reactions, are listed in Table 3.

Smith[120] also discusses the agreement between the literature values of ΔH_f° for different classes of organoaluminium compounds and his own results. He examined (1) the variation of ΔH_f° within each class of organoaluminium compounds as a function of their alkyl group, (2) the difference between the enthalpies of formation of aluminium compounds of different classes, and (3) the agreement between the enthalpies of reaction found experimentally (directly) and calculated from the enthalpies of formation of the reactants. This analysis showed, in particular, that Pawlenko's results discussed above[129,130] are incorrect. Thus, direct measurements[120] of the enthalpies of the reactions

$$^2/_3(C_2H_5)_3Al\,(l) + {}^1/_3AlCl_3\,(c) \rightarrow (C_2H_5)_2AlCl\,(l),$$

$$^1/_3(C_2H_5)_3Al\,(l) + {}^2/_3AlCl_3\,(c) \rightarrow C_2H_5AlCl_2\,(l)$$

yielded -5.3 ± 0.1 and -1.2 ± 0.3 kcal mol^{-1} respectively, while calculations of the corresponding enthalpies from the ΔH_f° for the reactants, obtained by Pawlenko[129,130], lead to unrealistic values for the above reactions of $+37 \pm 1$ and $+56 \pm 1$ kcal mol^{-1}.

There have been several studies[117,121-127] devoted to the investigation of the thermochemical properties of organic derivatives of gallium, indium, and thallium (Table 3). The satisfactory agreement between the values of ΔH_f° for liquid trimethylgallium calculated from its enthalpy of combustion[121] ($\Delta H_f^\circ = -19.1 \pm 1.7$ kcal mol^{-1}) and enthalpy of iodination[122] ($\Delta H_f^\circ = -18.6 \pm 2.2$ kcal mol^{-1}) suggests that the combustion method can be used successfully also for other gallium compounds.

V. COMPOUNDS OF GROUP IV NON-TRANSITION ELEMENTS

The recommended enthalpies of formation of the above substances are listed in Table 4.

In connection with the applications of organosilicon compounds in technology, numerous studies have been made on their thermochemistry. In most instances the enthalpies of formation of the compounds were calculated from their enthalpies of combustion measured in a stationary bomb calorimeter. The use of this method in such cases is extremely difficult owing to the formation of a film of silicon dioxide on combustion of the test compounds. The film

covers the test substance and hence hinders contact between it and oxygen, which precludes the attainment of complete combustion. In the present instance the combustion products can contain, together with CO_2, H_2O and SiO_2, elemental carbon and silicon, carborundum, carbon monoxide, and a wide variety of pyrolysis products of the initial compound. The exact analysis of the combustion product formed is frequently impossible, so that reliable heat corrections, associated with the incomplete oxidation of the initial compounds, could not be found.

Table 4. Standard enthalpies of formation of organic derivatives of Group IV non-transition elements (kcal mol^{-1}).*

Compound	ΔH_f^0	ΔH_f^0 (g)	References
$C_2H_3SiH_3$ (l)	−4±3	+1±3	131(SB)
$(CH_3)_2SiH_2$ (l)	−52±3	−47±3	131(SB)
$(CH_3)_2Si(n\text{-}C_3H_7)_2$ (l)	−56±8	—	131(SB)
$(CH_3)_3SiH$ (l)	−72±4	−66±4	131(SB)
$(CH_3)_3SiC_2H_3$ (l)	+4±1	—	133(RB)
$(CH_3)_4Si$ (l)	−61±1	−55±1	131(SB), 33(SB)
$C_2H_5SiH_3$ (l)	−32±3	−27±3	131(SB)
$(C_2H_5)_2SiH_2$ (l)	−49±5	−42±5	131(SB)
$(C_2H_5)_3SiH$ (l)	−49±5	−40±2	131(SB), 134(SB)
$(C_2H_5)_4Si$ (l)	−66±4	−56±4	131(SB), 33(SB), 135(SB), 136 (SB), 137(RB)
$(n\text{-}C_4H_9)SiH_3$ (l)	−38±5	−31±5	131(SB)
$(iso\text{-}C_4H_9)SiH_3$ (l)	−36±5	−29±5	131(SB)
$(C_6H_5)_4Si$ (c)	+44±1	+80±1	133(RB), 138(SB), 139(SB), 140(RB), 141(RB), 132(RB)
$(C_6H_5CH{=}CH)_4Si$ (c)	+174±6	—	142(SB)
$[(CH_3)_3Si]_2$ (l)	−96±2	−87±2	137(RB)
$[(C_2H_5)_3Si]_2$ (l)	−97±3	−82±3	135(SB), 136(SB)
$[(C_2H_5)_3Si]_2Hg$ (l)	−40±1	−26±2	143(SB)
$(CH_3)_3Si(OH)$ (l)	−130±1	−119±1	144(R)
$(CH_3)_3SiOC_2H_5$ (l)	−126±1	−117±1	145(R), 146(R)
$(CH_3)_2Si(OC_2H_5)_2$ (l)	−206±1	−196±1	147—149(SB)
$(CH_3)_3SiO\text{-}n\text{-}C_3H_7$ (l)	−133±1	−124±1	146(R)
$(CH_3)_3SiO\text{-}iso\text{-}C_3H_7$ (l)	−135±1	−127±1	146(R)
$(CH_3)_3SiO\text{-}t\text{-}C_4H_9$ (l)	−144±1	−135±1	146(R)
$(CH_3)_3SiOOC(CH_3)_3$ (c)	−126±3	−115±3	150(SB)
$(CH_3)_2HSiO(C_6H_4)(C_6H_5)$ (l)	—	−67±3	151(SB)
$(CH_3O)_3SiH$ (l)	−198±3	−189±3	152(SB)
$(CH_3O)_3SiCH_3$ (l)	−233±2	−225±2	153(SB)
$(CH_3O)_4Si$ (l)	−303±3	−293±3	152(SB), 154(SB)
$(C_2H_5)_2Si(OH)_2$ (c)	−218±1	—	147—149(SB)
$(C_2H_5O)Si(C_6H_5)_3$ (c)	−154±4	—	133(RB), 155(RB), 156(RB)
$(C_2H_5O)_2Si(n\text{-}C_3H_7)_2$ (l)	−224±2	—	147—149(SB)
$(C_2H_5O)_3SiH$ (l)	−228±2	−218±2	152(SB), 157(SB)
$(C_2H_5O)_3SiC_2H_3$ (l)	−247±1	−235±1	158(SB)
$(C_2H_5O)_4Si$ (l)	−330±5	−318±5	152(SB), 159(R), 157(SB)
$(C_2H_5OC_2H_4O)_3Si(C_2H_3)$ (l)	−470±3	—	160(SB)
$(iso\text{-}C_3H_7O)_4Si$ (l)	−355±5	−343±5	152(SB)
$[(CH_3)_3Si]_2O$ (l)	−195±1	−186±1	161(SB), 7(RB), 137(RB), 162(RB)
$[(CH_3O)_3Si]_2$ (l)	−458±1	−445±1	154(SB)
$[(CH_3O)_3Si]_2O$ (l)	−552±1	−539±1	154(SB)
$[(CH_3O)_2CH_3Si]_2O$ (l)	−424±3	−415±3	153(SB)
$[(CH_3O)_2C_2H_5Si]_2O$ (l)	−435±4	−425±4	153(SB)
$[(CH_3)_3SiO]_2Si(CH_3)_2$ (l)	−355±7	−345±7	161(SB)
$[(CH_3O)_3SiO]_2Si(OCH_3)_2$ (l)	−816±1	−803±1	154(SB)
$[(CH_3O)_2CH_3SiO]_2Si(CH_3)(OCH_3)$ (l)	−608±5	−598±5	153(SB)
$[(CH_3)_3SiOSi(CH_3)_2]_2O$ (l)	−534±8	−522±8	161(SB)
$[(CH_3)_3SiOSi(CH_3)_2O]_2Si(CH_3)_3$ (l)	−674±10	−661±10	161(SB)
CH_3SiCl_3 (l)	−146±1	−138±1	163—165(RB)
$(CH_3)HSiCl_2$ (l)	−104±1	−98±1	166(RB)
$(CH_3)_2HSiCl$ (l)	−97±1	−73±1	166(RB)
$(CH_3)_2SiCl_2$ (l)	−116±1	−108±1	163(RB), 167(R), 166(RB)
$(CH_3)_3SiCl$ (l)	−91.9±0.5	−84.5±0.5	163—165(RB), 168(R), 144(R), 146(R)
$(CH_3)_3SiBr$ (l)	−77±1	−69±1	144(R)
$C_2H_5SiCl_3$ (l)	−132±6	−126±6	169(SB)
$(C_6H_5)_2SiCl_2$ (l)	−66±1	−49±1	167(R), 156(RB)
$(C_6H_5)_3SiCl$ (c)	+12±4	—	156(RB)
$(C_2H_5O)_3SiCl$ (l)	−297±1	—	159(R)
$(CH_3)_3SiNHCH_3$ (l)	−63±1	−54±1	144(R)
$(CH_3)_3SiN(CH_3)_2$ (l)	−67±1	−59±1	144(R)
$(CH_3)_3SiN(C_2H_5)_2$ (l)	−89±1	−80±2	170(R)
$[(CH_3)_3Si]_2NH$ (l)	−124±1	−114±1	168(R), 144(R)
$[(CH_3)_3Si]_2NCH_3$ (l)	−116±1	−107±1	144(R)
$[(CH_3)_3Si]_3N$ (c)	−173±2	−160±3	144(R)
$(CH_3)_3Si(CH_2)_2NCH_2CH_2$ (l)	−26±1	—	174(SB)
$(CH_3)_3SiN{=}N{=}N$ (l)	+9±1	+17±2	175(R)
$(C_2H_5)_3SiN(C_2H_5)_2$ (l)	−88±1	−78±1	171(SB)
$[(C_2H_5)_2N]_3SiH$ (l)	−131±1	−117±1	171(SB)
$(CH_3)_2(C_2H_5O)Si(CH_2)_3NH_2$ (l)	−154±2	—	160(SB)

Table 4 (contd.).

Compound	ΔH_f^0	ΔH_f^0 (g)	Reference
$(CH_3)(C_2H_5O)_2Si(CH_2)_3NH_2$ (l)	−212±4	—	172(SB)
$(CH_3)(C_2H_5O)_2Si(CH_2)_2CN$ (l)	−231±2	—	160(SB)
$(CH_3)(C_2H_5O)_2Si(C_6H_4)NH(CH_3)$ (l)	−198±4	—	173(SB)
$(CH_3)_2(C_2H_5O)Si(CH_2)_5CHNH_2NHCH_3$ (l)	−177±2	—	173(SB)
$(C_2H_5O)_3Si(CH_2)_3NH_2$ (l)	−282±2	−271±2	176(SB)
$(C_2H_5O)_3Si(CH_2)_2CN$ (l)	−263±1	−257±1	160(SB)
$(CH_3)_3SiS(C_4H_9)$ (l)	−91±1	−81±1	144(R)
$(CH_3)_2Si(CH_2)_2CH_2$ (l)	−28±1	−20±1	133(RB), 162(RB), 177(RB)
cyclo-$[(CH_3)_2SiCH_2]_2$ (l)	−64±2	−54±2	162(RB), 177(RB)
cyclo-$[(CH_3)_2SiCH_2]_3$ (l)	−122±7	−111±7	162(RB), 177(RB)
$(CH_3)_2SiO(C_6H_4)(C_6H_4)$ (l)	—	−25±3	151(SB)
cyclo-$[(CH_3)_2SiO]_3$ (c)	−415±1	−402±1	147—149(SB)
cyclo-$[(CH_3)_2SiO]_4$ (c)	−543±2	−532±2	178(SB)
cyclo-$[(CH_3)HSiO]_5$ (c)	−591±3	—	179(SB)
cyclo-$[(CH_3)_2SiO]_5$ (c)	−687±2	−676±2	178(SB)
cyclo-$[(C_6H_5)_2SiO]_3$ (c)	−244±5	—	147—149(SB)
cyclo-$[(C_6H_5)_2SiO]_4$ (c)	−318±2	—	141(RB)
cyclo-[*cis*-$(CH_3)(C_6H_5)SiO]_3$ (c)	−321±2	—	180(RB), 181(RB), 133(RB)
cyclo-[*trans*-$(CH_3)(C_6H_5)SiO]_3$ (c)	−327±1	—	180(RB), 181(RB), 133(RB)
cyclo-$[(CH_3)(C_6H_5)SiO]_4$ (c)	−436±2	—	180(RB), 182(RB), 133(RB)
cyclo-$[(CH_3)(iso\text{-}C_3H_7O)SiO]_3$ (c)	−619±2	−609±2	178(SB)
cyclo-$[(CH_3)(iso\text{-}C_3H_7O)SiO]_4$ (c)	−843±2	−832±2	178(SB)
$(CH_3)_4Ge$ (l)	−28±2	−21±2	183(SB)
$(C_2H_5)_3GeH$ (l)	−40±2	−30±3	134(SB), 184(SB)
$(C_2H_5)_4Ge$ (l)	−51±2	−40±2	185(SB), 186(RB), 183(SB)
$(n\text{-}C_3H_7)_4Ge$ (l)	−73±1	−58±1	185(SB)
$(n\text{-}C_4H_9)_4Ge$ (l)	−92±1	−80±1	187(SB)
$(iso\text{-}C_4H_9)_4Ge$ (l)	−111±1	−100±1	187(SB)
$(C_6H_5)_2Ge(C{=}CH)_2$ (c)	+157±2	+189±2	188(SB)
$(C_6H_5)_4Ge$ (c)	+67±3	+105±4	138(SB), 189(SB), 190(RB), 191(RB)
$(C_6H_5CH_2)_4Ge$ (c)	+52±2	+96±3	192(RB), 193(RB)
$(C_6H_5CH{=}CH)_4Ge$ (c)	+199±3	—	194(SB)
$[(C_2H_5)_3Ge]_2$ (l)	−98±2	−83±2	184(SB)
$[(C_2H_5)_3Ge]_2Hg$ (l)	−32±1	−17±2	143(SB)
$[(iso\text{-}C_3H_7)_2Ge]_2Hg$ (l)	−74±1	−61±2	143(SB)
$[(C_6H_5)_3Ge]_2$ (c)	+107±2	+157±3	191(RB), 192(RB)
$(CH_3O)_4Ge$ (l)	−206±1	−196±1	196(SB)
$(C_2H_5O)Ge(CH_3)_3$ (l)	−95±2	−87±3	145(R)
$(C_2H_5O)_4Ge$ (l)	−245±1	−235±1	196(SB)
$(C_6H_5O)_4Ge$ (l)	−113±1	−104±1	196(SB)
$[(C_2H_5)_3Ge]_2O$ (l)	−151±2	−137±2	136(SB), 150(SB)
$(C_2H_5)_3GeOOC(CH_3)_3$ (c)	−120±1	−110±1	150(SB)
$(CH_3)_3GeCl$ (l)	−72±2	−64±3	145(R)
$(CH_3)_3GeBr$ (l)	−61±2	−52±3	145(R)
$(CH_3)_3GeN(CH_3)_2$ (l)	−37±2	−29±3	145(R)
$(C_2H_5)_3GeN(C_2H_5)_2$ (l)	−86±1	−75±2	171(SB)
$(CH_3)_3GeN{=}N{\equiv}N$ (l)	28±1	+37±2	175(R)
$(CH_3)_3GeS(n\text{-}C_4H_9)$ (l)	−65±2	−55±3	145(R)
$C(C_6H_5){=}[C(C_6H_5)]_2{=}C(C_6H_5)Ge(C{=}CH_2)$ (c)	+207±2	—	195(SB)
cyclo-$[(CH_3)_2GeO]_4$ (c)	−378±2	—	197(SB)
cyclo-$[(C_2H_5)_2GeO]_4$ (c)	−380±5	—	198(SB)
$(CH_3)_2SnH_2$ (l)	+14±1	+21±1	199(SB)
$(CH_3)_3SnH$ (l)	−2±1	+6±1	199(SB)
$(CH_3)_4Sn$ (l)	−12.6±0.5	−4.5±0.5	200(SB), 201(SB), 202(SB), 203(SB), 33(SB), 136(SB)
$(CH_3)Sn(C_2H_5)_3$ (l)	−54±1	—	201(SB)
$(CH_3)_2Sn(C_2H_5)_2$ (l)	−29±5	−19±5	201(SB)
$(CH_3)_3Sn(C_2H_5)$ (l)	−16±1	−7±1	201(SB), 203(SB)
$(CH_3)_3Sn(CH{=}CH_2)$ (l)	+13±1	+22±1	33(SB), 203(R)
$(CH_3)_3Sn(iso\text{-}C_3H_7)$ (l)	−21±1	−11±1	205(SB)
$(CH_3)_3Sn(t\text{-}C_4H_9)$ (l)	−29±1	−16±2	205(SB)
$(CH_3)_3Sn(C_6H_5)$ (l)	+14±1	+27±1	203(R), 204(R)
$(CH_3)_3Sn(CH_2C_6H_5)$ (l)	+8±2	+21±2	203(R), 204(R)
$[(CH_3)_3Sn]_2$ (l)	−19±1	−7±2	206(R), 203(SB)
$(C_2H_5)_2SnH_2$ (l)	+3±1	+10±1	199(SB)
$(C_2H_5)_3SnH$ (l)	−11±2	0±2	199(SB), 134(SB),
$(C_2H_5)_4Sn$ (l)	−23.0±0.5	−11.0±0.5	38(SB), 201(SB), 202(SB) 207(SB), 33(SB), 203(SB)
$(C_2H_5)_3Sn(CH{=}CH_2)$ (l)	+9±1	+21±2	33(SB)
$(C_2H_5)_2Sn(n\text{-}C_4H_9)_2$ (l)	−54±2	—	201(SB)
$[(C_2H_5)_3Sn]_2$ (l)	−52±2	−37±3	207(SB), 136(SB)
$(CH_2{=}CH)_4Sn$ (l)	+72±1	+84±2	33(SB)
$(CH_2{=}CH{-}CH_2)_4Sn$ (l)	−41±2	—	33(SB)
$(n\text{-}C_3H_7)_3SnH$ (l)	−32±1	—	208(R)
$(n\text{-}C_3H_7)_4Sn$ (l)	−50±1	−34±1	33(SB), 203(SB)
$(iso\text{-}C_3H_7)_4Sn$ (l)	−45±1	−29±2	33(SB), 205(SB)
$(n\text{-}C_4H_9)_3SnH$ (l)	−49±1	—	208(R)
$(n\text{-}C_4H_9)_4Sn$ (l)	−72.5±0.5	−52.7±0.7	201(SB), 203(SB), 33(SB)
$(iso\text{-}C_4H_9)_4Sn$ (l)	−79±1	—	33(SB)
$(cyclo\text{-}C_6H_{11})_4Sn$ (l)	−87±7	—	33(SB)
$(C_6H_{13})_4Sn$ (l)	−112±3	—	201(SB)
$(C_6H_5)_4Sn$ (c)	+98±1	+137±1	138(SB), 33(SB), 209(SB), 139(SB), 210(SB)
$[(C_6H_5)_3Sn]_2$ (c)	+158±2	+203±2	33(SB), 139(SB), 211(SB)
$(CH_3)_3SnOH$ (c)	−91±1	−76±2	145(R)
$(CH_3)_3Sn(OC_2H_5)$ (l)	−73±1	−63±2	145(R)
$(CH_3)_3SnOCOC_6H_5$ (c)	−118±2	—	136(SB)
$(C_2H_5)_3SnOOC(CH_3)_3$ (c)	−101±4	−89±4	150(SB)
$(C_2H_5)_3SnOCOC_6H_5$ (c)	−138±2	—	207(SB), 136(SB)

Table 4 (contd.).

Compound	ΔH_f^0	ΔH_f^0 (g)	Reference
$(C_2H_5)_3SnOOC(CH_3)_2C_6H_5$ (c)	−68±2	−55±2	150(SB)
$[(C_2H_5)_3Sn]_2O$ (l)	−102±3	−90±3	150(SB)
$(C_6H_5)_3SnOH$ (c)	+12±2	+43±2	212(SB)
$[(C_6H_5)_3Sn]_2O$ (c)	+99±2	+146±3	212(SB)
$(CH_3)SnCl_3$ (l)	−109±2	—	213(R)
$(CH_3)_2SnCl_2$ (l)	−81±2	—	213(R)
$(CH_3)_3SnCl$ (l)	−52±2	—	213(R)
$(CH_3)_3SnCl$ (c)	−59±1	−47±2	145(R)
$(CH_3)_3SnBr$ (l)	−44±1	−33±1	206(R), 203(SB)
$(CH_3)_3SnBr$ (c)	−48±1	−34±1	145(R)
$(CH_3)_3SnI$ (l)	−31±1	−20±1	206(R), 203(SB)
$(n\text{-}C_4H_9)_3SnBr$ (l)	−85±1	−65±3	203(R), 204(R)
$(C_6H_5)_2SnBr_2$ (c)	−5±1	—	203(R), 204(R)
$(C_6H_5)_3SnBr$ (c)	+45±1	—	203(R), 204(R)
$(CH_3)_3SnN(CH_3)_2$ (l)	−14±1	−5±2	145(R)
$[(CH_3)_3Sn]_2N(CH_3)$ (l)	−32±1	−20±2	145(R)
$[(CH_3)_3Sn]_3N$ (c)	−30±2	−15±3	145(R)
$(CH_3)_3SnN{=}N{\equiv}N$ (c)	+45±1	+60±2	175(R)
$(C_2H_5)_3SnN(C_2H_5)_2$ (l)	−50±1	−38±2	171(SB)
$[(n\text{-}C_4H_9)_3Sn]_2{=}C$ (l)	−86±1	—	214(SB)
$(n\text{-}C_4H_9)_3SnNCO$ (l)	−88±1	—	214(SB)
$(CH_3)_3SnS(n\text{-}C_4H_9)$ (l)	−47±1	−37±2	145(R)
$(CH_3)_4Pb$ (l)	+23.3±0.5	+32.4±0.5	6(RB)
$(C_2H_5)_4Pb$ (l)	+12.5±0.7	+26.0±0.8	5(RB)
$(C_6H_5)_4Pb$ (c)	+123±4	+161±4	215(RB), 216(RB)
$(C_6H_5)_2PbBr_2$ (c)	+8±4	+42±4	217(R), 218(R)
$(C_6H_5)_3PbBr$ (c)	+63±4	+95±4	217(R), 218(R)
$(C_6H_5)_2PbI_2$ (c)	+36±4	+69±4	217(R), 218(R)
$(C_6H_5)_3PbI$ (c)	+78±4	+109±4	217(R), 218(R)

*For the explanation of the Table, see the introduction.

The above factors led a number of workers to the assumption that all the values of ΔH_f° for silicon-containing substances obtained by the combustion method in a stationary bomb calorimeter are certain to be erroneous and do not merit any consideration. In particular, the values of ΔH_f° for silicon compounds found by the above method have been fully excluded from the monograph of Cox and Pilcher[1], the handbook of Wagman et al[10], Skinner's review[44], etc. However, in the majority of studies carried out using a stationary bomb calorimeter the investigators concerned made a detailed study of the products of incomplete combustion apart from creating the best possible conditions for the complete combustion of the starting material. This made it possible to apply the corresponding thermal corrections. The results of the above investigations may be suitable for various approximate calculations in cases where more accurate data are not available. For this reason, we have omitted from the present review only clearly erroneous results. Other values of ΔH_f° for silicon-containing compounds are included in Table 4 and are discussed regardless of the method used to determine them.

The enthalpies of combustion of a series of organosilicon compounds were first determined in a stationary bomb calorimeter by Reuther[152]. The lack of a detailed description of the method used precludes an assessment of the reliability of the results.

Tannenbaum et al.[131] measured the enthalpies of combustion of eleven organosilicon compounds. The substances, contained in glass or gelatine bulbs, were ignited in a nickel crucible having a number of apertures. The degree of combustion was checked by the visual inspection of the contents of the bomb after the experiments. The incomplete combustion products, in the form of dark spots on the inner surface of the bomb were observed even in the best experiments. Tannenbaum et al.[131] noted difficulties in creating conditions in the bomb which would ensure the complete combustion of the test compounds. For example, 25 combustions were carried out for vinylsilane and the necessary degree of combustion was achieved in only two experiments. For the remaining substances, only the results of the three best experiments were taken into account in calculating ΔH_f°. The authors believe[131] that the error of the ΔH_f° obtained ranges from −1.3 to +0.5%.

In his measurements of the enthalpies of combustion of polymethylsiloxanes, Thompson[161] used a novel method to ensure their complete combustion. The substance, enclosed in two bulbs of different strength, was placed in a glass crucible in the bomb. One of the bulbs was ruptured during the filling of the bomb with oxygen as a result of which the second stronger bulb was immersed in the liquid spilled out of the first bulb. At the required instant this liquid was ignited and, as a result of the evolution of heat, the second bulb exploded and, according to the author[161], the entire mass of the substance taken for the experiment was combusted, which he inferred from a visual inspection of the contents of the bomb after the experiment. The use of this combustion procedure involves difficulties associated with the preparation of bulbs capable of withstanding the oxygen pressure in the bomb and yet exploding on heating.

A series of studies on the measurements in a stationary bomb calorimeter of the enthalpies of combustion of organosilicon compounds of different structure were published by Tanaka and coworkers[147–149,153,154,178,179]. The liquid substances were ignited in glass or gelatine bulbs and solid substances were ignited in paper bags. The degree of combustion was inferred from the visual inspection of the solid combustion products formed. In his first studies Tanaka[147–149] did not report the difficulties encountered in attaining the complete combustion of the test compound. However, in later investigations[178,179] he noted the presence in the solid combustion products of, apart from amorphous SiO_2, amorphous carbon, silicon carbide, and a polymeric silicon-containing substance. The appropriate corrections were calculated in the interpretation of the experimental results.

Lautsch et al.[33] measured the enthalpies of combustion of tetramethyl- and tetraethyl-silanes. The substances were ignited in glass bulbs rolled up in a polyethylene film. However, complete combustion could not be achieved.

Several organosilicon compounds were investigated by Shaulov and coworkers[157,160,172,173,176]. The substances were placed in a bomb in polyethylene bulbs. The combustion products were analysed for carbon dioxide, unoxidised carbon, and silicon, and in the case of nitrogen-containing compounds, silicon nitride. It was established that the corrections for the presence of silicon and silicon nitride are insignificant and can be neglected.

A series of organosilicon compounds have also been combusted in a stationary bomb calorimeter in studies by the authors of the present review[134–136,150,171,174]. The liquid substances were ignited in polyethylene bulbs and the solid substances, in the form of several 0.1 g discs, were ignited in a thin platinum crucible. The analytical results for the solid combustion products showed that they contained as impurities unoxidised carbon and traces of unoxidised silicon and silicon carbide. For each substance, the experimental amount of CO_2 in the gaseous combustion products agreed, when account was taken of the incomplete combustion, to within 0.1% with the amount calculated from the chemical formula.

The use of the rotating bomb calorimeter method for organosilicon compounds is associated with two important conditions: the choice of the auxiliary substance ensuring a high degree of oxidation of the test compound and the choice of a solvent capable of rapidly dissolving the combustion

products formed. This method was first used by Good et al.[7] in a study of hexamethyldisiloxane. The substance was ignited in a mixture with trifluoromethylbenzene ($C_6H_5CF_3$). Trifluoromethylbenzene was chosen as the auxiliary substance because of the ease with which it can be purified and because of its ability to burn in the bomb calorimeter without the formation of carbon tetrafluoride. The mixture prepared in this way was ignited in a container of polyester film and the amount of energy consumed was ~69% in the combustion of trifluoromethylbenzene, ~25% in the combustion of hexamethyldisiloxane, and ~6% in the combustion of the film relative to the total amount of energy evolved during the experiment. The bomb was first charged with a specific amount of water or an aqueous HF solution, which came into contact with the combustion products on rotation of the bomb and reacted with the latter to form a solution of H_2SiF_6.HF. .H_2O. The enthalpy of formation of the resulting solution had been determined in preliminary experiments. In order to take into account a series of side effects, for example, the dissolution of carbon dioxide in aqueous solutions of H_2SiF_6 and HF, Good et al.[7] carried out the so called comparison experiments. In these experiments they combusted benzoic acid or liquid hydrocarbons; the amounts of the latter as well as the concentration of the aqueous solution of H_2SiF_2 and HF introduced into the bomb was selected in such a way that the final states of the reacting systems in the comparison experiments and the experiments involving the combustion of siloxane were as far as possible similar.

The enthalpy of formation of hexamethyldisiloxane obtained by Good et al.[7] was subsequently confirmed by Iseard et al.[137], who used a similar combustion method. However, they employed another auxiliary compound, namely *m*-trifluoromethylbenzoic acid ($C_6H_4CF_3COOH$). Iseard et al.[137] determined also the enthalpies of combustion of two other silicon compounds: tetraethylsilane and hexamethyldisilane. The combustion method proposed by Good[7] was also used by Genchel' et al.[162,177,180], who measured the enthalpies of combustion of several cyclic silicon compounds, and by Steele[132], who obtained an accurate value of ΔH_c° for tetraphenylsilane.

Another approach to the problem of the application of bomb calorimetric methods to silicon compounds was proposed by Gadzhiev[156]. He determined the enthalpies of combustion of a series of liquid chloromethylsilanes[156] by the explosive combustion method, which he developed[163–166]. This method consists in the vaporisation of part of the substance (not more than 10%) during the experiment and subsequent ignition of the mixture of its vapour with oxygen, which is stated[156,163–166] to cause the explosive combustion of both the gaseous and liquid parts of the substance with formation, apart from CO_2 and H_2O, of a stoichiometric amount of amorphous SiO_2. Gadzhiev and coworkers[133,140,141,155,156,181,182] recommend that solid organosilicon compounds be combusted in the presence of certain oxidants (potassium nitrate, potassium hypochlorite, benzoyl peroxide), which they say ensures the complete oxidation of the starting materials. However, one should point out that the value of ΔH_f° obtained in their studies[133,181,182] differ sharply from the corresponding data of other investigators[162,177,180] found using the more sophisticated combustion method developed by Good et al.[7] and used successfully in a later investigation[137]. This factor indicates the preliminary nature of both the methodological recommendations of Gadzhiev et al.[133,181,182] and of their results.

Failure to attain the complete combustion of organosilicon compounds in a stationary bomb calorimeter and the complexity of the experiments in a rotating bomb calorimeter led many investigators to resort to other methods for the thermochemical investigation of such substances. The study of their hydrolytic reactions proved to be extremely fruitful[144–146,159,167,168,170]. These reactions frequently take place at room temperature with formation of readily identifiable products. The widescale employment of the above procedure for the investigation of the methyl compounds of silicon has been favoured to a large extent by the fact that the enthalpy of formation of their main hydrolysis product (hexamethyldisiloxane) had been reliably established in the above investigations[7,137].

Despite the large number of organogermanium compounds synthesised and their practical importance, the study of their thermochemistry began comparatively recently namely in 1963, when the authors of the present review published the results of measurements of the enthalpies of combustion of tetraethylgermane and hexaethyldigermane[184]. As shown in one of the subsequent studies of the present authors[134,136,143,150,171] and also in the studies of Skinner[185] and Shaulov[183,187,189,196–198], organogermanium compounds are readily oxidised under the conditions of the stationary bomb calorimeter and the attainment of a high degree of their oxidation does not present special difficulties. All the above investigators ignited the test substances in polyethylene or polyester bulbs placed in a quartz crucible. In some cases the solid combustion products contained, together with hexagonal germanium dioxide, small amounts of unoxidised carbon and germanium, which were reliably taken into account by the appropriate corrections.

The combustion of organogermanium compounds in a rotating bomb calorimeter was first used by Bills and Cotton[186], who measured the enthalpy of combustion of liquid tetraethylgermane. The liquid in the bomb, used to dissolve the condensed combustion products, was an aqueous HF solution, which led to the formation of an aqueous solution of H_2GeF_6. This method was subsequently used in other studies[190,192] to determine the enthalpies of combustion of tetraphenylgermane, hexaphenyldigermane, and tetrabenzylgermane; however, the bomb liquid consisted of aqueous KOH. The enthalpies of solution in the above solvent of the germanium and carbon dioxides formed in the experiments were determined beforehand. The combustion products also contained a "solid residue", which did not dissolve in the bomb liquid. The authors[190,192] suggested that it consisted of a mixture of unoxidised carbon and the initial germanium compound. The correction taking into account the presence of this "solid residue" did not exceed 0.5% of the overall amount of energy evolved in the experiment.

It has been suggested[186] that the exact determination of the enthalpy of combustion of organogermanium compounds in a stationary bomb calorimeter is impossible owing to their incomplete oxidation in the corresponding experiments. However, the similarity of the values of ΔH_f° found for tetraethylgermane by the method of combustion in a stationary bomb calorimeter[183–185] (-52.2 ± 1.0, -52.6 ± 1.5, and -48.9 ± 1.0 kcal mol^{-1} respectively) and by the method of combustion in a rotating bomb calorimeter[186] (-50.4 ± 1.5 kcal mol^{-1}) suggests that reliable values of ΔH_f° can be obtained for germanium compounds also in stationary bomb calorimeters¶.

¶There is a sharp difference between the individual values of ΔH_f° for tetraphenylgermane found in a stationary bomb calorimeter[138,189] and between these and the result obtained by the rotating bomb calorimeter method[190]. However, it is apparently associated with the inadequate purity of the specimens investigated[138,189]. The error of Birr's result[138] and its possible cause were pointed out by Tel'noi and Rabinovich[139].

The only study in which reaction calorimetry was used to investigate the thermochemistry of germanium compounds is that of Baldwin et al.[145], who measured the enthalpies of hydrolysis of several trimethylgermane derivatives. The comparatively high error of the enthalpies obtained (±2 kcal mol^{-1}) is mainly due to the inaccuracy of the estimated enthalpy of formation of hexamethylgermanoxane (−136 ± 4 kcal mol^{-1}), formed in the hydrolysis of the above substances, which was used in the calculations.

The measurement of the enthalpies of combustion of organotin compounds presents no difficulties, since the latter are fully oxidised under the conditions of the stationary bomb calorimeter. This factor led to the accumulation in the literature of a large number of thermochemical data obtained by the combustion of organotin compounds in the stationary bomb calorimeter. Their combustion products contained in some cases unoxidised tin and carbon. However, in these experiments corrections for incomplete combustion could be determined exactly by heating the solid combustion product to constant weight and by the simultaneous determination of the carbon dioxide produced in this process[134,203]. In order to improve the combustion, the test substances are frequently placed in polyethylene or polyester bulbs. One should note that some of the investigations[138,200,201] in which the stationary bomb calorimeter method was applied to organotin compounds were experimentally imprecise and the difference between their results and those of the corresponding exact data[203,209,210] (Table 4) did not indicate any methodological complications arising in the study of the given substances in a stationary bomb calorimeter.

The existence of a large number of chemical reactions of organotin compounds suitable for calorimetric studies made it possible to determine the enthalpies of formation of many of these substances by reaction calorimetry. A study of the enthalpies of halogenation[204,205,208,213] and hydrolysis[145] proved to be the most fruitful. The methods of reaction calorimetry are particularly suitable for the determination of the enthalpies of formation of halogen-containing tin compounds whose combustion in a bomb calorimeter is complicated by a number of side reactions.

The combustion of organolead compounds in a stationary bomb calorimeter does not yield exact enthalpies of combustion because of the formation on combustion of a mixture of inorganic lead compounds which cannot be subjected to a reliable quantitative analysis. Good and coworkers[5,6] therefore used the method of combustion in a rotating bomb calorimeter in the study of tetramethyl- and tetraethyl-lead. A solution of nitric and arsenous acids was used as the bomb liquid, as a result of which the entire lead present in the combustion products was converted into Pb^{2+} ions. The test substances were combusted in a quartz crucible which was fairly inert in relation to the hot lead oxides formed. The use of glass bulbs and of a platinum crucible is inconvenient in this instance, since fused lead oxides or unoxidised lead react with glass and are fused together with platinum. Since explosive combustion is characteristic of tetramethyl-lead, it was diluted with a liquid-hydrocarbon before combustion and was placed in a polyester bag. The enthalpy of solution of tetramethyl-lead in the hydrocarbon as well as the enthalpy of solution of the carbon dioxide (formed in the experiments) in the final bomb solution were determined in special experiments. A combustion method analogous to that examined above was also used[215] in a study of tetraphenyl-lead.

The use of methods of reaction calorimetry for the determination of the enthalpies of formation of organolead compounds is limited to the studies of Butler et al.[217,218], who measured the enthalpies of halogenation of crystalline tetraphenyl-lead. The enthalpies of formation of certain bromo- and iodo-derivatives of the above compounds were calculated from the results (Table 4).

One must note that the literature values of the enthalpies of formation of organolead compounds, obtained by combustion in a stationary bomb calorimeter, are erroneous for the reasons examined above. For example, according to data[33] obtained in a stationary bomb calorimeter, the standard enthalpy of formation of crystalline $(C_6H_5)_4Pb$ is +221 ± 3 kcal mol^{-1}, while the use of the rotating bomb calorimeter[215] yields $\Delta H_f^\circ = +123 \pm 4$ kcal mol^{-1} for the same substance. All

Table 5. Standard enthalpies of formation of organic derivatives of Group V non-transition elements (kcal mol^{-1}).*

Compound	ΔH_f^0	ΔH_f^0 (g)	References	Compound	ΔH_f^0	ΔH_f^0 (g)	References
$(CH_3)_3P$ (l)	−30±1	−23±1	220(SB)	$(CH_3)_3PN(C_2H_5)$ (l)	−36±2	−22±2	230(R)
$(C_2H_5)_3P$ (l)	−21±3	−12±3	31(SB), 32(SB)	$(C_6H_5)_3PN(C_2H_5)$ (c)	+16±1	+34±2	230(R)
$(n\text{-}C_4H_9)_3P$ (l)	−28±7	—	221(R)	$[(C_2H_5)_2N]_3P$ (l)	−67±2	−53±3	235(R)
$(n\text{-}C_6H_{13})_3P$ (l)	−177±9	—	222(R)	$(CH_2)(C_6H_5NH)_2PO$ (c)	−86±6	—	226(SB)
$(C_6H_5)_3P$ (c)	+55±2	+78±3	223(SB), 224(SB)	$(C_2H_5)(C_6H_5NH)_2PO$ (c)	−89±3	—	226(SB)
$(CH_3O)_3P$ (l)	−176±1	−167±2	225(R)	$(C_2H_5)_2NPCl_2$ (l)	−81±1	—	236(R)
$(C_2H_5O)_3P$ (l)	−203±1	−193±1	225(R), 226(R)	$[(C_2H_5)_2N]_2PCl$ (l)	−78±2	—	236(R)
$(iso\text{-}C_3H_7O)_3P$ (l)	−232±2	−221±2	226(R)	$(n\text{-}C_4H_9)_3PS$ (l)	−56±7	—	237(R)
$(n\text{-}C_4H_9O)_3P$ (l)	−262±4	—	222(R)	$(C_2H_5O)_3PS$ (l)	−229±1	—	237(R)
$(C_6H_5)(OH)_2P$ (c)	−132±5	—	227(SB)	$(C_6H_5)_5C_4P$ (c)	+94±3	—	238(SB)
$(CH_3)(OH)_2PO$ (c)	−252±6	−240±6	228(R)	$(C_6H_5)(C_6H_4)_2P$ (c)	+45±2	—	238(SB)
$(C_2H_5)(OH)_2PO$ (c)	−251±2	−239±3	228(R), 231(R)	$(C_6H_5)_5C_4PO$ (c)	+53±5	—	238(SB)
$(C_6H_5)(OH)_2PO$ (c)	−211±3	—	227(SB)	$(C_6H_5)(C_6H_4)_2PO$ (c)	−21±6	—	238(SB)
$(C_6H_5)_2(OH)PO$ (c)	−125±6	—	227(SB)	cyclo-$[PN(CH_3)_2]_3$ (c)	−123±3	−105±4	239(SB)
$(CH_3)(ON)_2PO$ (c)	−350±2	—	229(SB)	cyclo-$[PN(C_6H_5)_2]_4$ (c)	+43±12	+61±12	239(SB)
$(CH_3)_3PO$ (c)	−115±2	−103±2	230(R)	cyclo-$[(CH_3N)_6P_4]$ (c)	−57±6	−42±6	240(SB)
$(n\text{-}C_4H_9)_3PO$ (c)	−110±7	—	232(SB)	cyclo-$[PN(cyclo\text{-}C_6H_{11}O_2)_2]_3$ (c)	−580±4	−562±5	239(SB)
$(n\text{-}C_6H_{13})_3PO$ (c)	−263±9	—	222(SB)	cyclo-$[C_6H_5NHP(O)NC_6H_5]_2$ (c)	−122±5	−92±5	240(SB)
$(C_6H_5)_3PO$ (c)	−26±1	+5±2	224(SB), 233(RB)	cyclo-$(CH_3NPCl_3)_2$ (c)	−209±2	−192±3	240(SB), 241(R)
$(C_2H_5O)_2(CH_3)PO$ (l)	−244±6	−231±7	226(R)	$(CH_3)_3As$ (l)	−4±1	+3±1	242(SB)
$(C_2H_5O)_3PO$ (l)	−296±1	−282±1	221(R), 224(SB) 234(SB)	$(C_2H_5)_3As$ (l)	+3±2	+13±2	31(SB), 32(SB)
				$(C_6H_5)_3As$ (c)	+71±2	+95±2	243(SB), 244(RB)
$(n\text{-}C_3H_7O)_3PO$ (l)	−315±4	−299±5	232(SB)	$(CH_3O)_3As$ (l)	−141.9±0.5	−131.6±0.5	245(R)
$(iso\text{-}C_3H_7O)_2(C_2H_5)PO$ (l)	−267±4	−252±4	226(R)	$(C_2H_5O)_3As$ (l)	−168.3±0.5	−156.2±0.6	245(R)
$(iso\text{-}C_3H_7O)_3PO$ (l)	−310±2	—	228(R)	$(n\text{-}C_3H_7O)_3As$ (l)	−189±1	−175±2	245(R)
$(n\text{-}C_4H_9O)(n\text{-}C_4H_9)_2PO$ (l)	−183±9	—	232(SB)	$(CH_3)_3Sb$ (l)	0±3	+8±3	247(SB)
$(n\text{-}C_4H_9O)_3PO$ (l)	−348±3	−331±3	232(SB), 234(SB)	$(C_2H_5)_3Sb$ (l)	+1±1	+11±1	31(SB), 32(SB)
$(iso\text{-}C_4H_9O)_3PO$ (l)	−347±8	—	234(SB)	$(C_6H_5)_3Sb$ (c)	+79±2	+104±3	223(SB)
$(C_6H_5O)_3PO$ (c)	−180±3	—	234(SB)	$(CH_3)_3Bi$ (l)	+37±2	+46±2	248(SB)
$(C_2H_5)PCl_2$ (l)	−72±4	—	228(R)	$(C_2H_5)_3Bi$ (l)	+40±2	+51±2	31(SB), 32(SB)
$(CH_3)POCl_2$ (c)	−148±6	−133±6	226(R)	$(C_6H_5)_3Bi$ (c)	+117±1	+143±2	243(SB), 219(RB)
$(C_2H_5)POCl_2$ (l)	−146±3	−136±3	226(R)				

*For the explanation of the Table, see the introduction.

the values of ΔH_f° calculated from the results of the combustion of organolead compounds in a stationary bomb calorimeter are therefore disregarded in this review and are not included in Table 4.

VI. COMPOUNDS OF GROUP V NON-TRANSITION ELEMENTS

The recommended enthalpies of formation of the above substances are listed in Table 5.

The determination of the enthalpies of combustion of organophosphorus compounds in a stationary bomb calorimeter has a number of characteristic features, which make it difficult to obtain sufficiently reliable results. Their combustion products contain, apart from CO_2 and H_2O, orthophosphoric acid (in aqueous solution), which, however, may be accompanied by other phosphorus-containing acids in solution: H_3PO_3, $H_4P_2O_7$, and $H_5P_3O_{10}$; the concentrations of the acids formed in different parts of the bomb differ significantly. This factor may appreciably distort the results of the calculation of the ΔH_f° of the test substance owing to the comparatively high enthalpies of solution of phosphoric acids in water. Furthermore, it is difficult to achieve the complete combustion of organophosphorus compounds—all the investigators have noted the presence of significant amounts of unoxidised carbon in their combustion products. In view of the corrosive nature of phosphoric acids in relation to the material of the crucible in which the test substance is to be combusted, the choice of the crucible is important.

The method of combustion in a stationary bomb calorimeter was used[226] in a study of two phosphoric acid dianilides. The combustion products were analysed for ortho-, pyro-, and meta-phosphoric acids. It was found that 93–96% of the phosphorus was oxidised to orthophosphoric acid. The authors[226] disregarded corrections for the formation of other acids. They also established that the concentration of the H_3PO_4 solution formed on combustion of the test substances was 0.5 M on the walls of the bomb and 2 M in the crucible and that the main bulk of the acid (~85%) was on the walls of the bomb. The difference between the concentrations of orthophosphoric acid in different parts of the bomb was taken into account in the interpretation of the experimental data. The error of the calculated ΔH_f° (Table 5) is several kcal mol^{-1}.

In the combustion of trimethylphosphine[220] magnesium ribbon was used to ignite the substance and to improve its combustion. However, its employment introduced additional difficulties owing to the formation of magnesium oxide in the combustion products, which partly dissolves in aqueous orthophosphoric acid. The trimethylphosphine combustion products were analysed to determine (a) the mass of magnesium oxide dissolved in phosphoric acid (an aqueous $MgHPO_4$ solution was formed), (b) to determine the mass of unoxidised carbon, (c) to test for the presence of lower phosphorus acids, and (d) to determine the masses of meta- and pyro-phosphoric acids. The analyses showed that orthophosphoric acid amounted to not less than 95% of the overall mass of all the phosphorus-containing acids formed. In the calculation of ΔH_c° corrections were applied for the presence of phosphorous acid, free carbon, etc. in the combustion products.

In another study[223] triphenylphosphine was combusted in polyethylene bulbs, which consumed ~60% of the energy evolved in the experiment. A mixture of H_3PO_4 and H_3PO_3 was detected in the combustion products. Corrections for the auxiliary materials and the presence of unoxidised carbon and phosphorus acid in the combustion products were applied in the calculations of ΔH_c°. The value $\Delta H_f^\circ = +52.9 \pm 3.6$ kcal mol^{-1} found by the author[223] agrees within the limits of experimental error with $+54.8 \pm 2.4$ kcal mol^{-1} obtained analogously in another investigation[224].

The enthalpies of combustion of a series of organophosphorus compounds were measured by Mortimer and coworkers[224, 238,239]. To improve the combustion, certain substances (discs) were placed in polyester bulbs. To prevent the scattering of the hot substances, the crucible was covered by a platinum gauze. The mass of the combusted compound was determined from the masses of CO_2 and free carbon found in the combustion products. It was assumed that all the auxiliary substances were completely combusted. Chemical analysis of the wash water from the bomb after the experiments demonstrated the presence of only one phosphorus-containing acid (H_3PO_4).

The method of measurement of ΔH_c° for phosphorus-containing substances was improved in a number of investigations[222,232,234]. Much attention was devoted to the selection of the material of the crucible, fairly inert with respect to the combustion products of the test compounds. Corundum crucibles, which proved in this respect to be better than stainless steel, titanium, quartz, or porcelain crucibles, were used. Together with orthophosphoric acids, a certain amount of pyrophosphoric acid was found in the combustion products, which conflicts with data obtained in investigations[224,238,239] where only orthophosphoric acids was found in the products. (Nikolaev et al.[234] explained this by the inaccuracy of the analytical methods employed in the earlier investigations[224,238,239].) In the interpretation of the experimental data account was taken of the thermal corrections for the enthalpy of solution of phosphoric acids and unoxidised carbon. The authors[222,232,234] explained the comparatively large error in the values of ΔH_c° obtained, amounting in certain cases to ~0.5%, by the impossibility of attaining the complete oxidation of phosphorus-containing substances under the conditions of the stationary bomb calorimeter.

The enthalpies of combustion of the three phosphorus-containing acids have been measured[227] in an adiabatic stationary bomb calorimeter not designed for precision measurement. Discs of the test substances were placed in a platinum crucible together with a disc of benzoic acid, which ensured a more complete combustion. Part of the water introduced into the bomb before the experiment wetted its inner walls, which tended to equalise the concentrations of the orthophosphoric acid formed in different parts of the bomb according to the authors[227]. The chemical composition of the wash water from the bomb after the experiments was determined by method proposed previously[224,238,239] and, as in those investigations, the authors[227] demonstrated the quantitative oxidation of phosphorus to orthophosphoric acid without the formation of other phosphoric acids.

The enthalpies of combustion of three cyclic phosphorus compounds containing also nitrogen and chlorine were determined by Fleig and Berke-Goehring[240] using a tantalum stationary bomb calorimeter. The substances were combusted together with paraffin. In the experiment with the chlorine-containing compound the bomb was charged with quartz wool impregnated with an aqueous solution of As_2O_3. Under these conditions, molecular chlorine, formed to some extent on combustion of the test compound, was fully reduced to HCl. Together with orthophosphoric acid, the authors detected small amounts of pyrophosphoric acid in the wash water from the bomb. However, the corrections due to the presence of the latter were insignificant and were therefore disregarded.

The possibility of the combustion of phosphorus compounds in a rotating bomb calorimeter has been examined in detail[233]. It was suggested that triphenylphosphine oxide be used as the standard substance for the thermochemical study of organophosphorus compounds[233]. A disc of the above compound was ignited in a small gold crucible by means of a polyethylene ribbon. The formation of soot in this case was insignificant. The bomb liquid consisted of an aqueous solution of perchloric acid. When the combustion product dissolved in it, only one phosphoric acid was formed, namely H_3PO_4. The amount of CO_2 found in the combustion products of triphenylphosphine oxide was 99.97 ± 0.01% of the amount calculated from its chemical formula. The enthalpy of combustion of the test compound was determined to within ±0.04% (which is significantly more accurate than the results obtained in the study of phosphorus-containing compounds in a stationary bomb calorimeter). $\Delta H_f^\circ = -26.2 \pm 1.0$ kcal mol^{-1}, calculated from the above heat of combustion, differs significantly from the value $\Delta H_f^\circ = -15.1 \pm 3.0$ kcal mol^{-1} found[224] in a stationary bomb calorimeter, which is probably due to the difficulty of the analysis of the combustion products formed when the authors' method is used[224].

The thermochemistry of a number of phosphorus-containing compounds has been studied by reaction calorimetry. In these studies the enthalpies of hydrolysis[228,230,231,241] or the enthalpies of oxidation of the test compounds by an aqueous solution of hydrogen peroxide[221,222,228,230] were frequently measured. Reliable thermochemical data have been obtained also by measuring the enthalpies of reaction of chlorine-containing phosphorus compounds with a cyclohexane solution of the corresponding alcohol and a substituted amine[225,226,235]. The role of the amines consisted in binding the hydrogen chloride formed in the processes. The experimental conditions selected ensured that the reactions took place at temperatures close to the standard temperature and the duration of the experiments in most cases did not exceed 60 min. The results of these investigations are presented in Table 5.

Mortimer and Skinner[249] were the first to investigate the thermochemistry of organoarsenic compounds. They showed that many of these compounds readily interact with iodine even at room temperature and that such reactions are extremely convenient for calorimetric study. The above workers measured[249,250] the enthalpies of the reactions

$$(CH_3)_2AsAs(CH_3)_2\ (l) + I_2\ (c) \rightarrow 2\,(CH_3)_2AsI\ (l),$$
$$C_6H_5AsH_2\ (l) + 2I_2\ (c) \rightarrow C_6H_5AsI_2\ (l) + 2HI\ (g),$$

occurring in methanol and carbon tetrachloride respectively. However, the results did not allow the calculation of ΔH_f° of any one arsenic-containing reactant. Later the enthalpies of formation of three alkoxyarsenic compounds were determined[245] from measurements of the enthalpies of their hydrolysis in the presence of an excess of NaOH. These reactions take place rapidly and quantitatively at room temperature. The presence of alkali is necessary for the rapid dissolution of the arsenic trioxide formed.

The applicability of the enthalpy of combustion method to arsenic compounds was first investigated by Long and Sackman[242], who measured ΔH_c° for trimethylarsenic in a stationary bomb calorimeter. They established that the combustion products of the above compound have a composition very difficult to analyse. Indeed, the combustion products contained unoxidised arsenic and carbon, solid As_2O_3, As_2O_4, and As_2O_5, and a solution containing arsenic(III) and arsenic(V) compounds. This made it necessary to develop a method for the exact analysis of the above mixture. The arsenic content found in the combustion product by the method developed above amounted on average to 99.8% of the expected value, which confirmed the validity of the proposed analytical procedure. The enthalpy of combustion of triethylarsenic has been measured[31-33] in a stationary bomb calorimeter and only one arsenic oxide (As_2O_3) was found in the combustion product.

The same method has been used[243] to investigate triphenylarsenic. A method proposed previously[242] was used to analyse the combustion products, among which the oxides As_2O_3, As_2O_4, and As_2O_5 were found. However, the enthalpy of formation of the above compound thus obtained (+93.6 ± 2.0 kcal mol^{-1}) differs appreciably from the reliable value of this quantity (+71.0 ± 2.0 kcal mol^{-1}) found by Mortimer and Sellers[244], who used the method of combustion in a rotating bomb calorimeter with aqueous NaOH as the bomb liquid. In this case dissolution of the combustion products in the bomb resulted in the formation of a solution of sodium arsenate, arsenite, carbonate, and hydroxide. The enthalpies of reaction of the combustion products with the bomb liquid, necessary for the calculation of ΔH_f° for the test compound, were measured[244] in a special calorimeter.

Few data are available for the thermochemical properties of organoantimony compounds. They were all obtained by the combustion of the test substances in a stationary bomb calorimeter. The enthalpy of combustion of trimethylantimony was determined by Long and Sackman[247] who inserted the test substance in thin-walled glass bulbs and then placed them in the bomb. Analysis of the solid combustion products showed that they consisted mainly of crystalline Sb_2O_4. Sb_2O_3, unoxidised antimony, and carbon were also found as impurities. The analytical method developed for this mixture made it possible to take into account accurately the products of the incomplete oxidation of the initial compound. The enthalpy of hydration of Sb_2O_3, specially measured in preliminary experiments, proved to be insignificant and was disregarded in the interpretation of the experimental data.

The enthalpy of combustion of triethylantimony has been measured[31-33]. The selected experimental conditions ensured the formation of only a single antimony oxide, namely Sb_2O_3. The enthalpy of combustion of triphenylantimony was determined by Birr[223]. To improve the combustion, the test substance was ignited in a polyethylene bag. The resulting solid combustion product consisted of a mixture of unoxidised carbon and the oxides Sb_2O_3 and Sb_2O_4. It was analysed by the method of Long and Sackman[247].

The enthalpies of combustion of trimethyl-, triethyl-, and triphenylbismuth have also been measured[31-33,243,246], by combustion in a stationary bomb calorimeter. Long and Sackman[246] placed samples of trimethylbismuth to be combusted in thin-walled glass bulbs, on which a magnesium ribbon, connected to an iron wire used for ignition, was wound. Only the bismuth oxide Bi_2O_3 was found in the solid combustion products. Small amounts of metallic bismuth and free carbon were found as impurities. Analysis for unoxidised bismuth and carbon was carried out after each experiment and the corrections due to their presence were taken into account in the calculation of ΔH_f° for the test substance.

Steele[219] determined the enthalpy of formation of triphenylbismuth by the rotating bomb calorimeter method. The bomb liquid was an aqueous HCl solution in which the bismuth-containing combustion products were converted into $BiCl_3$. The value $\Delta H_f^\circ[(C_6H_5)_3Bi(c)] = 117.0 \pm 1.2$ kcal mol^{-1} obtained in this investigation[219] is close to $\Delta H_f^\circ = 112 \pm 2$ kcal mol^{-1} found for the same compound by combustion in a stationary bomb calorimeter[243].

VII. COMPOUNDS OF GROUP VI NON-TRANSITION ELEMENTS

Among organic compounds containing Group VI non-transition elements, only sulphur-containing substances have been investigated in fair detail. The monograph of Cox and Pilcher[1] presents the enthalpies of formation (obtained as a rule by combustion in a rotating bomb calorimeter) for approximately 170 such compounds. As already mentioned in the introduction, these data are not repeated here.

As regards the thermochemistry of organic substances containing other Group VI non-transition elements, there have been only three studies in which the enthalpies of formation of organic compounds of selenium and tellurium were determined.

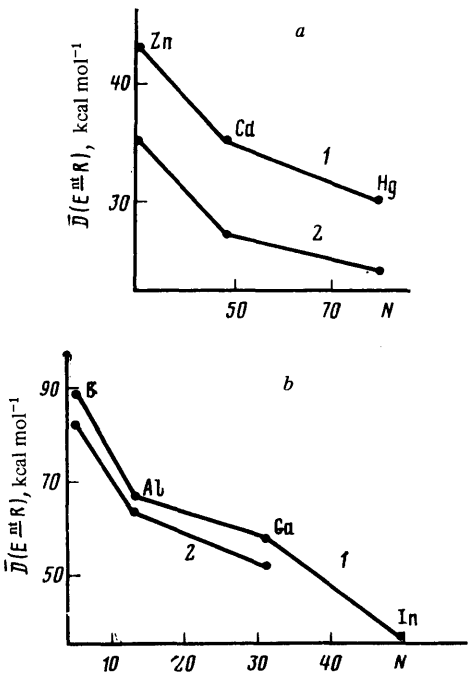


Figure 1. Variation of the average dissociation energy of the element–organic group bonds formed by Group II non-transition elements in the compounds $E^{nt}R_2$ (*a*) and Group III elements in the compounds $E^{nt}R_3$ (*b*) with increase of the atomic number of the element *N*; R: 1) CH_3; 2) C_2H_5.

The enthalpy of formation of liquid diethyl selenide, which is -23 ± 1 kcal mol^{-1}, has been calculated[251] from the results of the combustion of this substance in a stationary bomb calorimeter. It was combusted together with paraffin, which increased the degree of combustion. The same value of $\Delta H_f^\circ[(C_2H_5)_2Se(l)]$ was obtained[248] by measuring the enthalpy of reaction of diethyl selenide with an excess of bromine. After taking into account the enthalpy of vaporisation of this compound, which amounts to[248] 9.3 ± 0.4 kcal mol^{-1}, we obtain $\Delta H_f^\circ[(C_2H_5)_2Se(g)] = -14 \pm 1$ kcal mol^{-1}.

Barnes and Mortimer[252] calculated ΔH_f° for liquid diphenyl selenide from the enthalpy of combustion measured in a rotating bomb calorimeter and obtained $\Delta H_f^\circ = -54 \pm 1$ kcal mol^{-1}. The test substance was ignited in a polyester bag in a quartz crucible. Distilled water (50 cm^3), in which the combustion products obtained dissolved, was first placed in the bomb. The enthalpy of vaporisation of $(C_6H_5)_2Se$, amounting to 15.2 ± 0.6 kcal mol^{-1}, was calculated in the same study from its boiling point at different pressures. Taking into account this quantity, we have $\Delta H_f^\circ[(C_6H_5)_2Se(g)] = +69 \pm 1$ kcal mol^{-1}.

$\Delta H_f^\circ[(C_2H_5)_2Te(l)] = -3 \pm 1$ kcal mol^{-1} was calculated from measurements of the enthalpy of mixing of diethyl telluride with an excess of bromine and, after taking into account the enthalpy of vaporisation, equal to 10.0 ± 0.5 kcal mol^{-1}, the enthalpy of formation in the gaseous state was found to be $\Delta H_f^\circ[(C_2H_5)_2Te(g)] = +7 \pm 1$ kcal mole^{-1}.[248]

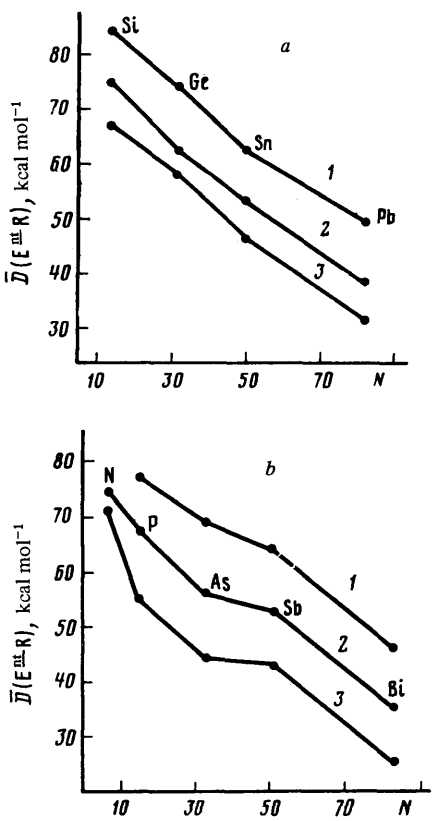


Figure 2. Variation of the average dissociation energy of the element–organic group bonds formed by Group IV non-transition elements in the compounds $E^{nt}R_4$ (*a*) and Group V elements in the compounds $E^{nt}R_3$ (*b*) with increase of the atomic number of the element; R: 1) C_6H_5; 2) CH_3; 3) C_2H_5.

VIII. THE AVERAGE DISSOCIATION ENERGIES OF THE CHEMICAL BONDS FORMED BY NON-TRANSITION ELEMENTS IN THEIR ORGANIC COMPOUNDS

The elucidation of the dependence of the strength of chemical bonds on the nature of the atoms involved in them is of considerable theoretical interest. However, determination of the dissociation energy of an individual bond in a

specified compound is usually a very difficult experimental problem. For this purpose one therefore frequently employs the average bond dissociation energies ($\bar{D}$). $\bar{D}$ is the enthalpy of the process

$$ER_n\ (g) \rightarrow E\ (g) + nR\ (g),$$

divided by the number of bonds n, where ER_n is the molecule of the given substance in the gaseous state, E the element, and R the atom, group, or ligand, also in the gaseous state. This quantity can be calculated by the formula

$$\bar{D}\ (E-R) = \frac{1}{n}\left\{\Delta H_f^0\ [E\ (g)] + n\Delta H_f^0\ [R\ (g)] - \Delta H_f^0\ [ER_n\ (g)]\right\},$$

from experimental (tabulated) enthalpies of formation of the reactants involved in the given reaction in the gaseous state.

Table 6. Average dissociation energies ($\bar{D}$) of element–organic group chemical bonds formed by Group II–VI non-transition elements (kcal mol^{-1}).

Compound	Bond	$\bar{D}$	Compound	Bond	$\bar{D}$
$(C_6H_5)_2Be$	C_6H_5—Be	80±3	(iso-C_4H_9)$_4$Ge	iso-C_4H_9—Ge	62±2
$(CH_3)_2Zn$	CH_3—Zn	43±1	$(C_6H_5)_4$Ge	C_6H_5—Ge	74±2
$(C_2H_5)_2Zn$	C_2H_5—Zn	35±1	$(C_6H_5CH_2)_4$Ge	$C_6H_5CH_2$—Ge	43±1
(n-C_3H_7)$_2$Zn	n-C_3H_7—Zn	38±3	$(CH_3O)_4$Ge	CH_3O—Ge	74±2
(n-C_4H_9)$_2$Zn	n-C_4H_9—Zn	39±3	$(C_2H_5O)_4$Ge	C_2H_5O—Ge	75±1
$(CH_3)_2Cd$	CH_3—Cd	35±1	$(C_6H_5O)_4$Ge	C_6H_5O—Ge	62±3
$(C_2H_5)_2Cd$	C_2H_5—Cd	27±1	$[(C_2H_5)_3Ge]_2$	C_2H_5—Ge	59±1
$(CH_3)_2Hg$	CH_3—Hg	30±1	$[(C_2H_5)_3Ge]_2O$	O—Ge(C_2H_5)$_3$	90±2
$(C_6H_5)_2Hg$	C_6H_5—Hg	24±1	$[(C_6H_5)_3Ge]_2$	C_6H_5—Ge	71±2
(n-C_3H_7)$_2$Hg	n-C_3H_7—Hg	24±1	$(CH_3)_4Sn$	CH_3—Sn	53±1
(iso-C_3H_7)$_2$Hg	iso-C_3H_7—Hg	20±1	$(C_2H_5)_4Sn$	C_2H_5—Sn	60±3
(n-C_4H_9)$_2$Hg	n-C_4H_9—Hg	27±2	$(C_2H_5)_4Sn$	C_2H_5—Sn	46±1
(iso-C_4H_9)$_2$Hg	iso-C_4H_9—Hg	26±2	(n-C_3H_7)$_4$Sn	n-C_3H_7—Sn	47±2
(iso-C_5H_{11})$_2$Hg	iso-C_5H_{11}—Hg	26±2	(iso-C_3H_7)$_4$Sn	iso-C_3H_7—Sn	43±2
$(C_6H_5)_2Hg$	C_6H_5—Hg	38±1	(n-C_4H_9)$_4$Sn	n-C_4H_9—Sn	47±2
$(CN)_2Hg$	CN—Hg	65±2	$(C_6H_5)_4Sn$	C_6H_5—Sn	62±2
$(CH_3)_3B$	CH_3—B	89±2	$[(CH_3)_3Sn]_2$	CH_3—Sn	52±2
$(C_2H_5)_3B$	C_2H_5—B	82±2	$[(C_2H_5)_3Sn]_2$	C_2H_5—Sn	48±2
(n-C_3H_7)$_3$B	n-C_3H_7—B	84±2	$[(C_2H_5)_3Sn]_2O$	O—Sn(C_2H_5)$_3$	79±3
(iso-C_3H_7)$_3$B	iso-C_3H_7—B	82±2	$[(C_6H_5)_3Sn]_2$	C_6H_5—Sn	60±2
(n-C_4H_9)$_3$B	n-C_4H_9—B	84±2	$[(C_6H_5)_3Sn]_2O$	O—Sn(C_6H_5)$_3$	80±3
(iso-C_4H_9)$_3$B	iso-C_4H_9—B	81±2	$(CH_3)_4Pb$	CH_3—Pb	38±1
(s-C_4H_9)$_3$B	s-C_4H_9—B	76±2	$(C_2H_5)_4Pb$	C_2H_5—Pb	31±1
(iso-C_5H_{11})$_3$B	iso-C_5H_{11}—B	84±2	$(C_6H_5)_4Pb$	C_6H_5—Pb	49±2
(cyclo-C_6H_{11})$_3$B	cyclo-C_6H_{11}—B	88±3	$(CH_3)_3N$	CH_3—N	74±1
(n-C_6H_{13})$_3$B	n-C_6H_{13}—B	82±2	$(C_2H_5)_3N$	C_2H_5—N	71±1
(n-C_7H_{15})$_3$B	n-C_7H_{15}—B	82±2	$(CH_3)_3P$	CH_3—P	67±1
(n-C_8H_{17})$_3$B	n-C_8H_{17}—B	82±2	$(C_2H_5)_3P$	C_2H_5—P	55±1
(s-C_8H_{17})$_3$B	s-C_8H_{17}—N	80±2	$(C_6H_5)_3P$	C_6H_5—P	77±2
$(C_6H_5)_3B$	C_6H_5—B	112±2	$(CH_3)_3PO$	$(CH_3)_3P$=O	139±2
$(CH_3O)_3B$	CH_3O—B	118±2	$(C_6H_5)_3PO$	$(C_6H_5)_3P$=O	133±3
$(C_2H_5O)_3B$	C_2H_5O—B	119±1	$(CH_3O)_3P$	CH_3O—P	83±2
(n-C_3H_7O)$_3$B	n-C_3H_7O—B	120±2	$(C_2H_5O)_3P$	C_2H_5O—P	83±1
(n-C_4H_9O)$_3$B	n-C_4H_9O—B	119±2	(iso-C_3H_7O)$_3$P	iso-C_3H_7O—P	84±2
$(C_6H_5O)_3B$	C_6H_5O—B	104±2	$(C_6H_5O)_3PO$	$(C_6H_5O)_3P$=O	150±1
$(CH_3)_2N)_3B$	$(CH_3)_2N$—B	96±2	$[(C_6H_5)_2N]_3P$	$(C_6H_5)_2N$—P	81±2
$(CH_3S)_3B$	CH_3S—B	87±3	(n-C_4H_9)$_3$PS	(n-C_4H_9)$_3$P=S	91±1
$(C_6H_5S)_3B$	C_6H_5S—B	79±3	$(C_2H_5O)_3PS$	$(C_2H_5O)_3P$=S	90±1
$(CH_3)_3Al$	CH_3—Al	67±1	$(CH_3)_3As$	CH_3—As	56±1
$(C_2H_5)_3Al$	C_2H_5—Al	64±1	$(C_2H_5)_3As$	C_2H_5—As	44±1
(n-C_3H_7)$_3$Al	n-C_3H_7—Al	63±2	$(C_6H_5)_3As$	C_6H_5—As	69±2
$(CH_3)_3Ga$	CH_3—Ga	59±1	$(CH_3O)_3As$	CH_3O—As	69±2
$(C_2H_5)_3Ga$	C_2H_5—Ga	52±2	$(C_2H_5O)_3As$	C_2H_5O—As	69±2
(n-C_4H_9)$_3$Ga	n-C_4H_9—Ga	56±2	(n-C_3H_7O)$_3$As	n-C_3H_7O—As	70±2
(iso-C_4H_9)$_3$Ga	iso-C_4H_9—Ga	55±2	$(CH_3)_3Sb$	CH_3—Sb	53±1
$(CH_3)_3In$	CH_3—In	37±1	$(C_2H_5)_3Sb$	C_2H_5—Sb	43±1
$(CH_3)_4Si$	CH_3—Si	75±1	$(C_6H_5)_3Sb$	C_6H_5—Sb	64±2
$(C_2H_5)_4Si$	C_2H_5—Si	67±1	$(CH_3)_3Bi$	CH_3—Bi	35±1
$(C_6H_5)_4Si$	C_6H_5—Si	84±2	$(C_2H_5)_3Bi$	C_2H_5—Bi	25±1
$(CH_3O)_4Si$	CH_3O—Si	102±2	$(C_6H_5)_3Bi$	C_6H_5—Bi	46±2
$(C_2H_5O)_4Si$	C_2H_5O—Si	101±2	$(CH_3)_2O$	CH_3—O	86±1
iso-$C_3H_7O)_4Si$	iso-C_3H_7O—Si	98±3	$(C_2H_5)_2O$	C_2H_5—O	85±1
$[(CH_3)_3Si]_2$	CH_3—Si	72±1	$(C_6H_5)_2O$	C_6H_5—O	102±2
$[(CH_3)_3Si]_2O$	O—Si(CH_3)$_3$	116±3	$(CH_3)_2S$	CH_3—S	71±1
$[(C_2H_5)_3Si]_2$	C_2H_5—Si	63±2	$(C_2H_5)_2S$	C_2H_5—S	68±1
$(CH_3)_4Ge$	CH_3—Ge	62±1	$(C_6H_5)_2S$	C_6H_5—S	83±2
$(C_2H_5)_4Ge$	C_2H_5—Ge	58±1	$(C_2H_5)_2Se$	C_2H_5—Se	60±2
n-C_3H_7—Ge	(n-C_3H_7)$_4$Ge	58±2	$(C_6H_5)_2Se$	C_6H_5—Se	70±2
n-C_4H_9—Ge	(n-C_4H_9)$_4$Ge	59±2	$(C_2H_5)_2Te$	C_2H_5—Te	48±2

Table 6 presents the values of $\bar{D}$(E–R) for a series of compounds of Group II–VI non-transition elements calculated by the authors of the review by this method from the data in Tables 1–5 in this review and in a handbook[11]. The data in Table 6 made it possible to establish the following relations for the dissociation energies $\bar{D}$ of the bonds formed by non-transition elements in their organic compounds.

1. In compounds $E^{nt}R_n$ of non-transition elements (E^{nt}) in the same Group of the Periodic System and with the same alkyl or phenyl group (R) and the same value of n, the average dissociation energy of the E^{nt}–R bond diminishes with increasing atomic number of the element E^{nt} down the Group (Figs. 1–3)†.

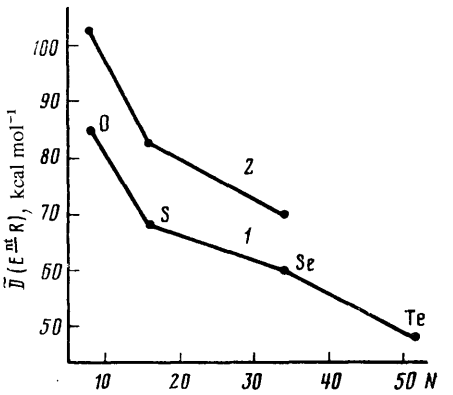


Figure 3. Variation of the average dissociation energy of the element–organic group bonds formed by Group VI non-transition elements in the compounds $E^{nt}R_2$ with increase of the atomic number of the element; R: 1) C_2H_5; 2) C_6H_5.

2. In all cases $\bar{D}(E^{nt}-C_6H_5) > \bar{D}(E^{nt}-CH_3) > \bar{D}(E^{nt}-C_2H_5) \cong \bar{D}(E^{nt}$-n-$C_3H_7) \cong \bar{D}(E^{nt}$-n-$C_4H_9)$.

3. The average dissociation energy of the E^{nt}–n-R bond exceeds by 1–4 kcal mol^{-1} $\bar{D}(E^{nt}$–iso-R). [The failure of $\bar{D}$(Ge-n-C_4H_9) and $\bar{D}$(Ge–iso-C_4H_9) to obey this rule is probably due to the inaccuracy of experimental data used to calculate these quantities.]

4. The average dissociation energies of the E^{nt}–OR bonds, where R is an alkyl group, exceed by 14±2 kcal mol^{-1} the corresponding values of $\bar{D}(E^{nt}$–$OC_6H_5)$. The high dissociation energies of the bonds formed by silicon and germanium with oxygen in the compounds $(R_3E)_2O$ compared with the corresponding values for $(RO)_4E$ are striking.

5. The average dissociation energies of the E–R bonds, where R is an alkyl or phenyl group and E = Si, Ge, or Sn, in the compounds ER_4 and $(ER_3)_2$ with the same elements and groups have similar values (Table 6). This corresponds to the equality, within the limits of the error of the determination, of the E–R bond lengths in the compounds ER_4 and $(ER_3)_2$ with identical E and R.[256–259]

†As a general relation, this was first established by the present authors[253]. In the compound E^tL_n of transition elements (E^t) belonging to the same Group and with the same ligand (L) and the same n, $\bar{D}(E^t$–L) increases with increasing atomic number of the element down the Group[254,255].

The values of $\bar{D}$(E–R) for compounds of the type $(ER_3)_2$ were calculated from the equation

$$\bar{D}(E-R) = {}^1/_6 \{6\Delta H_f^0[R(g)] + \Delta H_f^0[E_2(g)] - \Delta H_f^0[(ER_3)_2(g)]\}.$$

If, bearing in mind the observed similarity of the values of $\bar{D}$(E–R) in ER_4 and in $(ER_3)_2$, one assumes that $\bar{D}$(E–E) for the corresponding gas-phase molecules of E_2 and $(ER_3)_2$ are also similar, then we obtain the following values for the compounds $(ER_3)_2$: $\bar{D}$(Si–Si) ≅ 74 kcal mol^{-1}, $\bar{D}$(Ge–Ge) ≅ 66 kcal mol^{-1}, and $\bar{D}$(Sn–Sn) ≅ 45 kcal mol^{-1}.

Unfortunately there are no thermochemical data for the strength of the bonds between non-transition elements. a mass-spectrometric study[260] of the compounds $(C_5H_5)_3(CO)_3E^1E^2(CH_3)_3$, where E^1 = Cr, Mo, or W and E^2 = Ge or Sn, led to the following results:

Bond	Cr–Ge	Mo–Ge	W–Ge	Cr–Sn	Mo–Sn	W–Sn
D, kcal mole^{-1}	46.8	60.0	64.8	53.5	71.0	75.6

Thus $\bar{D}(E^1–E^2)$ increases with increasing atomic number of both the transition and non-transition element down the Groups of the Periodic System. In this case the behaviour characteristic of the bonds formed by transition metals, considered in detail in our previous reviews[245,255], is manifested.

REFERENCES

1. J.D.Cox and G.A.Pilcher, "Thermochemistry of organic and Organometallic Compounds", Acad. Press, London–New York, 1970.
2. D.R.Stull, E.F.Westrum, Jr., and G.C.Sinke, "The Chemical Thermodynamics of Organic Compounds" (Translated into Russian), Izd.Mir, Moscow, 1971.
3. M.Berthelot, Compt.rend., 129, 918 (1899).
4. L.H.Long and R.G.W.Norrish, Phil.Trans.Roy. Soc.A, 241, 587 (1949).
5. D.W.Scott, W.D.Good, and G.Waddington, J.Phys. Chem., 60, 1090 (1956).
6. W.D.Good, D.W.Scott, J.L.Lacina, and J.P.McCullogh, J.Phys.Chem., 63, 1139 (1959).
7. W.D.Good, J.L.Lacina, B.L.De Prater, and J.P.McCullough, J.Phys.Chem., 68, 579 (1964).
8. W.D.Good and M.Mansson, J.Phys.Chem., 70, 97 (1966).
9. N.K.Smith and W.D.Good, J.Chem.Eng.Data, 12, 570 (1967).
10. D.D.Wagman, W.H.Evans, V.B.Parker, J.Halow, S.M.Baidley, and R.H.Schumm, "Selected Values of Chemical Thermodynamic Properties", Nat.Bur. Stand., Washington, Technical Note 270-1 (1965); Technical Note 270-2 (1967); Technical Note 270-4 (1969); Technical Note 270-5 (1971).
11. Handbook, "Termicheskie Konstanty Veshchestv" (Thermal Constants of Substances), Izd.Akad.Nauk SSSR, Moscow, 1965, No.1; 1966, No.2; 1968, No.3; 1970, No.4; 1971, No.5; 1972, No.6; 1974, No.7; 1978, No.8.
12. L.V.Gurvich, G.V.Karachevtsev, V.N.Kondrat'ev, Yu.A.Lebedev, V.A.Medvedev, V.K.Potapov, and Yu.S.Khodeev, "Energii Razryva Khimicheskikh Svyazei. Potentsialy Ionizatsii i Srodstvo k Elektronu" (Chemical Bond Dissociation Energies, Ionisation Potentials, and Electron Affinities), Izd. Nauka, Moscow, 1974.
13. J.A.Kerr, Chem.Rev., 66, 465 (1966).
14. P.Gray and A.Williams, Chem.Rev., 59, 239 (1959).
15. T.Holm, J.Organomet.Chem., 77, 27 (1974).
16. Yu.A.Lebedev, E.A.Miroshnichenko, and A.M.Chaikin, Dokl.Akad.Nauk SSSR, 145, 1288 (1962).
17. P.A.Fowell and C.T.Mortimer, J.Chem.Soc., 3793 (1961).
18. R.Juza and E.Hullenbrand, Z.anorg.Chem., 273, 297 (1953).
19. J.M.Blanchard, R.D.Joly, J.M.Lettoffe, G.Perachon, and J.Thourey, J.chim.phys.et phys.-chim.biol., 71, 472 (1974).
20. J.Bousquet, J.M.Blanchard, R.D.Joly, J.M.Lettofe, G.Perachon, and J.Thourey, Bull.Soc.chim.France, 3, 478 (1975).
21. A.M.Chaikin, Zhur.Fiz.Khim., 36, 130 (1962)[Russ. J.Phys.Chem., No.1 (1962)].
22. J.Berkowitz, D.Bafus, and T.L.Brown, J.Phys. Chem., 65, 1380 (1961).
23. R.West and W.Glaze, J.Amer.Chem.Soc., 83, 3580 (1961).
24. M.Weiner, G.Vogel, and R.West, Inorg.Chem., 1, 654 (1962).
25. F.Glockling, R.J.Morrison, and J.W.Wilson, J.Chem. Soc., Dalton Trans., 94 (1973).
26. R.J.Irving and M.A.V.Ribeiro da Silva, J.Chem. Soc., 413 (1977).
27. H.S.Hull, A.F.Reid, and A.G.Turnbull, Inorg. Chem., 6, 805 (1967).
28. V.G.Genchel', E.V.Evstigneeva, and N.V.Petrova, Zhur.Fiz.Khim., 50, 1909 (1976)[Russ.J.Phys. Chem., No.7 (1976)].
29. W.Kakolowicz and E.Giera, Quatrieme Conference Internationale de Thermodynamique Chimique, Montpellier (France), 1, 73 (1975).
30. A.S.Carson, K.Hartley, and H.A.Skinner, Trans. Faraday Soc., 45, 1159 (1949).
31. W.F.Lautsch, Chem.Techn.(Berlin), 10, 419 (1958).
32. W.F.Lautsch, P.Erzberger, and A.Tröber, Wiss. Z.Techn.Hochschule Chem.Leuna–Merserburg, 1, 31 (1958).
33. W.F.Lautsch, A.Tröber, W.Zimmer, L.Mehner, W.Linck, H.M.Lehmann, H.Brandenburger, H.Körner, H.J.Metzchker, K.Wagner, and R.Kaden, Z.Chem., 3, 415 (1963).
34. A.S.Carson, K.Hartley, and H.A.Skinner, Proc. Roy.Soc.A, 195, 500 (1949).
35. K.Hartley, H.O.Pritchard, and H.A.Skinner, Trans. Faraday Soc., 46, 1019 (1950).
36. A.S.Carson, E.M.Carson, and B.Wilmshurst, Nature, 170, 320 (1952).
37. K.Hartley, H.Pritchard, and H.A.Skinner, Trans. Faraday Soc., 47, 254 (1951).
38. W.J.Jones, D.P.Evans, T.Gulwell, and D.C.Griffiths, J.Chem.Soc., 39 (1935).
39. C.T.Mortimer, H.O.Pritchard, and H.A.Skinner, Trans.Faraday Soc., 48, 220 (1952).
40. C.L.Chernick, H.A.Skinner, and J.Wadsö, Trans. Faraday Soc., 52, 1088 (1956).
41. D.M.Fairbrother and H.A.Skinner, Trans.Faraday Soc., 52, 956 (1956).
42. A.S.Carson and B.Wilmshurst, J.Chem.Thermodyn., 3, 251 (1971).
43. V.F.Kupriyanov, V.N.Alyasov, V.G.Tsvetkov, M.S.Sheiman, V.I.Buzulukov, V.P.Maslennikov, and Yu.A.Aleksandrov, Trudy po Khim. i Khim. Tekhnol.(Gor'kii), No.1, 80 (1974).
44. H.A.Skinner, Adv.Organomet.Chem., 2, 49 (1964).

45. A.S.Carson and H.A.Skinner, Nature, **165**, 484 (1950).
46. T.Holm, J.Organomet.Chem., **56**, 87 (1973).
47. W.H.Johnson, M.V.Kilday, and E.J.Prosen, J.Res. Nat.Bur.Stand., **65A**, 215 (1961).
48. L.Rosenblum, J.Org.Chem., **25**, 1652 (1960).
49. A.E.Pope and H.A.Skinner, J.Chem.Soc., 3704 (1963).
50. G.L.Gal'chenko and R.M.Varushchenko, Zhur. Fiz.Khim., **37**, 2513 (1963)[Russ.J.Phys.Chem., No.11 (1963)].
51. S.Tannenbaum and P.E.Schaeffer, J.Amer.Chem. Soc., **77**, 1385 (1955).
52. G.L.Gal'chenko, N.S.Zaugol'nikova, S.M.Skuratov, L.S.Vasil'ev, Yu.N.Bubnov, and B.M.Mikhailov, Dokl.Akad.Nauk SSSR, **169**, 587 (1966).
53. G.L.Gal'chenko and N.S.Zaugol'nikova, Zhur.Fiz. Khim., **41**, 1018 (1967)[Russ.J.Phys.Chem., No.5 (1967)].
54. E.A.Haseley, A.B.Garrett, and H.H.Sisler, J.Phys., Chem., **60**, 1136 (1956).
55. J.E.Bennet and H.A.Skinner, J.Chem.Soc., 2472 (1961).
56. G.L.Gal'chenko and N.S.Zaugol'nikova, Zhur.Fiz. Khim., **41**, 2181 (1967)[Russ.J.Phys.Chem., No.9 (1967)].
57. A.Finch, P.J.Gardner, E.J.Pearn, and G.B.Watts, Trans.Faraday Soc., **63**, 1880 (1967).
58. W.J.Cooper and J.E.Masi, J.Phys.Chem., **64**, 682 (1960).
59. T.Charnley, H.A.Skinner, and N.B.Smith, J.Chem.Soc., 2288 (1952).
60. G.L.Gal'chenko, N.S.Zaugol'nikova, S.M.Skuratov, L.S.Vasil'ev, A.Ya.Bezmenov, and B.M.Mikhailov, Dokl.Akad.Nauk SSSR, **166**, 103 (1966).
61. G.L.Gal'chenko, N.S.Zaugol'nikova, S.M.Skuratov, A.Ya.Bezmenov, L.S.Vasil'ev, Yu.N.Bubnov, and B.M.Mikhailov, Zhur.Fiz.Khim., **41**, 3034 (1967) [Russ.J.Phys.Chem., No.12 (1967)].
62. J.E.Bennet and H.A.Skinner, J.Chem.Soc., 2150 (1962).
63. G.L.Gal'chenko, R.M.Varushchenko, Yu.M.Bubnov, and B.M.Mikhailov, Zhur.Obshch.Khim., **32**, 284 (1962).
64. G.L.Gal'chenko, M.M.Ammar, S.M.Skuratov, Yu.N.Bubnov, and B.M.Mikhailov, Vestnik Moskov. Gos.Univ., Ser.Khim., No.2, 3 (1965).
65. G.L.Gal'chenko, R.M.Varushchenko, Yu.M.Bubnov, and B.M.Mikhailov, Zhur.Obshch.Khim., **32**, 2405 (1962).
66. J.T.F.Fenwick and J.W.Wilson, J.Chem.Soc., Dalton Trans., **13**, 1324 (1972).
67. J.W.Wilson and J.T.F.Fenwick, J.Chem.Thermodyn., **5**, 431 (1973).
68. H.A.Skinner and T.F.S.Tees, J.Chem.Soc., 3378 (1953).
69. A.Finch and P.J.Gardner, Trans.Faraday Soc., **62**, 3314 (1966).
70. A.Finch, P.J.Gardner, and G.B.Watts, Chem. Comm., 1054 (1967).
71. A.Finch, P.J.Gardner, N.Hill, and K.Hussian, J.Chem.Soc., Dalton Trans., 2543 (1973).
72. H.A.Skinner and N.B.Smith, J.Chem.Soc., 3930 (1954).
73. H.A.Skinner and N.B.Smith, J.Chem.Soc., 4025 (1953).
74. G.L.Gal'chenko, E.P.Brykina, L.I.Chirkova, L.S.Vasil'ev, and B.M.Mikhailov, Zhur.Fiz.Khim., **47**, 1606 (1973)[Russ.J.Phys.Chem., No.6 (1973)].
75. G.L.Gal'chenko, E.P.Brykina, V.K.Pavlovich, Yu.N.Bubnov, and B.M.Mikhailov, Dokl.Akad.Nauk SSSR, **43**, 2034 (1969).
76. G.L.Gal'chenko, M.M.Ammar, S.M.Skuratov, Yu.N.Bubnov, and B.M.Mikhailov, Vestnik Moskov. Gos.Univ., Ser.Khim., No.3, 10 (1965).
77. G.L.Gal'chenko, E.P.Brykina, L.I.Chirkova, B.K.Pavlovich, and N.N.Shcheglova, "V Vsesoyuznaya Konferentsiya po Kalorimetrii, Tezisy Dokladov" (The Vth All-Union Conference on Calorimetry. Abstracts of Reports), Moscow, 1971, p.121.
78. G.L.Gal'chenko, E.P.Brykina, N.N.Shcheglova, L.S.Vasil'ev, and B.M.Mikhailov, Izv.Akad.Nauk SSSR, Ser.Khim., 200 (1973).
79. G.L.Gal'chenko, Nguyen Zanh Ni, E.P.Brykina, O.G.Boldyreva, V.A.Dorokhov, and B.M.Mikhailov, Trudy po Khim. i Khim.Tekhnol.(Gor'kii), No.4, 17 (1975).
80. Nguyen Zanh Ni, Candidate's Thesis, Moscow State University, Moscow, 1977.
81. R.E.McCoy and S.H.Bauer, J.Amer.Chem.Soc., **78**, 2061 (1956).
82. E.P.Kirpichev, Yu.I.Rubtsov, L.V.Titov, and M.D.Levicheva, Zhur.Neorg.Khim., **16**, 56 (1971).
83. E.P.Kirpichev, Yu.I.Rubtsov, T.V.Sorokina, L.V.Titov, and L.A.Gavrilova, Zhur.Fiz.Khim., **48**, 2097 (1974) [Russ.J.Phys.Chem., No.8 (1974)].
84. E.P.Kirpichev, Yu.I.Rubtsov, T.V.Sorokina, L.V.Titov, and S.P.Psikha, "VII Vsesoyuznaya Konferentsiya po Kalorimetrii, Tezisy Dokladov" (The VIIth All-Union Conference on Calorimetry. Abstracts of Reports), Moscow, 1977, p.111.
85. G.L.Gal'chenko, E.P.Brykina, R.M.Varushchenko, L.S.Vasil'ev, and B.M.Mikhailov, Zhur.Fiz.Khim., **47**, 1609 (1973)[Russ.J.Phys.Chem., No.6 (1973)].
86. H.A.Skinner and N.B.Smith, J.Chem.Soc., 2324 (1954).
87. A.Finch, P.J.Gardner, and G.B.Watts, Trans. Faraday Soc., **63**, 1603 (1967).
88. A.Finch, P.J.Gardner, and E.J.Pearn, Trans. Faraday Soc., **62**, 1072 (1966).
89. A.Finch and P.J.Gardner, J.Chem.Soc., 2985 (1964).
90. G.L.Gal'chenko, Nguyen Zanh Ni, E.P.Brykina, O.G.Boldyreva, V.A.Dorokhov, and B.M.Mikhailov, Vestnik Moskov.Gos.Univ., Ser.Khim., No.4, 404 (1977).
91. G.L.Gal'chenko, L.N.Martynovskaya, and V.I.Stanko, Dokl.Akad.Nauk SSSR, **186**, 1328 (1969).
92. G.L.Gal'chenko, L.N.Martynovskaya, and V.I.Stanko, Zhur.Obshch.Khim., **40**, 2410 (1970).
93. V.I.Pepekin, Yu.N.Matyushin, V.N.Kalinin, Yu.A.Lebedev, L.I.Zakharkin, and A.Ya.Apin, Izv.Akad.Nauk SSSR, Ser.Khim., 268 (1971).
94. V.K.Pavlovich, Candidate's Thesis, Moscow State University, Moscow, 1978.
95. G.L.Gal'chenko, L.V.Kulakova, V.N.Siryatskaya, and A.F.Zhigach, Vestnik Moskov.Gos.Univ., Ser. Khim., No.6, 3 (1969).
96. G.L.Gal'chenko, L.N.Martynovskaya, V.I.Stanko, and Yu.V.Gol'tyapin, Dokl.Akad.Nauk SSSR, **188**, 587 (1969).
97. G.L.Gal'chenko, L.N.Martynovskaya, and V.I.Stanko, Zhur.Obshch.Khim., **40**, 2415 (1970).
98. G.L.Gal'chenko, V.K.Pavlovich, L.M.Kovba, V.I.Stanko, Yu.V.Gol'tyapin, A.I.Klimova, Yu.A.Lebedev, and E.A.Miroshnichenko, Trudy po Khim. i Khim.Tekhnol.(Gor'kii), No.1, 3 (1974).
99. G.L.Gal'chenko, L.N.Martynovskaya, V.I.Stanko, and Yu.V.Gal'tyapin, Zhur.Obshch.Khim., **41**, 141 (1971).

100. G.L.Gal'chenko, V.K.Pavlovich, Yu.V.Gal'tyapin, and V.I.Stanko, Trudy po Khim. i Khim.Tekhnol. (Gork'kii), No.4, 12 (1975).
101. G.I.Gal'chenko, V.K.Pavlovich, Yu.V.Gal'tyapin, and V.I.Stanko, Dokl.Akad.Nauk SSSR, **216**, 561 (1974).
102. G.L.Gal'chenko, L.N.Martynovskaya, V.I.Stanko, and A.I.Klimova, Dokl.Akad.Nauk SSSR, **193**, 341 (1970).
103. G.L.Gal'chenko, V.K.Pavlovich, R.M.Varushchenko, A.I.Druzhinina, V.N.Siryatskaya, and A.F.Zhigach, Dokl.Akad.Nauk SSSR, **238**, 865 (1978).
104. B.C.Smith, L.Thakur, and M.A.Wassef, J.Chem. Soc.(A), 1616 (1967).
105. B.C.Smith, L.Thakur, and M.A.Wassef, Canad.J. Chem., **48**, 1936 (1970).
106. C.T.Mortimer and P.W.Sellers, J.Chem.Soc., 1978 (1963).
107. A.Tröber and C.Stricker, Wiss.Z.Techn.Hochschule Chem.Leuna–Merserberg, **8**, 34 (1966).
108. Yu.Kh.Shaulov, G.O.Shmyreva, and V.S.Tubyanskaya, Zhur.Fiz.Khim., **39**, 105 (1965)[Russ.J.Phys. Chem., No.1 (1965)].
109. V.Fic, Chem.prümysl., **16**, 607 (1966).
110. G.O.Shmyreva, G.B.Sakharovskaya, A.F.Popov, I.N.Korneev, and A.A.Smolyaninova, Zhur.Fiz. Khim., **45**, 467 (1971)[Russ.J.Phys.Chem., No.2 (1971)].
111. Yu.Kh.Shaulov, V.S.Tubyanskaya, E.V.Evstigneeva, and G.O.Shmyreva, Zhur.Fiz.Khim., **38**, 1779 (1964) [Russ.J.Phys.Chem., No.7 (1964)].
112. G.O.Shmyreva, R.M.Golosova, G.B.Sakharovskaya, A.S.Popov, and N.N.Korneev, Zhur.Fiz.Khim., **48**, 770 (1974)[Russ.J.Phys.Chem., No.3 (1974)].
113. J.W.Wilson, J.Chem.Soc.(A), 981 (1971).
114. Y.Kawasaki, T.Tanaka, and R.Okawara, Technol. Reports Osaka Univ., **13**, 537 (1963).
115. J.O.Hill and R.J.Irving, J.Chem.Soc.(A), 971 (1966).
116. R.J.Irving and M.A.Ribero da Silva, J.Chem.Soc., Dalton Trans., 1257 (1975).
117. K.J.Cavel and G.Pilcher, J.Chem.Soc., Faraday Trans.I, **10**, 1590 (1977).
118. R.J.Irving and M.A.V.Ribero da Silva, J.Chem.Soc., Dalton Trans., 1940 (1976).
119. Yu.Kh.Shaulov and G.O.Shmyreva, Zhur.Fiz.Khim., **42**, 1916 (1968) [Russ.J.Phys.Chem., No.8 (1968)].
120. M.B.Smith, J.Organomet.Chem., **76**, 171 (1974).
121. L.H.Long and J.F.Sackman, Trans.Faraday Soc., **54**, 1797 (1958).
122. P.A.Fowell and C.T.Mortimer, J.Chem.Soc., 3734 (1958).
123. Yu.Kh.Shaulov, V.G.Genchel', R.M.Aizatullova, and G.S.Pesotskii, Zhur.Fiz.Khim., **46**, 2379 (1972) [Russ.J.Phys.Chem., No.9 (1972)].
124. G.M.Kol'yakova, I.B.Rabinovich, and E.N.Zorina, Dokl.Akad.Nauk SSSR, **209**, 616 (1973).
125. R.J.Irving and G.W.Walter, J.Chem.Soc.(A), 2690 (1969).
126. W.D.Clark and S.J.W.Price, Canad.J.Chem., **46**, 1683 (1968).
127. H.Hull and A.G.Turnbull, Inorg.Chem., **6**, 2020 (1967).
128. G.L.Gal'chenko, Doctoral Thesis, Moscow State University, Moscow, 1972.
129. S.Pawlenko, Chem.Ber., **100**, 3591 (1967).
130. S.Pawlenko, Chem.Ber., **102**, 1937 (1969).
131. S.Tannenbaum, S.Kaye, and G.F.Lewenz, J.Amer. Chem.Soc., **75**, 3753 (1953).
132. W.V.Steele, J.Chem.Thermodyn., **10**, 445 (1978).
133. G.G.Nurullaev, Candidate's Thesis, Institute of Physics, Academy of Sciences of Azerbaijan SSR, Baku, 1975.
134. V.I.Tel'noi, G.M.Kol'yakova, I.B.Rabinovich, and N.S.Vyazankin, Dokl.Akad.Nauk SSSR, **185**, 374 (1969).
135. V.I.Tel'noi, I.B.Rabinovich, and G.A.Razuvaev, Dokl.Akad.Nauk SSSR, **159**, 1106 (1964).
136. V.I.Tel'noi and I.B.Rabinovich, Zhur.Fiz.Khim., **40**, 1556 (1966)[Russ.J.Phys.Chem., No.7 (1966)].
137. B.S.Jseard, J.B.Pedley, and J.A.Treverton, J.Chem.Soc.(A), 19, 3095 (1971).
138. K.H.Birr, Z.anorg.Chem., 315, 175 (1962).
139. V.I.Tel'noi and I.B.Rabinovich, Zhur.Fiz.Khim., **39**, 2314 (1965)[Russ.J.Phys.Chem., No.9 (1965)].
140. S.N.Hajiev, H.G.Nurullaev, L.N.Martynovskaya, and A.M.Mosin, Quatrieme Conference Internationale de Thermodynamique Chimique, Montpellier (France), 1, 229 (1975).
141. S.N.Gadzhiev, V.A.Klyuchnikova, G.A.Lobanov, K.K.Kerimov, A.G.Kuznetsov, and L.N.Martynovskaya, "VII Vsesoyuznaya Konferentsiya po Kalorimetrii, Tezisy Dokladov" (The VIIth All-Union Conference on Calorimetry. Abstracts of Reports), Moscow, 1977, p.114.
142. K.H.Birr and C.Sarafidis, Z.anorg.Chem., 311, 97 (1961).
143. G.M.Kol'yakova, I.B.Rabinovich, N.S.Vyazankin, and E.N.Gladyshev, Dokl.Akad.Nauk, SSSR, **204**, 356 (1972).
144. J.C.Baldwin, M.F.Lappert, J.B.Pedley, and J.A.Treverton, J.Chem.Soc.(A), 1980 (1967).
145. J.C.Baldwin, M.F.Lappert, J.B.Pedley, and J.S.Poland, J.Chem.Soc., Dalton Trans., 1943 (1972).
146. P.Sellers, Quatrieme Conference Internationale de Thermodynamique Chimique, 1, 237 (1975).
147. T.Tanaka, U.Takahashi, R.Okawara, and T.Watase, J.Chem.Phys., 19, 1330 (1951).
148. T.Tanaka, U.Takahashi, R.Okawara, and T.Watase, J.Chem.Phys., **22**, 957 (1954).
149. T.Tanaka, Bull.Chem.Soc.Japan, **28**, 15 (1955).
150. E.G.Kiparisova, I.B.Rabinovich, and Yu.A.Aleksandrov, Dokl.Akad.Nauk SSSR, **200**, 1116 (1971).
151. V.G.Genchel', T.L.Krasnova, A.M.Mosin, and E.A.Chernyshev, Zhur.Obshch.Khim., 30, 1742 (1970).
152. H.Reuther, Chem.Techn.(Berlin), **2**, 331 (1950).
153. T.Tanaka, Bull.Chem.Soc.Japan, **32**, 1258 (1959).
154. T.Tanaka and T.Watase, J.Chem.Phys., 22, 1268 (1954).
155. S.N.Gadzhiev, Dokl.Akad.Nauk Azerb.SSR, **22**, 37 (1966).
156. S.N.Gadzhiev, Doctoral Thesis, Institute of Physics, Academy of Sciences of Azerbaijan SSR, Baku, 1972.
157. Yu.B.Nadzhafov and Yu.Kh.Shaulov, Zhur.Fiz. Khim., **38**, 2975 (1964)[Russ.J.Phys.Chem., No.12 (1964)].
158. V.G.Genchel', A.M.Mosin, and Yu.Kh.Shaulov, Zhur.Fiz.Khim., **43**, 967 (1969)[Russ.J.Phys.Chem., No.4 (1969)].
159. T.Filicroft and H.A.Skinner, J.Chem.Soc., 3355 (1956).
160. Yu.B.Nadzhafov, V.B.Losev, and Yu.Kh.Shaulov, Zhur.Fiz.Khim., **46**, 1835 (1972)[Russ.J.Phys. Chem., No.7 (1972)].
161. R.Thompson, J.Chem.Soc., 1908 (1953).

162. V.G.Genchel', N.V.Demidova, N.S.Nametkin, L.B.Gusel'nikov, E.A.Volnina, E.N.Burdasov, and V.N.Vdovin, Izv.Akad.Nauk SSSR, Ser.Khim., 10, 2337 (1976).
163. S.P.Gadzhiev, M.Ya.Agarunov, Yu.R.Nagdalieva, T.Kh.Azisov, V.N.Chebotarev, and F.A.Namazov, Izv.Akad.Nauk Azerb.SSR, 3, 57 (1966).
164. S.N.Hajiev and M.J.Agarunov, J.Organomet.Chem., 22, 305 (1970).
165. M.Ya.Agarunov and S.N.Gadzhiev, Dokl.Akad.Nauk SSSR, 185, 577 (1969).
166. S.N.Hajiev and M.J.Agarunov, J.Organomet.Chem., 11, 415 (1968).
167. M.A.Ring, H.R.O.Neal, A.H.Kadhim, and F.Jappe, J.Organomet.Chem., 5, 124 (1966).
168. A.E.Beezer and C.T.Mortimer, J.Chem.Soc.(A), 514 (1966).
169. S.N.Gadzhiev and M.Ya.Agarunov, Zhur.Fiz.Khim., 39, 239 (1965)[Russ.J.Phys.Chem., No.1 (1965)].
170. A.P.Claydon and C.T.Mortimer, J.Chem.Soc., 3212 (1962).
171. G.N.Kol'yakova, I.B.Rabinovich, and N.S.Vyazankin, Dokl.Akad.Nauk SSSR, 200, 111 (1971).
172. Yu.Kh.Shaulov, Yu.B.Nadzhafov, and K.I.Sevast'yanova, Zhur.Obshch.Khim., 36, 697 (1966).
173. Yu.B.Nadzhafov, V.B.Losev, and Yu.Kh.Shaulov, Zhur.Fiz.Khim., 39, 1220 (1965)[Russ.J.Phys.Chem., No.5 (1965)].
174. V.V.Lebedev, L.Ya.Tsvetkova, E.G.Kiparisova, V.N.Perchenko, G.A.Sytov, and I.B.Rabinovich, Vysokomol.Soed., 17A, 626 (1975).
175. S.O.Adeosun, Inorg.Nuclear Chem.Letters, 12, 301 (1976).
176. Yu.B.Nadzhafov and Yu.Kh.Shaulov, Plast.Massy, No.3, 16 (1965).
177. V.G.Genchel', N.V.Demidova, E.N.Buradsov, E.A.Volnina, and L.E.Guselnikov, "II Vsesoyuznaya Konferentsiya po Termodinamike Organicheskikh Soedinenii, Tezisy Dokladov" (The IInd All-Union Conference on the Thermodynamics of Organic Compounds. Abstracts of Reports), Gorky, 1976 p.7.
178. T.Tanaka, Bull.Chem.Soc.Japan, 33, 282 (1960).
179. T.Tanaka, Technol.Repts.Osaka Univ., 8, 437 (1958).
180. R.M.Aizatullova and V.G.Genchel', "VI Vsesoyuznaya Konferentsiya po Kalorimetrii, Tezisy Dokladov" (The VIth All-Union Conference on Calorimetry. Abstracts of Reports), Tbilisi, 1973, p.133.
181. S.N.Gadzhiev, G.G.Nurullaev, A.G.Kuznetsova, and K.A.Karasharli, "VI Vsesoyuznaya Konferentsiya po Kalorimetrii, Tezisy Dokladov" (The VIth All-Union Conference on Calorimetry. Abstracts of Reports), Tbilisi, 1973, p.155.
182. G.G.Nurullaev and S.N.Gadzhiev, Azerb.Khim. Zhur., No.2, 28 (1975).
183. Yu.Kh.Shaulov, A.K.Fedorov, and V.G.Genchel', Zhur.Fiz.Khim., 43, 1336 (1969)[Russ.J.Phys.Chem., No.5 (1969)].
184. I.B.Rabinovich, V.I.Tel'noi, N.V.Karyakin, and G.A.Razuvaev, Dokl.Akad.Nauk SSSR, 149, 324 (1963).
185. A.E.Pope and H.A.Skinner, Trans.Faraday Soc., 60, 1404 (1964).
186. J.L.Bills and F.A.Cotton, J.Phys.Chem., 68, 806 (1964).
187. Yu.Kh.Shaulov, E.M.Vygodskaya, and A.K.Fedorov, Zhur.Fiz.Khim., 44, 268 (1970)[Russ.J.Phys.Chem., No.1 (1970)].
188. B.V.Lebedev, V.I.Milov, L.Ya.Tsvetkova, N.K.Lebedev, E.G.Kiparisova, and A.A.Evstropov, Zhur.Fiz.Khim., 49, 1592 (1975)[Russ.J.Phys.Chem., No.6 (1975)].
189. Yu.Kh.Shaulov, A.K.Fedorov, and V.G.Genchel', Zhur.Fiz.Khim., 44, 262 (1970)[Russ.J.Phys.Chem., No.1 (1970)].
190. G.P.Adams, A.S.Carson, and P.G.Laye, Trans.Faraday Soc., 65, 113 (1969).
191. A.S.Kana'an, J.Chem.Thermodynamics, 6, 191 (1974).
192. A.S.Carson, E.M.Carson, P.G.Laye, J.A.Spencer, and W.V.Steele, Trans.Faraday Soc., 66, 2459 (1970).
193. W.V.Steele, Ann.Reports Progress Chem., 71, 103 (1974).
194. K.H.Birr and D.Kräft, Z.anorg.Chem., 311, 235 (1961).
195. B.V.Lebedev, V.I.Milov, E.G.Kiparisova, A.M.Sladkov, and L.K.Luneva, Zhur.Fiz.Khim., 49, 2716 (1975)[Russ.J.Phys.Chem., No.10 (1975)].
196. Yu.Kh.Shaulov, A.K.Fedorov, G.Ya.Zueva, G.V.Borisyuk, and V.G.Genchel', Zhur.Fiz.Khim., 44, 2081 (1970)[Russ.J.Phys.Chem., No.8 (1970)].
197. E.A.Volchkova, D.D.Smol'yaninova, V.G.Genchel', I.L.Lopatkina, and Yu.Kh.Shaulov, Zhur.Fiz.Khim., 46, 1837 (1972)[Russ.J.Phys.Chem., No.7 (1972)].
198. V.G.Genchel', A.I.Toporkova, Yu.Kh.Shaulov, and D.D.Smol'yaninova, Zhur.Fiz.Khim., 48, 1837 (1974)[Russ.J.Phys.Chem., No.7 (1974)].
199. W.F.Lautsch, A.Trober, W.Zimmer, L.Mehner, W.Linck, H.M.Lehmann, H.Brandenburger, H.Korner, H.J.Metzschker, K.Wagner, and R.Kaden, Z.Chem., 4, 441 (1964).
200. E.R.Lippincot and M.C.Tobin, J.Amer.Chem.Soc., 75, 4141 (1953).
201. C.R.Dillard, E.H.McNeil, D.E.Simmons, and J.B.Yeldell, J.Amer.Chem.Soc., 80, 3607 (1958).
202. A.A.Balandin, E.I.Klabunovskii, M.G.Kozina, and O.D.Ul'yanova, Izv.Akad.Nauk SSSR, Ser.Khim., 1, 12 (1958).
203. J.V.Davies, A.E.Pope, and H.A.Skinner, Trans. Faraday Soc., 59, 2233 (1963).
204. J.B.Pedley and H.A.Skinner, Trans.Faraday Soc., 55, 544 (1959).
205. D.J.Coleman and H.A.Skinner, Trans.Faraday Soc., 62, 1721 (1966).
206. J.B.Pedley, H.A.Skinner, and C.L.Chernick, Trans. Faraday Soc., 53, 1612 (1957).
207. I.B.Rabinovich, V.I.Tel'noi, P.N.Nikolaev, and G.A.Razuvaev, Dokl.Akad.Nauk SSSR, 138, 852 (1961).
208. W.F.Stack, G.A.Nash, and H.A.Skinner, Trans. Faraday Soc., 61, 2122 (1965).
209. A.E.Pope and H.A.Skinner, Trans.Faraday Soc., 60, 1402 (1964).
210. G.Adams, A.S.Carson, and P.G.Laye, J.Chem. Thermodyn., 1, 393 (1969).
211. A.S.Carson, P.G.Laye, J.A.Spencer, and W.V.Steele, J.Chem.Thermodyn., 2, 659 (1970).
212. A.S.Carson, J.Franklin, P.G.Laye, and H.Morris, J.Chem.Thermodyn., 7, 763 (1975).
213. G.A.Nash, H.A.Skinner, and W.F.Stack, Trans. Faraday Soc., 61, 640 (1965).
214. E.Z.Zhuravlev, V.D.Selivanov, V.F.Gerega, and Yu.I.Dergunov, Zhur.Obshch.Khim., 43, 1095 (1973).
215. A.S.Carson, P.G.Laye, J.A.Spencer, and W.V.Steele, J.Chem.Thermodyn., 4, 783 (1972).

216. A.S.Kanaan and T.I.Morrison, J.Chem.Thermodyn., 9, 423 (1977).
217. R.A.Butler, A.S.Carson, P.G.Laye, and W.V.Steele, J.Organometal Chem., 24, C11 (1970).
218. R.A.Butler, A.S.Carson, P.G.Laye, and W.V.Steele, J.Chem.Thermodyn., 8, 1153 (1976).
219. W.V.Steele, J.Chem.Thermodyn., 11, 187 (1979).
220. L.H.Long and J.F.Sackman, Trans.Faraday Soc., 53, 1606 (1957).
221. C.L.Chernick and H.A.Skinner, J.Chem.Soc., 1401 (1956).
222. A.V.Nikolaev, Yu.A.Afanas'ev, and A.D.Starostin, Izv.Sibir.Otd.Akad.Nauk SSSR, Ser.Khim.Nauk, Issue 6, No.14, 3 (1968).
223. K.H.Birr, Z.anorg.Chem., 306, 21 (1960).
224. A.F.Bedford and C.T.Mortimer, J.Chem.Soc., 1622 (1960).
225. C.L.Chernick, H.A.Skinner, and C.T.Mortimer, J.Chem.Soc., 3936 (1955).
226. E.Neale, L.T.D.Williams, and V.T.Moore, J.Chem. Soc., 422 (1956).
227. A.Finch, P.J.Gardner, K.S.Hussain, and R.A.Melaugh, J.Chem.Thermodyn., 7, 881 (1975).
228. E.Neale and L.T.D.Williams, J.Chem.Soc., 2485 (1955).
229. R.Thompson, J.Chem.Soc., 3292 (1952).
230. A.P.Claydon, P.A.Fowell, and C.T.Mortimer, J.Chem.Soc., 3284 (1960).
231. G.Geiseler, K.Quitzsch, and M.Kockert, Z.phys. Chem.(Leipzig), 218, 367 (1961).
232. A.D.Starostin, A.V.Nikolaev, and Yu.A.Afanas'ev, Izv.Akad.Nauk SSSR, Ser.Khim., 1303 (1966).
233. A.J.Head and D.Harrop, Quatrieme Conference Internationale de Thermodynamique Chimique, 1, 19 (1975).
234. A.V.Nikolaev, Yu.A.Afanas'ev, and A.D.Starostin, Dokl.Akad.Nauk SSSR, 168, 351 (1966).
235. P.A.Fowell and C.T.Mortimer, J.Chem.Soc., 2913 (1959).
236. J.R.Van Wazer and L.Maier, J.Amer.Chem.Soc., 86, 811 (1964).
237. C.N.Chernick, J.B.Pedley, and H.A.Skinner, J.Chem.Soc., 1851 (1957).
238. A.F.Bedford, D.M.Heinekey, I.T.Miller, and C.T.Mortimer, J.Chem.Soc., 2932 (1962).
239. A.F.Bedford and C.T.Mortimer, J.Chem.Soc., 4649 (1960).
240. H.Fleig and M.Berke-Goehring, Z.anorg.Chem., 376, 215 (1970).
241. F.A.Fowell and C.T.Mortimer, Chem.Ind.(London), 444 (1960).
242. L.H.Long and J.F.Sackman, Trans.Faraday Soc., 52, 1201 (1956).
243. K.H.Birr, Z.anorg.Chem., 311, 92 (1961).
244. C.T.Mortimer and P.W.Sellers, J.Chem.Soc., 1965 (1964).
245. T.Charnly, C.T.Mortimer, and H.A.Skinner, J.Chem. Soc., 1181 (1953).
246. L.H.Long and J.F.Sackman, Trans.Faraday Soc., 50, 1177 (1954).
247. L.H.Long and J.F.Sackman, Trans.Faraday Soc., 51, 1062 (1955).
248. V.G.Tsvetkov and B.I.Kozyrkin, Trudy po Khim. i Khim.Tekhnol.(Gor'kii), No.7, 73 (1978).
249. C.T.Mortimer and H.A.Skinner, J.Chem.Soc., 4331 (1952).
250. C.T.Mortimer and H.A.Skinner, J.Chem.Soc., 3189 (1953).
251. H.Merten and H.Schlütter, Ber.Deut.chem.Ges., 69B, 1364 (1936).
252. D.S.Barnes and C.T.Mortimer, J.Chem.Thermodyn., 5, 371 (1973).
253. I.B.Rabinovich, V.I.Tel'noi, and V.P.Nistratov, Trudy po Khim. i Khim.Tekhnol.(Gor'kii), No.2, 30 (1972).
254. V.I.Tel'noi and I.B.Rabinovich, Trudy po Khim. i Khim.Technol.(Gor'kii), No.2, 12 (1972).
255. V.I.Tel'noi and I.B.Rabinovich, Uspekhi Khim., 46, 1337 (1977)[Russ.Chem.Rev., No.8 (1977)].
256. L.O.Brockway and H.O.Jenkins, J.Amer.Chem.Soc., 58, 2032 (1936).
257. L.O.Brockway and N.R.Davidson, J.Amer.Chem. Soc., 63, 3287 (1941).
258. L.E.Sutton, "Table of Interatomic Distances and Configuration in Molecules and Ions", The Chemical Society, London, 1958.
259. L.Z.Jensovsky, Z.Chem., 3, 453 (1963).
260. D.I.Gardin, S.A.Keppie, M.F.Lappert, and M.R.Litzow, J.Chem.Soc.(A), 2262 (1971).

Institute of Chemistry at the
Lobachevskii Gorky State University

Translated from *Uspekhi Khimii*, 49, 1174-1187 (1980) U.D.C. 54.36:541.122:541.145.15

Methods of Calculating pK_{BH^+} for Weak Bases

Yu.L.Khaldna

Methods of calculating pK_{BH^+} for weak bases from spectrometric data are discussed, with special emphasis on methods based on the principle of free energy linearity. It is shown that the ionisation of a weak base in a strongly acid medium is described by two quantities: pK_{BH^+} and the solvation parameter. 77 references.

CONTENTS

I. Introduction 623
II. Present state of the acidity function method 623
III. The Yates-McClelland method 625
IV. The Bunnett-Olsen method 625
V. The MCP and Cox-Yates method 627
VI. Calculation of pK_{BH^+} without using the indicator ratio 628

I. INTRODUCTION

Over 2000 papers on the basicity of weak bases have been published in the last 20 years[1]. Various aspects of this problem are dealt with in special reviews and monographs[1-10]. The basis of any discussion of the basicity of weak bases is still the Brønsted–Lowry scheme[11,12]

$$BH^+ \rightleftharpoons B + H^+, \quad (1)$$

where B and BH^+ denote the weak base and its conjugate acid respectively. The equilibrium (1) is characterised by the basicity constant of the base[4,5]

$$K_{BH^+} = a_B a_{H^+}/a_{BH^+}. \quad (2)$$

Within the framework of this approach specific solvation phenomena involving both the B and the BH^+ form of the bases are not considered in detail. The influence of these factors on the position of the equilibrium (1) is allowed for by varying the appropriate activity coefficients (f_B and f_{BH^+}).

The basicity of weak bases is usually studied in strongly acid media, where the equilibrium (1) lies very far towards the left. The binary water–sulphuric acid and water–perchloric acid systems are most frequently used, and the indicator ratio[4,5] $I = [B]/[BH^+]$ of the base is determined as a function of the composition of the medium for different concentrations of H_2SO_4 or $HClO_4$.

Up to 1970 the I values were determined mostly by u.v. spectroscopy[4,5]:

$$I = [B]/[BH^+] = (\varepsilon - \varepsilon_{BH^+})/(\varepsilon_B - \varepsilon), \quad (3)$$

where ε_B, ε_{BH^+}, and ε are the molar absorption coefficients of the B form, the BH^+ form, and their mixture respectively. This method can be used to study the basicity of bases whose solubility is very low, because it can handle concentrations as low as 10^{-4}–10^{-5} mole litre^{-1}. However the u.v. spectra are often complicated by the so-called medium effects, resulting in lack of constancy of ε_B and ε_{BH^+} under conditions when the shift of the equilibrium (1) is extreme[13,14]. Various methods have been proposed to overcome this difficulty, but we shall not discuss them here because they are examined in detail in Bernshtein and Kaminskii's book[15].

Following recent developments and improvement in NMR spectroscopy this technique has been widely used since 1970 to determine the indicator ratio of weak bases in water–strong acid systems. Very dilute solutions of the weak bases can be used in the PMR method: in most cases the concentration of the weak base is varied between 0.005 and 0.15 mole litre^{-1}.[16-24] The main disadvantage of the PMR method is that the shift of the signal is very sensitive to specific solvation effects[23,25-28]. Therefore the ^{13}C NMR method is preferable, in principle, because its signal is generated from a nucleus close to the basicity centre[28]. However the signal from the ^{13}C nucleus is ~64 times weaker than the signal from ^1H (assuming equal numbers of carbon and hydrogen atoms in a constant magnetic field)[29], and therefore the ^{13}C NMR method requires a higher concentration of the base B in solution (usually 0.5–1.0 mole litre^{-1}).[29-31]

In both the PMR and the ^{13}C NMR method the indicator ratio is calculated by the equation[30]

$$I = [B]/[BH^+] = (\nu - \nu_{BH^+})/(\nu_B - \nu), \quad (4)$$

where ν_B, ν_{BH^+}, and ν are the characteristic frequencies for the B form, the BH^+ form, and their mixture respectively.

There is still some doubt about the degree of agreement of I values calculated by Eqn.(4) using NMR data for different nuclei (^1H, ^{13}C, and even ^{31}P). Thus some substantial discrepancies between I values obtained from NMR data for different nuclei have been pointed out[23,24].

In spite of these difficulties we shall assume throughout this review that the effect of the composition of the water–strong acid system on the indicator ratio of the weak base is known, either from u.v. spectroscopy or from NMR (^1H or ^{13}C) data.

II. PRESENT STATE OF THE ACIDITY FUNCTION METHOD

Once the I values have been determined from Eqns.(3) or (4) and from experimental data as a function of the concentration of H_2SO_4 or $HClO_4$ we have to choose a method of calculating the basicity constant of the weak base. The classical approach is to use the appropriate acidity function[4]

$$pK_{BH^+} = H_X - \lg I, \quad (5)$$

where H_X is the acidity function, which describes the extent of protonation of the base B. This method of calculating pK_{BH^+} was widely used up to the late 1960's, because it was thought that all electrically neutral bases which are protonated according to Eqn.(1) must follow the Hammett acidity function H_0.[5,32,33] However more than 10 mutually inconsistent acidity functions have now been reported[4,20,32-48]:

$$H_X = -\lg a_{H^+} - \lg \frac{f_X}{f_{XH^+}}, \quad (6)$$

where f_X and f_{XH^+} are the activity coefficients of the indicator X and of its ionised form XH^+. Since the acidity function ceased to be unique, the Hammett postulate[4,5]

$$f_X/f_{XH^+}=f_B/f_{BH^+} \quad (7)$$

became the exception rather than the rule[1,10]. If the condition (7) is not satisfied in the concentration range of the strong acid for which the I values have been calculated by Eqn.(3) it follows that the pK_{BH^+} value given by Eqn.(5) is not a thermodynamic quantity[4,18]. From the practical point of view we have to decide whether the published acidity function describes the protonation of the base under study with sufficient precision (see below)[25]. It is essential to bear in mind that pK_{BH^+} values calculated by using different acidity functions cannot be intercompared directly, in the sense that the most negative values of pK_{BH^+} will not necessarily correspond to the base which is protonated to 50% ("half-protonation") in the most concentrated acid solution.

In recent years pK_{BH^+} values have been calculated from Eqn.(5) only in some special cases, such as studies of the basicity of a series of structurally similar compounds protonated according to some acidity function H_X common to the whole series. Correct application of this method of calculating pK_{BH^+} implies a test of the precision with which the protonation of the base under study is described, in each case, by the given acidity function H_X. For this purpose, Eqn.(5) is conveniently re-written[32]

$$\lg I=aH_X-pK_{BH^+}, \quad (8)$$

where a is the slope of the plot of $\lg I$ against H_X [often referred to as $d(\lg I)/dH_X$].[4,7] Eqn.(8) is solved by least squares, minimising the deviations in $\lg I$.[49] If the protonation of the given base corresponds to the function H_X the regression coefficient of a will be close to unity (as confirmed by considering the width of the confidence interval of the a values)[49]. It is usually assumed that the base B is protonated according to H_X if $a=1\pm0.1$.[14,32]

In addition to the a coefficient, we can calculate pK_{BH^+} and its confidence interval by the least squares method. When applying Eqn.(8) we should remember that the $\lg I$ values are not uniformly precise; the most precise values are those close to zero[15,50,51]. Usually when the modulus of $\lg I$ is greater than unity the value is so inaccurate that its use in Eqn.(8) is not permissible[15]. To allow for the uneven accuracy of $\lg I$ values we can attach to them the weight $w=[s(\lg I)]^{-2}\cdot\text{const}$, where the standard deviation of the determination of $\lg I$ is calculated by the equation[15,32,50-52]

$$s(\lg I)=\pm0.434\,\frac{I+1}{I\Delta R}\sqrt{s_{BH^+}^2+(I+1)^2s^2+I^2s_B^2}, \quad (9)$$

in which $\Delta R=\varepsilon_B-\varepsilon_{BH^+}$ [or $\Delta R=\nu_B-\nu_{BH^+}$, see Eqns.(3) and (4)]; s_{BH^+}, s, and s_B are the standard deviations of the determination of ε_{BH^+} (or ν_{BH^+}), ε (or ν), and ε_B (or ν_B) respectively. If $s_{BH^+}=s=s_B$ we can write[15,32]

$$w=1200\,I^2/(1+I)^2(1+I+I^2). \quad (10)$$

The factor 1200 is introduced into Eqn.(10) in order to make $w=100$ for $I=1$.[15]

The view that each weak base is protonated according to its own acidity function is now widely held[1,7,10,30,39]. Hence the condition $d(\lg I)/dH_X=1$ will apply to a series of bases only if the individual acidity functions (H_B) vary linearly with H_X, with a unit slope. We note from Eqn.(6) that all the acidity functions contain the term $\lg a_{H^+}$, which is a parameter of the medium and is independent of the nature of the weak base X. The dependence of $\lg a_{H^+}$ on the composition of the water–sulphuric acid or water–perchloric acid system is fairly accurately known, though the results of different workers for concentrated solutions show some discrepancies (see Table 1).

Table 1. Values of $\lg a_{H^+}$ for aqueous solutions of sulphuric and perochloric acid at 25 °C.

Acid concn., wt.%	H_2SO_4 solution		$HClO_4$ solution	
	Ref.53	Ref.54	Ref.53	Ref.54
5	0.01	−0.12	−0.02	−0.04
10	0.63	0.49	0.56	0.78
20	1.77	1.58	1.91	2.05
30	2.90	2.70	3.26	3.36
40	4.31	4.10	4.97	4.98
50	6.00	5.72	7.22	7.11
60	7.97	7.44	—	9.41
70	—	9.48	—	—

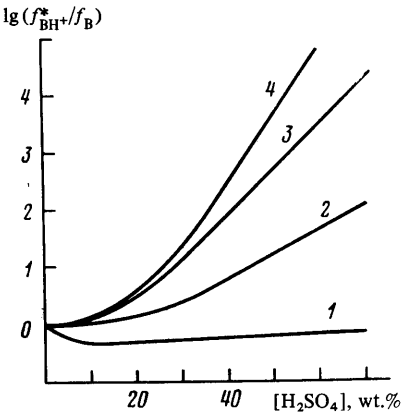


Figure 1. Plots of $\lg(f^*_{BH^+}/f_B)$ against concentration of sulphuric acid in the H_2O–H_2SO_4 system: *1*) for olefins, *2*) for *N*,*N*′-dimethyl substituted aromatic amines (H_0''' indicators[39]), *3*) for substituted aromatic amines (H_0' indicators[32]), *4*) for substituted benzamides (H_A indicators[34]).

It follows from the above that the non-coincidence of different acidity functions is probably due to differences in the dependence of $\lg f_X/f_{XH^+}=\phi$ on the acid concentration for different types of base. The activity coefficient of the non-ionised form f_X can be determined relatively easily either from solubility data or from the distribution coefficient[5,7,10]. It is found that for bases of different structure the variation of f_X with concentration of H_2SO_4 (or $HClO_4$) can be very different: this problem is considered in detail in a special review article[10]. The activity coefficient of the ionised form (f_{XH^+}) is not measurable, and therefore (as suggested by Boyd[6,55]) f_{XH^+} is replaced by the ratio

$$f^*_{XH^+}=f_{XH^+}/f_{Et_4N^+} \quad (11)$$

whose variation with the concentration of H_2SO_4 (or $HClO_4$) can be measured.

The method of determining $f^*_{XH^+}$ is discussed in Refs.6, 55, and 56. It is assumed that the screening of the positive charge on the nitrogen atom by the ethyl groups ensures that the Et_4N^+ ion cannot undergo specific solvation[6,26,57]. Since this type of solvation is the main reason for the deviation of the activity coefficients from unity we can write $f_{Et_4N^+}=1$ for all solutions (from those in pure water to those in concentrated solutions of acids)[6,26,53]. However the ratio $f_X/f^*_{XH^+}$ is found to depend both on the concentration of the strong acid and on the nature of the base X (see Fig.1). We shall not dwell on the reasons for the deviation of f_X and $f^*_{XH^+}$ from unity because they are discussed at length in review articles[1,7,10].

The difference between two arbitrarily chosen acidity functions (H_X and H_Y) at a given concentration of the strong acid is determined by the expression

$$H_X - H_Y = \lg \frac{f_Y f_{XH^+}}{f_{YH^+} f_X}, \qquad (12)$$

from which we can judge the correctness of independently obtained[7,10] values of $f_X/f^*_{XH^+}$ and $f_Y/f^*_{YH^+}$. This type of test has shown that the difference between acidity functions can be calculated from the values of $f_X/f^*_{XH^+}$ and $f_Y/f^*_{YH^+}$.[20,58] Therefore there is no longer any doubt that in general, for any acidity function H_X, the ratio $f_X/f_{XH^+} \neq 1$.[1,10] This is what makes compliance with the Hammett postulate (7) a rare event, and detracts from the value of the classical method of calculating pK_{BH^+}.[58-62]

III. THE YATES–McCLELLAND METHOD

This method was developed[63] because an acidity function H_X for which $d(\lg I)/dH_X = 1.00$ could not be found for many weak bases. According to Yates and McClelland, to a first approximation a simple proportionality always exists between the quantities H_X and H_0:[63]

$$H_X = mH_0. \qquad (13)$$

Inserting (13) into (5) we obtain the Yates equation for calculating pK_{BH^+}:[63]

$$\lg I = mH_0 - pK_{BH^+}. \qquad (14)$$

This equation can be solved by least squares with allowance for the unequal precision of the $\lg I$ values [see Eqns.(9) and (10)].

The pK_{BH^+} value calculated by Eqn.(14) expresses the basicity of the substance B in its own individual acidity scale $H_B = -\lg a_{H^+} f_B/f_{BH^+}$: in other words this value of pK_{BH^+} gives us the H_B value for a solution in which $\lg I = 0$.[14] Often instead of pK_{BH^+} one calculates the H_0 value for a solution in which $\lg I = 0$, i.e. the quantity $H_0^{(1/2)}$. Inserting $\lg I = 0$ into Eqn.(14) we obtain

$$H_0^{(1/2)} = \frac{1}{m} pK_{BH^+}. \qquad (15)$$

The H_0 value at half-protonation of the unknown base ($H_0^{1/2}$) is often identified[32,33] with the pK_{BH^+} value of the base in the H_0 acidity scale[9,17,19,64,65].

The Yates–McClelland method relies on the assumption of a direct proportionality between H_X and H_0 [Eqn.(13)]. This linear variation is obeyed only approximately in practice, with a break near $H_0 = 0$, since in this pH region $m = 1$ for all values of H_X (see Fig.2). As a result, the pK_{BH^+} values calculated by Eqn.(14) lose some of their physical significance, and they cease to be thermodynamic quantities referred to a standard state in water. In the most favourable case these pK_{BH^+} values can be treated as referred to a standard state in an acid solution for which $H_0 = 0$ (i.e. 4.8 wt.% H_2SO_4 or 4.0 wt.% $HClO_4$).

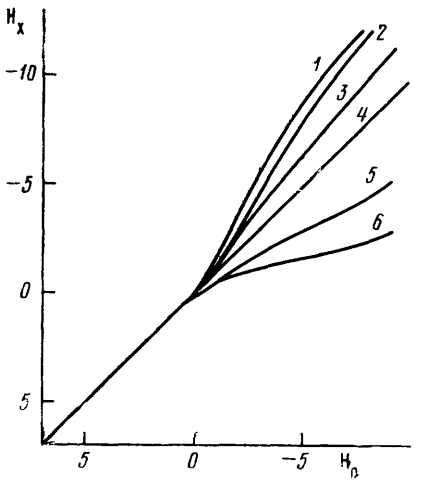


Figure 2. Plots of different acidity functions (H_X) against H_0 [32] in aqueous solutions of sulphuric acid at 25 °C: *1*) $H_{R'}$,[43] *2*) H_C,[35] *3*) H_0''',[39] *4*) H_0,[32] *5*) H_A,[34] *6*) H_{ROH}.[40]

IV. THE BUNNETT–OLSEN METHOD

The Bunnett–Olsen method[66] of calculating pK_{BH^+} is based on the linear expression

$$\lg Q_1 = a \lg Q_2 + b, \qquad (16)$$

where $Q_1 = [B_1][H^+]/[B_1H^+]$; $Q_2 = [B_2][H^+]/[B_2H^+]$; B_1 and B_2 are arbitrarily chosen weak bases; the concentration $[H^+]$ is taken to be numerically equal to the molar concentration of H_2SO_4 or $HClO_4$.[66] The validity of the linear relationship (16) has been tested[58,66,67] for several bases B_1 and B_2: the equation was found to be generally applicable, deviations from it being smaller than experimental error[67].

In order to obtain an equation for calculating pK_{BH^+}, Bunnett and Olsen[66] standardised their reference scale, i.e. the choice of the base B_2. They defined their standard base as a hypothetical primary aromatic amine with $pK_{BH^+} = 0$, for which $\lg [B_2]/[B_2H^+] = H_0$, and

$$\lg Q_2 = H_0 + \lg [H^+]. \qquad (17)$$

We should stress that the choice of the acidity function H_0 as the reference scale has no fundamental significance: in principle H_0 in Eqn.(17) can be replaced by any similar acidity function. The function H_0 is chosen simply because it has been carefully measured and is widely known.

After combining (17) and (16) and simplifying we obtain the expression

$$H_0 - \lg I_1 = \Phi(H_0 + \lg [H^+]) - b, \qquad (18)$$

where $I = [B_1]/[B_1H^+]$ and $\Phi = 1 - a$. If the condition $\Phi = \text{const}$ is obeyed at all concentrations, from the standard state in water (for which $H_0 - \lg [H^+] = 0$) to the acid solutions used for measuring I_1, we can easily see that $-b = pK_{B_1H^+}$ (since

in the standard state $H_0 - \lg I_1 = pK_{BH^+}$). Inserting $-b = pK_{B_1H^+}$ into Eqn.(18) we arrive at the Bunnett–Olsen equation for $pK_{B_1H^+}$:[66]

$$H_0 - \lg I_1 = \Phi(H_0 + \lg [H^+]) + pK_{B_1H^+} . \quad (19)$$

When applying Eqn.(19) we must make allowance for the uneven precision of the $\lg I_1$ values [see (9) and (10)], and treat the H_0 and $[H^+]$ values as exactly known.

By comparing formulae (5) and (19) we can easily show that[1,68]

$$H_X + \lg [H^+] = (1-\Phi)(H_0 + \lg [H^+]). \quad (20)$$

This relationship between the acidity functions H_X and H_0 is free from the shortcomings found in the simpler Yates–McClelland formula (13). It does not show the characteristic break near $H_0 = 0$ given by Eqn.(13) (see Figs.2 and 3), since both $H_X + \lg [H^+]$ and $H_0 + \lg [H^+]$ tend towards zero as we approach the standard state in water. According to the expression (20), plotted in Fig.3, we can judge the constancy of the parameter Φ in all cases from water to concentrated solutions of strong acids. We see from Fig.3 that Φ = const in moderately concentrated solutions of acids. At high concentrations of H_2SO_4 the quantity Φ is often not constant. This effect introduces some uncertainty into the pK_{BH^+} values obtained by Eqn.(19) through a long extrapolation (from concentrated solutions of acids).

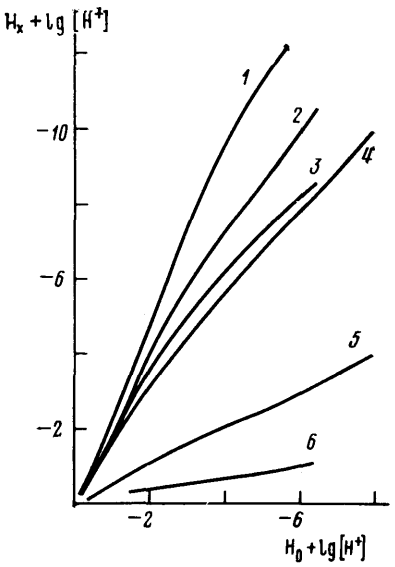


Figure 3. Relationship between the acidity functions according to Bunnett and Olsen[66,68] [see Eqn.(20), aqueous solutions of sulphuric acid at 25 °C]: *1)* $H_X = H_R$,[43] *2)* $H_X = -\lg a_{H^+}$,[54] *3)* $H_X = H_M$,[42] *4)* $H_X = H_0$,[32] *5)* $H_X = H_A$,[34] *6)* $H_X = H_{ROH}$.[40]

The possible error range of the pK_{BH^+} values obtained from Eqn.(19) was evaluated[69,70] by noting that in principle the function H_0 in that equation can be replaced by any analogous acidity scale. The criterion for the validity of such a scale is the linearity of expressions of the type of (20). If the standard base B_2 in Eqn.(16) is taken to be a hypothetical base with $pK_{BH^+} = 0$ which is protonated without specific solvation effects, i.e. according to the $\lg a_{H^+}$ acidity scale, Eqns.(19) and (20) become, respectively,

$$-\lg a_{H^+} - \lg I_1 = \Phi(-\lg a_{H^+} + \lg[H^+]) + pK_{B_1H^+}, \quad (21)$$

$$H_X + \lg[H^+] = (1-\Phi)(-\lg a_{H^+} + \lg[H^+]). \quad (22)$$

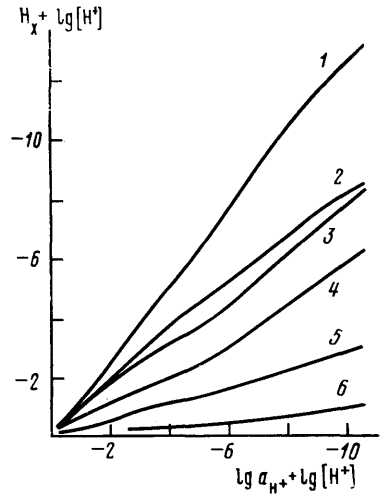


Figure 4. Variation of $H_X + \lg [H^+]$ with $(-\lg a_{H^+} + \lg M)$ for different acidity functions H_X in aqueous solutions of sulphuric acid at 25 °C: *1)* $H_X = H_R$,[43] *2)* $H_X = H_M$,[42] *3)* $H_X = H_0''$,[39] *4)* $H_X = H_0$,[32] *5)* $H_X = H_A$,[34] *6)* $H_X = H_{ROH}$.[40]

We note from Fig.4 that the proportionality (i.e. the condition Φ = const) is more accurately obeyed by Eqn.(22) than by the analogous expression in terms of H_0 [Eqn.(20), see Fig.3].[70] Therefore the $pK_{B_1H^+}$ values calculated by (21) are more nearly equal to the corresponding thermodynamic quantities than those calculated by (19). For $pK_{BH^+} > -3$ the difference between the pK_{BH^+} values given by formulae (19) and (21) is insignificant[69]. However for very weak bases with $pK_{BH^+} < -3$ the discrepancy between the pK_{BH^+} values given by (19) and (21) can be as high as three units of pK_{BH^+}.[69] These discrepancies arise primarily from the loss of linearlity of Eqn.(20) at high concentrations of the strong acid[70].

Because of the wide use made of the Bunnett–Olsen method it is becoming generally assumed that in order to characterise the basicity of a weak base quantitatively we need to know the solvation parameter Φ as well as pK_{BH^+}. This interpretation of the parameter Φ was originally proposed by Hammett[68], and further developed by Modena and Scorrano[1]. The solvation parameter Φ is independent of pK_{BH^+} for a weak base, but is determined by the nature of the base. It is normalised to give $\Phi = 1$ for water[1,20] and $\Phi = 0$ for primary amines[1,66]. Different types of weak bases are assigned the following values of Φ:[1] aryl carbinols from −1.02 to −1.59, azulenes −0.70, tertiary aromatic amines from −0.33 to −0.48, amides from +0.42 to +0.55, alcohols +0.85, etc. The relationship between the value of Φ and the solvation effects during the protonation of weak bases is discussed in Ref.1.

In order to compare Φ with m we note, from Eqn.(14), that at high acid concentrations the quantity $\lg [H^+]$ is small in comparison to the absolute value of H_0. Hence under these conditions Eqn.(19) is equivalent to Eqn.(14) with $m = 1 - \Phi$, which can be confirmed by directly comparing the values of m and $1 - \Phi$.[1]

Both the classical Bunnett–Olsen equation (20) and its modification [Eqn.(22)] are linear free energy functions. Thus from Eqns.(20) and (22) respectively we can obtain[66,69]

$$\lg \frac{f_{H^+} f_X}{f_{XH^+}} = (1 - \Phi) \lg \frac{f_{H^+} f_B}{f_{BH^+}}, \quad (23)$$

$$\lg \frac{f_{XH^+}}{f_X} = \Phi \lg f_{H^+}. \quad (24)$$

These expressions indicate linear relationships between the changes in free energy of the corresponding particles.

V. THE MCP AND COX–YATES METHODS

Bunnett and Olsen's expression (23) was critically examined by an Italian group of workers (Marziano, Cimino, and Passerini, abbreviated to MCP), who concluded[71] that the Hammett acidity function H_0 should not be used to construct a comparative scale of $\lg (f_{H^+} f_B / f_{BH^+})$ [in Eqn.(20)]. Instead, they suggested a description of weak bases involving partially overlapping ionisation regions[71]:

$$\lg \frac{[X]}{[XH^+]} + \lg [H^+] = n_X \left(\lg \frac{[B]}{[BH^+]} + \lg [H^+] + pK_{BH^+} \right) - pK_{XH^+}, \quad (25)$$

where $[H^+]$ is the molar concentration of strong acid, and X is a slightly weaker base than B. The linear relationship (25) allows us to determine pK_{XH^+} for the next indicator X of a given series, and the corresponding slope of the plot of Eqn.(25):

$$n_X = \lg \frac{f_{H^+} f_X}{f_{XH^+}} \Big/ \lg \frac{f_{H^+} f_B}{f_{BH^+}}. \quad (26)$$

Applying Eqn.(25) to the next indicator Y of the series (with $pK_{YH^+} < pK_{XH^+}$) we can evaluate n_Y:

$$n_Y = \lg \frac{f_{H^+} f_Y}{f_{YH^+}} \Big/ \lg \frac{f_{H^+} f_X}{f_{XH^+}}. \quad (27)$$

By stepwise repetition of this procedure we can determine all the slopes n_X, n_Y, ..., n_Z up to that of the weaker base Z. Assuming that n_X, n_Y, ..., n_Z are constant, i.e. that differentials of the type of $d(\lg f_{H^+} f_Y / f_{YH^+}) / d(\lg f_{H^+} f_X / f_{XH^+})$ are independent of the I value [defined by Eqn.(3)] of the base, we can easily relate the first term B of a given series to the subsequent terms X, Y, ..., Z:

$$\lg \frac{f_{H^+} f_B}{f_{BH^+}} = \frac{1}{n_X} \lg \frac{f_{H^+} f_X}{f_{XH^+}} = \frac{1}{n_X n_Y} \lg \frac{f_{H^+} f_Y}{f_{YH^+}} = \ldots = \frac{1}{n_X n_Y \ldots n_Z} \lg \frac{f_{H^+} f_Z}{f_{ZH^+}} = -M_c. \quad (28)$$

Eqn.(28) was used to calculate the "function of the activity coefficients" M_c [71] in terms of n_X, n_Y, ..., n_Z and of the quantity

$$\lg \frac{f_{H^+} f_Z}{f_{ZH^+}} = -pK_{ZH^+} - \lg \frac{[Z][H^+]}{[ZH^+]}. \quad (29)$$

If the function M_c is known the pK_{BH^+} value of an arbitrarily chosen weak base B can be obtained from the linear expression[71]

$$\lg I + \lg [H^+] = n_B M_c - pK_{BH^+} \quad (30)$$

using the method of least squares and allowing for the unequal precision of the I values given by Eqn.(3) [see Eqn.(10)].

Unfortunately the M_c scales calculated from different series of weak bases do not coincide† when the solution contains more than 40 wt.% of H_2SO_4.[71] The authors recommend the use of the M_c scale calculated from the ionisation of Hammett indicators (whose protonation proceeds in the same sense as the acidity function H_0).[71] Therefore the MCP group developed a new method of calculating the M_c scale from all possible values of I for the whole of the ionisation region (usually $0.1 \leq I \leq 1$). However their following paper[72] gives only the new M_c values for aqueous solutions of sulphuric acid (see Table 2) without describing the method of calculating M_c.

Table 2. Values of M_c, X, and $\lg c_{H^+}$ for aqueous solutions of sulphuric and perchloric acid.

Acid concn., wt.%	H_2SO_4 solution			$HClO_4$ solution	
	$-10 \cdot M_c$ (Ref.72)	X (Ref.73)	$\lg c_{H^+}$ (Ref.73)	X (Ref.73	$\lg c_{H^+}$ (Ref.69)
5	0.172	0.103	−0.205	0.091	−0.293
10	0.354	0.231	0.117	0.212	0.018
15	0.555	0.387	0.315	0.371	0.209
20	0.785	0.573	0.461	0.571	0.349
25	1.053	0.790	0.577	0.819	0.459
30	1.358	1.038	0.674	1.116	0.552
35	1.706	1.317	0.757	1.468	0.633
40	2.096	1.628	0.828	1.879	0.705
45	2.526	1.969	0.891	2.354	0.773
50	2.999	2.345	0.945	2.908	0.833
55	3.514	2.763	0.992	3.561	0.891
60	4.075	3.238	1.033	4.337	0.941
65	4.682	3.795	1.069	5.241	0.977
70	5.338	4.459	1.097	6.220	1.022
74	5.896	5.080	1.118	6.983	1.057
80	6.786	6.150	1.143	—	—
84	7.427	6.906	1.133	—	—
90	8.547	7.985	0.996	—	—
95	9.808	8.989	0.654	—	—
99	—	10.754	−0.153	—	—

At approximately the same time (1976–1977) and independently of the MCP group Cox and Yates[73] also worked on this problem. Accepting the universality of Eqn.(23), they wrote it in the form of

$$\lg \frac{f_{H^+} f_B}{f_{BH^+}} = m^* \lg \frac{f_{H^+} f_{B^*}}{f_{B^*H^+}} = m^* X, \quad (31)$$

where B* is a hypothetical standard base. The quantity X is identical to $-M_c$, but Cox and Yates prefer to call it the "excess acidity"[73]. They calculate the pK_{BH^+} value of the weak base B by the equation[73]

$$-\lg I - \lg c_{H^+} = m^* X + pK_{BH^+}, \quad (32)$$

where c_{H^+} is the concentration of hydrated protons in solution (see Table 2). This equation can be solved by least squares allowing for the uneven precision of the I values [see Eqn.(10)].

† The discrepancies between the M_c scales arise from the use of I values [obtained by Eqn.(3)] in the overlap regions of successive indicators where the modulus of $\lg I$ is greater than (0.7–1.1) and the uncertainty in its determination is relatively high [see Eqn.(10)].

Unlike the MCP group[72], Cox and Yates describe in great detail the mathematical procedures adopted in the calculation of X.[73] Without reproducing their algorithm, we shall only point out that the X values are obtained by an iterative method, using the equation

$$X = \frac{1}{m^*}(-\lg I - \lg c_{H^+} - pK_{BH^+}), \qquad (33)$$

in which arbitrary values of pK_{BH^+} and m^* are inserted at first. The first, approximate estimate of the scale is then used to obtain more precise values of pK_{BH^+} and m^* by Eqn. (32), and so on. The procedure is repeated until the values of X become invariant[73]. These workers used I values obtained by Eqn.(3) over the whole ionisation region for 165 bases in solutions containing 0–99.5 wt.% H_2SO_4, and for 76 bases in solutions containing 0–78 wt.% of $HClO_4$.

The X scales for aqueous solutions of sulphuric acid and perchloric acid are given in Table 2. We can see that in general the X values are close to the $-M_c$ values multiplied by 10 (the introduction of this scaling factor affects only the solvation parameter). In spite of this similarity the pK_{BH^+} values calculated by using X and M_c respectively differ by more than 0.3 units of pK_{BH^+}.[73] Of course, this conclusion applies to the pK_{BH^+} values obtained with the original M_c scale[71], to which the authors themselves no longer subscribe, but as yet no pK_{BH^+} values appear to have been obtained from the new M_c scale[72]. Its authors[72] are themselves unwilling to apply the new scale until the method of calculating pK_{BH^+} has been improved so that the quoted uncertainty limits can reflect the uncertainty limits of the M_c scale [see Eqn.(30)].

Extensive comparisons of pK_{BH^+} values obtained by using the X scale [Eqn.(32)], the Bunnett–Olsen method [Eqn.(19)], and the acidity function [Eqn.(5)] are given in the Tables of Ref.73. In most cases the pK_{BH^+} values are not very different (within ±0.2 pK_{BH^+} unit), but differences in excess of 1 pK_{BH^+} unit are occasionally found. We note that Eqns.(5) and (32) will give identical pK_{BH^+} values only if all the indicators used to construct the acidity function H_X have the same m^* value [to within ±0.1,[74] see Eqn.(32)].

VI. CALCULATION OF pK_{BH^+} WITHOUT USING THE INDICATOR RATIO

All the methods of calculating pK_{BH^+} discussed so far use the indicator ratio I, calculated by Eqn.(3) or (4). Recent developments in the application of computers make it possible to calculate pK_{BH^+} (and the solvation parameter) directly from experimental results, i.e. from the ε or ν values, without going through the stage of determining I by Eqns.(3) or (4).[20,75] This approach involves the following steps. From Eqn.(3) we readily obtain

$$\varepsilon = \frac{I\varepsilon_B + \varepsilon_{BH^+}}{1 + I} \qquad (34)$$

and a similar expression is obtained from Eqn.(4). Then, using any of the above methods of calculating pK_{BH^+} [i.e. using Eqn.(8), (14), (19), (21), (30), or (32)], we find the variation of $\lg I$ with pK_{BH^+} for the medium parameter P and the solvation parameter S (relating H_0, H_X, c_{H^+}, X, and M_c to the medium parameters P; and m, Φ, n, and m^* to the solvation parameters S):

$$\lg I = F(pK_{BH^+}, P, S),$$

whence

$$I = 10^{F(pK_{BH^+}, P, S)}. \qquad (35)$$

Inserting (35) into (34) we obtain a system of k transcendental equations ($k \geq 3$) with two unknowns (pK_{BH^+} and S). The problem now reduces to finding values of pK_{BH^+} and S which minimise a function of the difference between calculation and experiment such as

$$\Psi = \sum_{i=1}^{i=k} (\varepsilon_{i,\text{calc}} - \varepsilon_{i,\text{exper}})^2 . \qquad (36)$$

Because of the non-linearity of the system of equations the minimum of the function Ψ cannot be found by the standard methods of regression analysis. The problem must therefore be solved by one of the iteration methods commonly used[76] to solve systems of equations. These include Newton's method and its modifications[76], the method of steepest descent[76], and the coefficient variation method[77]. The best choice of method for solving the system of transcendental equations depends on the type of computer to be used and on the availability of appropriate subprograms.

We note that in principle this method of treating experimental data allows us to determine not only pK_{BH^+} and S, but also one of the parameters of the limiting forms[20] (ε_B or ε_{BH^+}) which appear in Eqn.(34). In this case we evaluate three rather than two unknowns from the system of transcendental equations ($k \geq 4$). However there is a risk of being caught up in the "numbers game": the risk is greatest when the plot of ε against composition of the medium lacks a clear plateau near the limiting form ε_B or ε_{BH^+}.

Thus in recent years the methods of calculating pK_{BH^+} for weak bases have undergone some radical changes. The acidity function method [Eqn.(5)] and the Yates–McClelland method [Eqn.(14)] are no longer at the forefront. The former was abandoned when the limitations of the Hammett postulate (7) (leading to a multiplicity of acidity functions) were realised. The Yates–McClelland method proved too empirical and approximate, as well as relying on the basic acidity function devoid of physical significance (H_0).

These older methods are now being replaced by new methods based on the principle of free energy linearity (FEL) [see Eqn.(23)]. Of these, the Bunnett–Olsen method has proved most popular so far [Eqn.(20)], but since it relies on the acidity function H_0 based on the Hammett postulate (7) its use cannot be recommended. Some of the even newer methods are free from this shortcoming: these include the essentially identical MCP method (based on the M_c function) and Cox–Yates method (based on the X function). The advantages of these methods include: firstly, that the calculation of pK_{BH^+} by using the function X (or M_c) relies on a very simple and clear theoretical foundation (the assumption that the FEL principle (23) applies), and secondly that these methods do not require the use of a multitude of acidity functions. Each strong-acid system is characterised by a single function of the X (or M_c) type, and each weak base has two parameters (pK_{BH^+} and m^*) which describe its ionisation. The parameter m^* can be treated as a measure of the solvation interactions with the medium (thus we note that $m^* \cong 1 - \Phi$ [73]).

However, while stressing these favourable aspects of the new methods, we must repeat that a discrepancy still exists between the X and M_c scales, which points to a need for greater efforts on developing and unifying scales of the type of X.

REFERENCES

1. E.M.Arnett and G.Scorrano, Adv.Phys.Org.Chem., **13**, 84 (1976).
2. E.M.Arnett, "Progress in Physical Organic Chemistry", Vol.1, Wiley, New York–London–Sydney, 1963, p.223.

3. N.C.Deno, "Survey of Progress in Chemistry", Vol.2, Academic Press, New York, 1964, p.155.
4. C.H.Rochester, "Acidity Functions", Academic Press, London–New York, 1970,
5. M.I.Vinnik, Uspekhi Khim., **35**, 1922 (1966) [Russ. Chem.Rev., No.11 (1966)].
6. R.H.Boyd, "Solute–Solvent Interactions", Marcel Dekker, New York, 1969, p.97.
7. Yu.L.Khaldna, Reakts.Sposobn.Org.Soed., **5**, 489 (1968).
8. G.A.Olah and A.M.White, Chem.Rev., **70**, 561 (1970).
9. M.Liler, "Reaction Mechanisms in Sulphuric Acid", Academic Press, New York, 1971.
10. K.Yates and R.A.McClelland, "Progress in Physical Organic Chemistry", Vol.11, Wiley, New York–London–Sydney, 1974, p.323.
11. J.N.Brønsted, Rec.Trav.chim., **42**, 718 (1923).
12. T.M.Lowry, Chem.Ind., **42**, 43 (1923).
13. C.C.Greig and C.D.Johnson, J.Amer.Chem.Soc., **90**, 6453 (1968).
14. G.F.Tereshchenko, T.I.Smirnova, G.I.Koldobskii, V.A.Ostrovskii, A.S.Enin, and L.I.Bagal, Zhur.Org. Khim., **8**, 236 (1972).
15. I.Ya.Bernshtein and Yu.L.Kaminskii, "Spektrometricheskii Analiz v Organicheskoi Khimii" (Spectrometric Analysis in Organic Chemistry), Izd.Khimiya, Leningrad, 1975, p.155.
16. G.C.Levy, J.D.Cargioli, and W.Racela, J.Amer.Chem. Soc., **92**, 6238 (1970).
17. M.Liler, J.Chem.Soc.B, 334 (1971).
18. A.Levi, G.Modena, and G.Scorrano, J.Amer.Chem.Soc., **96**, 6585 (1974).
19. P.Haake, R.D.Cook, and G.H.Hurst, J.Amer.Chem. Soc., **89**, 2650 (1967).
20. P.Bonvicini, A.Levi, V.Lucchini, G.Modena, and G.Scorrano, J.Amer.Chem.Soc., **95**, 5960 (1973).
21. D.W.Earls, J.Chem.Soc., Perkin Trans.II, 1641 (1976).
22. W.J.Spillane and J.B.Thompson, J.Chem.Soc., Perkin Trans.II, 580 (1977).
23. N.K.Skvortsov, G.F.Tereshchenko, B.I.Ionin, and A.A.Petrov, Zhur.Obshch.Khim., **46**, 521 (1976).
24. N.K.Skvortsov, G.F.Tereshchenko, B.I.Ionin, and A.A.Petrov, Zhur.Obshch.Khim., **43**, 981 (1973).
25. G.Scorrano, Acc.Chem.Res., **6**, 132 (1973).
26. T.A.Modro, W.F.Reynolds, and K.Yates, Canad.J. Chem., **54**, 1439 (1976).
27. A.Koeberg-Telder and H.Cerfontain, J.Chem.Soc., Perkin Trans.II, 226 (1975).
28. H.Cerfontain, A.Koeberg-Telder, and C.Kruk, Tetrahedron Letters, **42**, 3639 (1975).
29. G.C.Levy and G.L.Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists" (Translated into Russian), Izd.Mir, Moscow, 1975, p.17.
30. R.A.McClelland and W.F.Reynolds, Canad.J.Chem., **54**, 718 (1976).
31. Yu.R.Siigur, M.Myagi, Yu.L.Khaldna, and E.T.Lippmaa, Reakts.Sposobn.Org.Soed., **8**, 267 (1971).
32. C.D.Johnson, A.R.Katritzky, and S.A.Shapiro, J. Amer.Chem.Soc., **91**, 6654 (1969).
33. S.A.Attiga and C.H.Rochester, J.Chem.Soc., Perkin Trans.II, 1624 (1974).
34. J.T.Edward and S.C.Wong, Canad.J.Chem., **55**, 2492 (1977).
35. M.Reagan, J.Amer.Chem.Soc., **91**, 5506 (1969).
36. R.L.Hinman and J.Long, J.Amer.Chem.Soc., **86**, 3796 (1964).
37. T.G.Bonner and J.Phillips, J.Chem.Soc.B, 650 (1966).
38. C.Tissier and M.Tissier, Bull.Soc.chim.France, 2109 (1972).
39. E.M.Arnett and G.W.Mach, J.Amer.Chem.Soc., **86**, 2671 (1964).
40. D.J.Lee and R.Cameron, J.Amer.Chem.Soc., **93**, 4724 (1971).
41. K.Yates and R.A.McClelland, J.Amer.Chem.Soc., **95**, 3055 (1973).
42. T.K.Rodima and Yu.L.Khaldna, Reakts.Sposobn.Org. Soed., 7, 391 (1970).
43. M.J.Cook, N.L.Dassanayke, C.D.Johanson, A.R.Katritzky, and T.W.Toone, J.Amer.Chem.Soc., **97**, 760 (1975).
44. P.Bonvicini, A.Levi, V.Lucchini, and G.Scorrano, J.Chem.Soc., Perkin Trans.II, 2267 (1972).
45. J.Janata and G.Jansen, J.Chem.Soc., Faraday Trans., 1656 (1972).
46. J.Mindl and M.Vecera, Coll.Czech.Chem.Comm., **36**, 3621 (1971).
47. J.T.Edward, I.Lantos, G.D.Derdall, and S.C.Wong, Canad.J.Chem., **55**, 812 (1977).
48. S.R.Lockerente, P.van Brandt, and A.Bruylants, Bull.Sci.Acad.roy.Belge, **58**, 23 (1972).
49. V.P.Spiridonov and A.A.Opatkin, "Matematicheskaya Obrabotka Fiziko-khimicheskikh Dannykh" (The Mathematical Treatment of Physicochemical Data), Izd. Moskov.Univ., Moscow, 1970.
50. A.J.Kresge and H.J.Chen, Anal.Chem., **41**, 74 (1969).
51. V.C.Armstrong and R.B.Moodie, J.Chem.Soc.B, 275 (1968).
52. Yu.R.Siigur and Yu.L.Khaldna, Reakts.Sposobn.Org. Soed., 7, 211 (1970).
53. T.A.Modro, K.Yates, and J.Janata, J.Amer.Chem.Soc., **97**, 1492 (1975).
54. Yu.L.Khaldna and I.A.Koppel', Reakts.Sposobn.Org. Soed., 13, 89 (1976).
55. R.H.Boyd, J.Amer.Chem.Soc., **85**, 1555 (1963).
56. T.K.Rodima and Yu.L.Khaldna, Reakts.Sposobn.Org. Soed., 7, 1273 (1970).
57. B.S.Krumgal'z, K.P.Mishchenko, and D.G.Traber, Teor.Eksper.Khim., 7, 98 (1971).
58. K.Yates, H.Wai, G.Welch, and R.A.MacClelland, J.Amer.Chem.Soc., **95**, 418 (1973).
59. E.M.Arnett, R.P.Quirk, and J.J.Burke, J.Amer.Chem. Soc., **92**, 1260 (1970).
60. K.Yates and S.A.Shapiro, Canad.J.Chem., **50**, 581 (1972).
61. R.Passerini, N.C.Marziano, and P.Traverso, Gazzetta, **105**, 901 (1975).
62. A.J.Kresge, H.J.Chen, L.E.Hakka, and J.Kouba, J.Amer.Chem.Soc., **93**, 6174 (1971).
63. K.Yates and R.A.McClelland, J.Amer.Chem.Soc., **89**, 2686 (1967).
64. P.Olavi, I.Virtanen, and M.Maikkula, Tetrahedron Letters, **47**, 4855 (1968).
65. D.W.Farlow and R.B.Moodie, J.Chem.Soc.B, 334 (1970).
66. J.F.Bunnett and F.Olsen, Canad.J.Chem., **44**, 1899 (1966).
67. N.C.Marziano, P.G.Traverso, and R.C.Passerini, J.Chem.Soc., Perkin Trans.II, 306 (1977).
68. L.P.Hammett, "Physical Organic Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1972, p.355.
69. Yu.L.Khaldna, I.A.Koppel', and Kh.I.Kuura, Reakts. Sposobn.Org.Soed., **14**, 212 (1977).
70. Yu.L.Khaldna, I.A.Koppel', and Kh.I.Kuura, Reakts. Sposobn.Org.Soed., **15**, 13 (1978).
71. N.C.Marziano, G.M.Cimino, and R.C.Passerini, J.Chem.Soc., Perkin Trans.II, 1915 (1973).

72. N.C.Marziano, P.G.Traverso, A.Tomasin, and R.C.Passerini, J.Chem.Soc., Perkin Trans.II, 309 (1977).
73. R.A.Cox and K.Yates, J.Amer.Chem.Soc., **100**, 3861 (1978).
74. R.A.Cox and R.Stewart, J.Amer.Chem.Soc., **98**, 488 (1976).
75. R.I.Zalevski and G.E.Dunk, Canad.J.Chem., **47**, 2263 (1969).
76. V.L.Zaguskin, "Spravochnik po Chislennym Metodam Resheniya Uravnenii" (Handbook of Numerical Methods of Solving Equations), Fizmatgiz, Moscow, 1960.
77. Yu.L.Khaldna, Ucheb.Zap.Tartu.Univ., No.384, 118 (1976).

Tartu State University
Analytical Chemistry Department

Translated from *Uspekhi Khimii*, **49**, 1188-1213 (1980) U.D.C. 541.49:541.571.53

Outer-sphere Interactions in Solutions of Labile Complexes

Yu.A.Makashev and V.E.Mironov

The principal methods for the investigation of outer-sphere interactions in solutions of labile inner-sphere complexes are arranged systematically and analysed. The modern views on the thermodynamics and structure of outer-sphere complexes are discussed and the reliability of certain hypotheses and models is examined from the standpoint of the comparison of the results of different experimental methods and theoretical ideas. A number of features of the outer-sphere interaction in solutions are formulated in relation to outer-sphere associated species formed by 3*d* metals, using certain data about the associated species of *s*, *p*, and *f* metals as well as outer-sphere associated species of inert complex cations.
The bibliography includes 203 references.

CONTENTS

I. Introduction 631
II. Methods for the investigation of the outer-sphere interaction of labile complex cations 631
III. Outer-sphere complexes of transition metals (*d* metals) 634
IV. Outer-sphere complexes of non-transition (*s*, *p*), lanthanide, and actinide elements (*f* metals) 637
V. Certain features of the outer-sphere interaction of labile outer-sphere complexes 639

I. INTRODUCTION

Outer-sphere interaction is a phenomenon as common as the formation of inner-sphere complexes[1]. Certain problems of the theory and practice of outer-sphere association in solutions have been examined in a number of reviews[2-10]. However, in these studies attention was concentrated on the outer-sphere complexes (OSC) formed by inert Werner complexes, i.e. complexes which are formed and dissociated at a low rate and which are saturated with respect to the coordination number of the central atom[1-8]. As regards labile complexes or complexes which rapidly exchange ligands, over a period shorter than 1 min for a 50% degree of reaction, outer-sphere reactions involving them have been investigated mainly in relation to complex anions[2,3] such as $[ZnBr_4]^{2-}$, $[BiCl_6]^{3-}$, $[Fe(SCN)_6]^{3-}$, and $[AgCl_2]^-$.

Complex cations, for example, $[Co(NH_3)_6]^{3+}$, $[Cr(H_2O)_6]^{3+}$, and $[Rh(NH_3)_5Cl]^{2+}$ usually function as the coordination centres of the OSC. Anions, both simple and complex, play the role of ligands in the vast majority of cases. This can be explained by the high tendency of anions to exhibit electron-donating properties. Inert complex anions are probably capable of forming an outer (second) coordination sphere of a definite configuration, which has been confirmed by numerous investigations[1-14]. The ability of labile complex cations, for example $[Ni(NH_3)_6]^{2+}$ and $[Co(H_2O)_6]^{2+}$ to undergo outer-sphere interaction and procedures for its investigation have not so far been the subject of independent reviews. At the same time the number of systems with labile inner-sphere complexes is many times greater than the number of systems with inert compounds and the interactions in such systems are much more complicated.

Together with the increased theoretical interest in labile outer-sphere complexes[1-10], the latter also attract attention from the practical point of view, particularly in the field of homogeneous catalysis[1,12,15] and in the regulation of biological molecular processes—oxygen and energy transfer in cells, ionic equilibria in the reactions of enzymes, and other most important biological phenomena[12].

The equilibria in labile systems containing outer-sphere complexes and the thermodynamic interpretation of the experimental results associated with them have been transformed into an important and serious problem[5-10], in view of the almost simultaneous occurrence of both inner-sphere and outer-sphere interactions.

The aim of the present review is to examine critically methods for the experimental investigation of the outer-sphere interaction of labile complex cations with different ligands, to survey and analyse literature data on the thermodynamics of this type of OSC, to carry out a comparison with the results of the study of the OSC of inert cations, and to outline certain ways in which this field in the chemistry of coordination compounds can be developed.

II. METHODS FOR THE INVESTIGATION OF THE OUTER-SPHERE INTERACTION OF LABILE COMPLEX CATIONS

There exist various approaches to methods for the investigation of the outer-sphere interactions of labile complex cations as a function of an inner-sphere process, which complicates the study of the OSC.

1. Outer-Sphere Interaction Uncomplicated by Inner-Sphere Complex Formation

The most convenient method for the investigation of outer-sphere interactions for labile complex cations of different composition involves carrying out experiments in solutions containing an excess of inner-sphere ligands. This excess should almost completely suppress the dissociation of the inner sphere and should not influence appreciably the formation of the OSC investigated. This situation can only be created in systems with comparatively stable inner-sphere compounds. The absence of measurable dissociation of the inner-coordination sphere makes it possible to study the formation of OSC by any methods used in the investigation of labile inner-sphere interaction.

The formation of 1 : 1 OSC can be represented in the general form as follows:

$$[ML_N] + A \rightleftarrows [ML_N] \ldots A$$

where L and A are inner- and outer-sphere ligands (the charges have been omitted) and N is the limiting coordination number of the first sphere.

Potentiometry, which is one of the most exact and widely used methods for the investigation of inner-sphere complex formation, has been employed in the study of the association of tris(ethylenediamine)cadmium with sulphate ions in 3.0 N

aqueous solutions of mixtures of sodium perchlorate and sulphate[11,13]. Measurements were made of the changes in the e.m.f.'s of cells with ion transport comprising a cadmium amalgam electrode, where diffusion potentials were determined experimentally[13]. The dissociation of tris(ethylenediamine)-cadmium(II) was suppressed by an excess of ethylenediamine. The measured changes in the e.m.f. were related to the formation of OSC of the type $[CdEn_3](SO_4)_n^{2-2n}$ only; the values of n and the stability constants were determined by Leden's method[1].

The changes in the solubilities of a number of sparingly soluble salts containing the tris(ethylenediamine)nickel(II) ion in solutions with increasing concentrations of outer-sphere ligands and in the presence of a constant excess of ethylenediamine served as a basis for the determination of the stability constants of the OSC $[NiEn_3].L_n^{z-zn}$, where z is the charge of the ligand and L are chloride, sulphate, thiosulphate, and carbonate ions. The conductimetric method has been used[15] to study the monoligand OSC of tris(ethylenediamine)- and tris(propylenediamine)-cobalt(II) in aqueous solutions at low ionic strengths. The thermochemical method[14] led to the determination of the stability constants and enthalpies and entropies of formation of a number of tris-(ethylenediamine)nickel(II) OSC.

Electronic spectroscopy using charge transfer bands in the ultraviolet has been employed in the investigation of the OSC of tris(ethylenediamine)cobalt(II)[15,16] and a number of other cations[17]. The NMR method yielded information about the thermodynamics and structure of numerous OSC of tris(pyrazolyl)borate[18–22] as well as bis(acetylacetone)dipyridinecobalt(II)[23] in several non-aqueous solvents such as cyclohexanone or chloroform. The absorption of ultrasound has been used to investigate the OSC of tris(1,10-phenanthroline)zinc(II).[24] Extraction has been used for the same complexes and mixed complexes with acetylacetone[25]. It served as a basis also for the determination of the formation constants of the OSC of tetra(γ-picoline)dicyanatocobalt(II).[26] The influence of the composition of the external medium on the width of the EPR spectral line has been demonstrated[27].

The high stability of the hydration shell of alkali and alkaline earth metal cations as well as lanthanide ions in many instances makes it possible to investigate numerous OSC of the aquo-complexes of these metals with simple and complex anions using various research techniques[28,29]. However, in such systems there is a possibility of the superposition of the inner-sphere effect on the outer-sphere association. The degree of such superposition depends greatly on the stability of the hydration shell and the nature of the outer-sphere ligands.

2. Simultaneous Formation of Inner- and Outer-Sphere Complexes

The simultaneous formation of inner-sphere complexes (ISC) and OSC is frequently encountered in systems containing aquated cations. The effect of the outer-sphere interaction is then manifested to the maximum extent before the formation of the first inner-sphere complex[1] and is sharply reduced in subsequent coordination stages.

Processes involving the joint formation of monoligand inner- and outer-sphere complexes from an aquated metal ion $M(H_2O)_N$ and the ligand (here and in the general cases discussed below the ionic charges are omitted to simplify the formulation) can be represented by the equations:

$$\begin{array}{ccc} M(H_2O)_N + L & \overset{k_{1,2};\,\omega_{01}}{\rightleftharpoons} & [M(H_2O)_N]\cdot L \\ \uparrow\downarrow & & \uparrow\downarrow \\ & \beta_{n,0} & \\ & \rightarrow & [M(H_2O)_{N-n}L] + nH_2O \end{array} \qquad (1)$$

where n is the number of binding sites in the ligand in the given process. Thus the inner-sphere complexes examined are labile and the OSC are formed at very high rates[3,4], the equilibrium constants for the formation of 1 : 1 complexes can be characterised by the following expressions:

$$\omega_{01} = \frac{\{[M(H_2O)_N]\cdot L\}}{\{[M(H_2O)_N]\}\cdot\{L\}}, \qquad (2)$$

$$\beta_{10} = \frac{\{[M(H_2O)_{N-1}\cdot L]\}\cdot\{H_2O\}}{\{[M(H_2O)_N]\}\cdot\{L\}}. \qquad (3)$$

The square brackets define the Werner coordination sphere and the braces denote activity or concentration if the activity coefficients are constant. The subscripts to the constants indicate the number of attached inner- and outer-sphere ligands.

The ratio of the constants represented by Eqns.(2) and (3) characterises the conversion of the OSC into the inner-sphere complex:

$$K_\Pi = \frac{\{[M(H_2O)_{N-1}\cdot L]\}\cdot\{H_2O\}}{\{[M(H_2O)_N]\cdot L\}} = \frac{\beta_{10}}{\omega_{01}}. \qquad (4)$$

In systems with labile complexes it is difficult to separate the effects of the formation of inner- and outer-sphere species for their quantitative assessment. The majority of physicochemical properties or quantities (electrical conductivity, electrode potential, optical density, heat of formation, and others), characteristic of OSC and ISC, are manifested as the general property of the solution. The reactions involving the formation of OSC and ISC under equilibrium conditions are virtually identical with the parallel reactions and any property of the solution is related to the amounts of complexes by the general expression

$$\bar{P} = \sum_{i=0}^{i=n} \alpha_i\, p_i, \qquad (5)$$

where α_i are the fractions of different types of complexes and p_i are the partial values of a certain physicochemical parameter $\bar{P}$ for each type of complex. Since it is impossible to obtain the exact value of p_i either experimentally or theoretically, only an approximate solution of Eqn.(5) and an approximate determination of β_{10} and ω_{01} are possible[1,37,39,40,45,46].

The majority of the formation constants of the complexes determined previously and compiled in the literature[28,29] contain information about the overall stability of two components:

$$K = \frac{\{[M(H_2O)_N]\cdot L\}\cdot(1/\{H_2O\}) + \{[M(H_2O)_{N-1}\cdot L]\}}{\{[M(H_2O)_N]\}\cdot\{L\}} = \beta_{10} + \omega_{01}. \qquad (6)$$

At the present time extensive data have accumulated, which permit a separate estimation of the β_{10} and ω_{01} with a certain degree of approximation.

The spectrophotometric method has been greatly developed for the solution of problems of outer-sphere interactions. Changes in absorption in the visible region in the electronic spectra of d and f metals have been observed in a large number of examples[37,38] for solutions containing inner-sphere forms[31–34]. We may note that the presence of OSC does not affect the intensity and positions of the absorption bands in the visible part of the spectrum, but affects the absorption in the ultraviolet, where intense charge-transfer bands are present[34,35]. In many cases[36–38] it is possible to assign the absorption bands to different types of complexes. The difficulty of the quantitative determination of β_{10} and ω_{01} is associated, as for a number of other methods, with the fact that the partial molar extinction coefficients of the OSC and ISC (ε_{01} and ε_{10}) are unknown. These quantities can be estimated approximately[39,40]. The neglect of one of the forms present in smaller amounts[41–44] yields doubtful results,

because the degree of approximation to the exact stability constants[45,46] is difficult to determine.

The most successful approach probably involves the use of the change in the activity of water in the course of the formation of the ISC [see Eqn.(1)]. Spectrophotometric measurements for aqueous organic solutions make it possible to obtain separately the values of β_{10} and ω_{01}.[45,47] A disadvantage of this method is the necessity to extrapolate the formation "constants", more precisely coefficients, characterising the equilibria in non-aqueous solutions to the conditions in an aqueous solution.

Using a familiar method[48] for the calculation of the stability constants of 1 : 1 complexes in the visible region of the spectrum, where $\varepsilon_{01} = \varepsilon_{00}$, it is possible to obtain the following relation[45]:

$$\frac{d\bar{\varepsilon}}{d[L]} = \frac{1}{\beta_{10}^{org}(\varepsilon_{10} - \varepsilon_{00})}\left(\frac{\varepsilon_{00} - \bar{\varepsilon}}{[L]}\right)^2, \qquad (7)$$

where ε_{10} and ε_{00} are the molar extinction coefficients of the ISC and the free metal respectively.

The values of $\varepsilon_{10} - \varepsilon_{00}$ and ε_{10} can be found from $\beta_{10}^{org}(\varepsilon_{10} - \varepsilon_{00})$ and β_{10}^{org} (obtained for an aqueous–non-aqueous solution) by extrapolating the experimental values to the concentration ranges where absolute non-aqueous and aqueous solutions exist. In this case the errors due to the slight changes in absorption in the region of transitions in the electronic absorption spectrum forbidden by the selection rule are usually added to the inaccuracies associated with the extrapolation.

The method of chemical relaxation developed by Eigen and his coworkers[49-51] theoretically makes it possible to find separately the formation constants of OSC and ISC, provided that there is a significant difference between the kinetics of their formation. For $k_{12} = 10^{10} - 10^{12}$ mol s^{-1} [see Eqn.(1)], the constant k_{23} is frequently in the range 10^3–10^9 s^{-1}. If it is possible to obtain separately the relaxation times corresponding to the formation of the OSC and the ISC, then the problem of the calculation of their formation constants can be solved unambiguously. In practice one usually obtains a single relaxation time corresponding to the slow state of the process, i.e. the formation of the ISC. This relaxation time (τ) depends on both the fast and slow processes:

$$\tau^{-1} = \frac{k_{12}([M] + [L])k_{23} + k_{21}k_{32}}{k_{21} + k_{23}}, \qquad (8)$$

where [M] and [L] are equilibrium concentrations.

Bearing in mind that $k_{21} \gg k_{23}$, we obtain

$$\tau^{-1} = k_{23}\omega_{01}([M] + [L]) + k_{32},$$

where $\omega_{01} = k_{12}/k_{21}$.

Thus the values of $k_{form} = k_{23}\omega_{01}$ and $k_{diss} = k_{32}$, obtained from kinetic experiments, make it possible to determine β_{10}:

$$K = k_{23}\omega_{01}/k_{32} = K_{II}\omega_{01} = (\beta_{10}/\omega_{01})\,\omega_{01} = \beta_{10}.$$

The difficulty consists in the determination of the exact relaxation data under standard conditions. Using this method, Eigen and Tamm[50] calculated the equilibrium constants K_{II} for a series of 3*d* aquo-anions in sulphate solutions.

In some kinetic studies it has been suggested that the amplitude and form of the relaxation curve be used[52,53] to calculate the parameters of the equilibria involving OSC and ISC when these are present jointly. The two methods yield a difference between the stability constants approximately by a factor of two. The experimental accuracy of the kinetic data is still unsatisfactory for the determination of reliable data for the stability of the OSC. More than others, this method can yield an unambiguous solution, provided that the experimental technique is improved and is applied more widely to problems of the OSC.

During recent years, the NMR and EPR methods have contributed greatly to the study of outer-sphere interaction[54-58]. The separation of the effects with their aid as well as other methods is difficult owing to the rapid exchange of the ligands in the inner sphere of labile complexes[59,72]. The difference between the two forms of complexes in solution is limited by the condition $1/\tau = (\sqrt{2})\pi\Delta\nu_0$, where $1/\tau$ is the rate of the exchange reaction and $\Delta\nu_0$ is the difference between the frequencies of maximum absorption for the two forms in the absence of exchange. Thus, when the lifetime of any one form is too short ($< 10^{-3}$ s), i.e. there is rapid exchange, then ν_{10} and ν_{01} cannot be determined separately. This obtains virtually for all labile complexes.

However, the NMR and EPR methods yield very valuable structural data, obtained under the conditions of a slow exchange of atoms containing resonating nuclei or electrons[55,56]. For example, the formation of ISC together with OSC in solutions of certain copper salts has been demonstrated from the change in the *g*-factor[57,58]. OSC in the presence of different anions have been found on the basis of the line width in the hyperfine structure of the EPR spectrum of manganese(II).[60-62]

Comparison of the variations of the signal intensity and the hyperfine splitting line width in the EPR spectra made it possible to find the ratio of the OSC and ISC in solutions of the dithionate[63-65] and perchlorate[66] of manganese(II).

The NMR chemical shifts[67-69], the relaxation times[70], and the paramagnetic shift[71-76] in the resonance of the ^{1}H, ^{19}F, ^{17}O, and (to a lesser extent) heavier nuclei have been used to investigate outer-sphere interactions. In most cases the formation of a mixture of ISC and OSC was noted in solutions of inorganic salts of transition metals (Cu, Mn, Co, Ni), including solutions where complex anions were present: SiF_6^{2-}, GeF_6^{2-}, SnF_6^{2-}, and BF_4^-.[71,74-76] An attempt has been made[71] to calculate β_{10} and ω_{01} for compounds of a series of metals with the above ligands from the changes in the paramagnetic shifts of the ^{19}F signal. However, the assumptions made led to extremely approximate equilibrium constants.

Relatively inert complexes, for example aluminium sulphates[77,78], give rise to resonance absorption bands of the ISC $[Al(H_2O)_5(SO_4)]^+$ and the hexa-aquo-form $[Al(H_2O)_6]^{3+}$, which can be determined separately, but no calculations have been made by the NMR method on the two forms of complexes present jointly in these systems.

The possibility of using the rate of exchange of water in the aquo-ions of metals in the presence of non-aqueous additives has been demonstrated[74-76,79]. In this case differences are observed between the chemical shifts of inner- and outer-sphere water. The development of this method apparently makes it possible to differentiate quantitatively the OSC and ISC in mixed solvents.

The "probe" method has been used[80] to investigate the outer-sphere interaction of labile aquo-ions of the elements in the first transition series. Methylene chloride and carbon tetrachloride have been used as the outer-sphere probes. On the basis of measurements of the longitudinal (T_1) and transverse (T_2) proton relaxations, the formation of a series of OSC $[H_4Mn(H_2O)_6]_nCl_m$, where $n = 2$–4 and $m = 4$–6, in manganese(II) chloride solutions has been demonstrated[81].

In certain favourable cases vibrational spectroscopy has been used successfully as a quantitative and qualitative method for the study of outer-sphere interactions. The characteristic absorption of SCN^-, CN^-, SO_4^{2-}, and PO_3^- ions serves as a source of information about the OSC and ISC in solutions of many metal salts[82-87]. For example, the absorption bands due to the stretching vibrations of the S–O bond in the sulphate ion in the range 850–1400 cm^{-1} make it possible to identify ISC and OSC. It has been possible to demonstrate approximately[82] the presence of 8, 50, and 12% of ISC in

sulphate solutions of nickel(II), indium(III), and cerium(III) salts. Analogous data have been obtained for sulphate solutions of aluminium(III)[83,84] as well as Mn^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+} in the presence of SCN^-.[85-87]

The difficulties in the quantitative estimation of the ratio of the concentrations of OSC and ISC are due to the lability of the complexes and the necessity for an accurate determination of the absorption intensity in aqueous solutions. Qualitative data have been obtained for solutions of metal perchlorates, nitrates, and sulphates from Raman spectra[88-92].

The potentiometric method has been used recently[93-95] for the simultaneous detection and subsequent calculation of the formation constants of the OSC and ISC in solutions of copper(II) chloride and bromide and manganese(II), cobalt(II), and zinc(II) chlorides. These studies were performed for a variable salt composition, which entailed the variation of the activity of water. The equilibrium constants were determined by extrapolating the concentration "constants" obtained to zero and unit activities of water. The dependence of the composition of the complexes on the activity of water, discussed above [see Eqn.(1)], and not the method of measurement plays the main role in this instance. The disadvantages of the method include the necessity to measure the equilibrium constants under non-equivalent conditions in the ionic medium and inaccurate extrapolation.

The calorimetric method sometimes makes it possible to solve the problem of whether OSC or ISC predominate. Owing to the liberation of water molecules [see Eqn.(1)] from the inner sphere on formation of the OSC, the values of $\Delta H°$ and $\Delta S°$ should be more positive when the inner sphere complex does not form strong covalent bonds. On this basis, the complexes formed in solution can be assigned either to the inner-sphere type (the ΔH and ΔS for the complex formation reactions are more positive than for the reactions involving other ligands) or to the outer-sphere type. This method of identification can be referred to as the thermodynamic criterion. Hypotheses concerning the application of a thermodynamic criterion of the type of complex formation on this basis have been put forward by both Vasil'ev and Yatsimirskii[96-100] and subsequently in Ahrland's papers[9,10].

Comparison of the values of $\Delta H°$ and $\Delta S°$ for labile and inert complexes makes it possible to make a qualitative choice in a number of instances between inner- and outer-sphere compounds[9,10,101-107]. A more reliable application of this principle is hindered by the lack of thermodynamic complex formation data obtained by calorimetric measurements and referred to zero ionic strength.

The inner- and outer-sphere complexes can be identified by measuring the specific volumes or compressibilities of solutions[108]. The sensitivity of solutions to pressure should be greater when ISC predominate[108-111]. This can be explained by the theoretically greater compressibility of ISC solutions compared with OSC solutions, because the degrees of hydration and electrostriction change more on formation of ISC. For example, the changes in the partial molar volumes of solutions for manganese(II) and magnesium(II) sulphates[109] are from −7,4 to −10 ml mol^{-1} and from −9.5 to 6.9 ml mol^{-1} when the concentration is changed from 5×10^{-4} M to 2×10^{-2} M respectively. The different directions of the changes $\overline{\Delta V}$ permit a conclusion concerning the different types of complexes formed.

The proof of the influence of the outer sphere of aquocations on the structure and properties of the solutions has also been obtained from compressibility data[110,111]. On the other hand, dilatometric measurements of the compressibilities of cobalt(III) complexes[111] in solutions containing OSC and ISC do not allow the formulation of a criterion for differentiating between these two types of complexes although the changes $\overline{\Delta V}$ for complexes with similar structures were regular.

An effective although rarely used method for the investigation of OSC in solutions is X-ray diffraction. The results of the determination of the interatomic distances in the OSC $[M(H_2O)_6]^{2+}...Cl^-$, where M = Cd(II), Co(II), or Cu(II), have been published[112]. The M–Cl distance is 4.42 Å. The distances for the ISC are much smaller: 2.27–2.60 Å.[113] The existence of OSC has been established by X-ray diffraction for associated gadolinium chloride species[114] in which the Gd–Cl distances are 4.5–5.0 Å, while in the ISC the Gd–Cl bond length is 2.8 Å.

The above brief survey of experimental methods leads to the conclusion that the study of inner- and outer-sphere complex formation is on the whole developing rapidly and involves the employment of the latest methods. Important structural results have been obtained with the aid of microwave spectroscopy, chemical relaxation, and X-ray diffraction. On the other hand, the study of the equilibria and the thermodynamics of the ISC and OSC in labile systems is advancing slowly. The problem can be probably to a large extent solved by devising apparatus whereby one can measure chemical relaxation with a high accuracy and by developing experimental and computational NMR techniques in combination with the development of the theory of solutions[115-117].

III. OUTER-SPHERE COMPLEXES OF TRANSITION METALS (*d* METALS)

Unambiguous information about the thermodynamics of the structure of OSC has been obtained for systems where outer-sphere association is not complicated by the inner-sphere interaction. Unfortunately such studies have been made only for a small number of OSC and should be extended further.

Data have now been obtained[14] on the association of tris(ethylenediamine)nickel(II) in 3.0 *N* aqueous sodium perchlorate solutions containing also the sodium salt of the ligand (Table 1). It follows from these results that the stability of the OSC decreases in the following sequence of outer-sphere anions: $S_2O_3^{2-} > SO_4^{2-} > CO_3^{2-} > Cl$, which is analogous to the sequence for tris(ethylenediamine)cobalt(III) [4] and many other inert complexes[15,30]. The existence of this sequence has been explained[4] by the changes in the charges and polarisabilities of the anions.

Table 1. The overall association constants of tris(ethylenediamine)nickel(II) with certain anions in 3.0 *N* solutions of sodium perchlorate and the sodium salt of the ligand at 25.0 °C according to solubility data[14] for $[NiEn_3]SO_4$.

Ligand ion	ω_{01}	ω_{02}
Chloride	0.08	—
Sulphate	0.70 (0.66) *	0.20 (0.57) *
Carbonate	0.58	0.06
Thiosulphate	0.92 (0.83) **	0.16 (0.22) **

* The solubilities of $[NiEn_3][PtCl_6]$ are indicated in brackets.

** According to the solubility of $[NiEn_3]S_2O_3$.

The enthalpies (−1.7 kcal g-ion^{-1}) and entropies (−5.7 e.u.) of formation show[14] that the addition of a sulphate ion to tris(ethylenediamine)nickel takes place as a result of the enthalpy component of the free energy. On the other hand,

inert tris(ethylenediamine) complexes combine with sulphate ions as a result of the increase of entropy[4]. The causes of this phenomenon require explanation.

It is of interest to note that tris(ethylenediamine)cadmium(II) forms associated species with sulphate ions having the same equilibrium constant[11] as the species formed by tris(ethylenediamine)nickel(II). This demonstrates the influence of the charge of the complex cation on the association and a very small contribution of other factors. However, tris(ethylenediamine)cobalt(II)[16] has a much smaller capacity for interaction with sulphate ions, which conflicts with the conclusion that the charge exerts the dominant influence. We believe that the properties of the OSC noted here have still been very little investigated and require extensive tests in relation to other examples.

A number of studies[18-22] of the OSC of labile but extremely strong complexes of cobalt(II), the inner sphere of which is saturated by the tridentate tripyrazolylmethane ligands, have been published. The OSC were studied by NMR. Measurements were made of the chemical shifts of the proton or ^{19}F signals for the outer-sphere ligands consisting of different molecules and ions. The outer-sphere ligands were pyridine, aniline (or its substituted derivatives), methanol, acetonitrile, acetone, benzene, hexane, hexafluorophosphorus(V), etc. It was shown that neutral molecules add to the outer sphere along the z axis[18,19], while anions add along the x axis[21]. This difference was explained by the contribution of electrostatic and van der Waals forces to the formation of outer-sphere bonds. The contribution of the latter was confirmed[22] by the increase of the association constants with increase of the dipole moment of the solvent. The results of these studies demonstrated the presence in the outer-sphere of a different configuration which determines the catalytic effect[20].

An analogous study by NMR was carried out[23] for bis(acetylacetone)dipyridinecobalt(II) in cyclohexanone. The stepwise interaction with chloroform and methyl chloride was investigated and it was observed that the outer-sphere association takes place as a result of the decrease of enthalpy accompanied by a sharp diminution of entropy (−20 e.u. in each coordination stage). It was shown that the outer-sphere ligands are coordinated via hydrogen atoms directed towards the inner-sphere ligands in the equatorial plane.

Table 2. The extinction coefficients ($\bar{\varepsilon}$) of copper(II), cobalt(II), and nickel(II) ions in 1 M Li_nL solutions at an ionic strength of 3.0 ($LiClO_4$).

Ligand ion	Cu^{2+} (λ = 800 nm)	Type of complex	Co^{2+} (λ = 510 nm)	Type of complex	Ni^{2+} (λ = 720 nm)	Type of complex
Perchlorate	11.9	OSC	5.5	OSC	2.2	OSC
Sulphate	12.1	OSC	5.6	OSC	2.3	OSC
Fluoride	>12.5	OSC,ISC	5.5	OSC	2.2	OSC
Chloride	22.1	ISC	6.0	OSC	2.2	OSC
Bromide	21.8	ISC	5.9	OSC	2.2	OSC

An extraction study[26] demonstrated the occurrence of successive double addition of chloroform to the outer-sphere of dithiocyanatotetrakis(γ-picoline)cobalt(II) via hydrogen bonds formed between chloroform and the picoline π electrons.

However, in the case of labile ISC systems the greatest amount of data has been obtained for acido-OSC formed by the complexations of transition elements of the first series with F^-, Cl^-, Br^-, SO_4^{2-}, NO_3^-, etc. In these systems both types of complex formation occur simultaneously, inner- and outer-sphere associated species being produced. In such cases the absorption spectrum in the visible region, due to the breakdown of symmetry in the inner sphere, undergoes a change in intensity. Table 2 presents data concerning the variation of the absorption of certain cations under comparable conditions[39,101-103].

Table 3. Thermodynamic data for inner- and outer-sphere complex formation (at 25 °C) involving inert and labile complexes according to the equilibria:

$$[ML_6]^{n+} + A^z \rightleftarrows [ML_6]^{n+}\cdot A^z \rightleftarrows [ML_5\cdot A]^{n-z} + H_2O$$

Compn. of complex in soln.	ΔH°, kcal mol^{-1}	ΔS°, cal mol^{-1} K^{-1}	Ionic strength	Type of complex	Refs.
$[Cr(H_2O)_5SO_4]^+$	7.2	29	1.0*	ISC	10
$[Cr(H_2O)_6]^{3+}\cdot SO_4^{2-}$	0	5	1.0*	OSC	10
$[Cr(H_2O)_5Cl]^{2+}$	5.0	23.3	0	ISC	118
$[Cr(H_2O)_5Cl]^{2+}$	6.6	—	5.1	ISC	119
$[Cr(H_2O)_6]^{3+}\cdot Cl^-$	−0.43	−1.7	1.0	OSC	120
$[Co(NH_3)_5SO_4]^+$	3.7	17	1.0	ISC	32,10
$[Co(NH_3)_5SO_4]^+\cdot SO_4^{2-}$	1.6	16.5	0	OSC	126
$[Co(NH_3)_5Cl]^{2+}\cdot SO_4^{2-}$	−4.1**	−6.2	0.3	OSC	121
$[Co(NH_3)_5Br]^{2+}\cdot SO_4^{2-}$	0.85	16	0	OSC	126
$[Co(NH_3)_5Br]^{2+}\cdot SO_4^{2-}$	0.7	15	0	OSC	126
$[Co(NH_3)_5(H_2O)]^{3+}\cdot SO_4^{2-}$	−0.3	4	1.0	OSC	32,10
$[Co(NH_3)_6]^{3+}\cdot Cl^-$	0.6	—	1.0	OSC	122
$[Co(NH_3)_6]^{3+}\cdot SO_4^{2-}$	−0.5	14.2	0	OSC	126
$[Rh(NH_3)_5Cl]^{2+}\cdot SO_4^{2-}$	1.1	17	0	OSC	125
$[Rh(NH_3)_5Cl]^{2+}\cdot CO_3^{2-}$	4.9	22	0.5	OSC	125
$[Rh(NH_3)_5Cl]^{2+}\cdot CO_3^{2-}$	1.0	16	0	OSC	125
$[IrEn_3]^{3+}\cdot CO_3^{2-}$	−0.2	13.7	0	OSC	125
$[CoEn_3]^{3+}\cdot SO_4^{2-}$	2.0	10	0.5	OSC	125
$[CoEn_3]^{3+}\cdot SO_4^{2-}$	1.4	14	0	OSC	125
$[CoEn_3]^{3+}\cdot SO_4^{2-}$	−0.5	13.5	0	OSC	126
$[CoEn_3]^{3+}\cdot SO_4^{2-}$	0.3	6.5	0.5	OSC	126
$[Co\,Dipy_3]^{3+}\cdot SO_4^{2-}$	−8	−13	0	OSC	15
$[Co\,Phen_3]^{3+}\cdot SO_4^{2-}$	−6	−10	0	OSC	15
$[CuCl]^+$	2.9	7.0	3.0	ISC	101
$[CuCl]^+$	3.2	10.6	4.0	ISC	127
$[NiCl]^+$	1.10	2.9	4.0	OSC,ISC	127
$[CoCl]^+$	0.62	1.3	4.0	OSC	127
$[MnCl]^+$	1.40	4.5	4.0	ISC,OSC	127
$[ZnCl]^+$	1.2	4.8	4.0	ISC,OSC	127
$[FeCl]^{2+}$	4.2	16	1.0	ISC	10
$[FeCl]^{2+}$	3.4	16	3.7	ISC	10
$[CuBr]^+$	3.0	7.5	3.0	ISC	101
$[CuBr]^+$	0.9	2.8	2.0	ISC,OSC	123
$[CuBr]^+$	1.0	3.0	2.0	ISC,OSC	123
$[NiBr]^+$	0.08	−0.27	2.0	OSC	123
$[NiBr]^+$	2.8	5.5	3.0	ISC,OSC	101
$[CoBr]^+$	2.20	3.5	3.0	ISC,OSC	101
$[CoBr]^+$	0.15	0	2.0***	OSC	123
$[ZnBr]^+$	0.0	−2.75	4.5	OSC	124
$[CuSO_4]$	1.22	14.6	0	ISC,OSC	10,123
$[CuSO_4]$	0.38	2.0	4.0	OSC	127
$[NiSO_4]$	0.41	14.1	0.0	OSC	10
$[NiSO_4]$	0.58	3.0	3.0	OSC	101
$[NiSO_4]$	−0.11	2.2	4.0	OSC	127
$[CoSO_4]$	0.50	13.9	0	OSC	10
$[CoSO_4]$	0.62	3	3.0	OSC	101
$[CoSO_4]$	−0.64	0.1	4.0	OSC	127
$[FeSO_4]$	0.56	12.0	0	OSC	123
$[MnSO_4]$	0.61	15.2	0	OSC	10
$[MnSO_4]$	2.3	7	3.0	ISC,OSC	101
$[MnSO_4]$	1.4	4.5	4.0	ISC,OSC	127
$[ZnSO_4]$	0.63	13.5	0	OSC	123
$[ZnSO_4]$	0.72	3.5	3.0	OSC	101
$[ZnSO_4]$	0.57	4.7	4.0	OSC	127
$[NiS_2O_3]$	0.11	1.2	1.0	OSC	105
$[CoS_2O_3]$	0.12	1.2	1.0	OSC	105
$[CuF]^+$	3.2	15.5	3.0	ISC	103
$[MnF]^+$	3.6	10.5	3.0	ISC	103
$[CoF]^+$	3.3	14.0	3.0	ISC	103
$[NiF]^+$	1.4	8.0	3.0	OSC,ISC	103
$[ZnF]^+$	2.2	11.5	3.0	OSC,ISC	103
$[CuClO_4]^+$	−1.55	−6.8	1.0	OSC	106
$[NiClO_4]^+$	−1.26	−5.8	1.0	OSC	106
$[CoClO_4]^+$	−0.65	−1.2	1.0	OSC	106
$[MnClO_4]^+$	−1.24	−5.4	1.0	OSC	106
$[ZnClO_4]^+$	−1.04	−4.0	1.0	OSC	106

* At 60 °C.

** Determined from the temperature variation of the formation constant.

*** At 40 °C.

The results in Table 2 indicate at least the coexistence of OSC and ISC for the majority of associated copper(II) species and predominantly ISC for cobalt(II) and nickel(II).

The results of the measurements of the heats of formation of these complexes lead to the same conclusion. Table 3 presents the experimental $\Delta H°$ and $\Delta S°$ obtained by different workers together with qualitative estimates of the dominant types of complexes in the reaction mixture. The data for inert complexes, which form only OSC, are included as selection criteria.

The numerical data in Table 3 permit the utilisation of the thermodynamic criterion described above and lead to a conclusion concerning the dominant type of complex formation in systems comprising the labile compounds. The analogy with inert OSC in terms of thermodynamic properties is apparently fully justified, since kinetic properties should not influence the thermodynamics of the compounds. The OSC of inert "hydrophilic" complex cations are characterised by low values of ΔH and as a rule by positive values of ΔS, while the corresponding quantities for the ISC are more positive. Ionic strength has little influence on the ΔH for the complexes but, it apparently should have a significant influence on the entropies of formation of the OSC, since in this case the outer sphere is desolvated[105,106]. On the other hand, careful calorimetric measurements for the OSC formed by inert complexes[15,30,125,126] demonstrated that the entropy is approximately constant at $\Delta S° \cong 15$ e.u. for "hydrophilic" complex cations of any charge and doubly charged anions at zero ionic strength. By analogy, it is sometimes possible to decide which type of OSC predominates in the case of labile aquo-complexes and other "hydrophilic" complexes (Table 3).

In conformity with the thermodynamic criterion, the majority of the results obtained agree with spectroscopic measurements on solutions of salts of 3*d* metals. Unfortunately the amount of calorimetric data on complex formation at zero ionic strength is still inadequate. The development of studies on these lines is essential. On the other hand, one should point out the limitations of the thermodynamic criterion. It is inapplicable to "soft" acceptors and donors and to "hydrophobic" ions {see the OSC of $[CoDipy_3]^{3+}$ and $[CoPhen_3]^{3+}$, Table 3} whose hydration and solvation processes contribute less to the free energy[9,10,15,30].

Aruga[105,106] assigned the monoligand associated cobalt(II) and nickel(II) thiosulphate species in solutions as well as the manganese(II), cobalt(II), nickel(II), copper(II), and zinc(II) nitrate and chlorate species predominantly to the class of outer-sphere complexes in view of the negative values of ΔS at an ionic strength of 1.0. For $\Delta S = -1.2 - -6.8$ e.u., ΔH was $-0.65 - -1.55$ kcal mol^{-1}, which apparently characterises the interaction of ions of class *a*.

Larsson[107] calculated $\Delta S°$ for the dissociation of the OSC of the type MSO_4, where $M^{2+} = Mg^{2+}$, Zn^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, or Ca^{2+}. These functions were found to be in the range between -14.7 and -17.8 e.u. Theoretically the partial molar entropies $\Delta S°$ for the OSC differ from those for the ISC by the entropy of liberation of water (7.3 e.u.). Then judging from the $\Delta S°$, zinc(II) and magnesium(II) sulphates should exist in the form of the OSC, while calcium(II) and cadmium(II) should be predominantly in the form of ISC.[107]

As mentioned above, the stability constants of the ISC and OSC can be determined separately with certain approximations, but in the majority of methods no estimate of the degree of approximation is made. The most reliable results have been so far obtained by relaxation and spectrometric methods, the dependence of the equilibria on the composition of the solvent being used in the latter case. Table 4 gives a systematic list of the results of the determination of the stability constants of the OSC and ISC by different methods in systems comprising labile complexes. Table 4 also includes the results of the determinations of the overall stability constants for systems in which the appearance of both types of compounds has been demonstrated, the type of complex being determined on the basis of the experimental criteria of each method.

Many of the results in Tables 3 and 4 demonstrate unambiguously the dominance of the outer-sphere interaction in aqueous solutions of the salts of many ions of 3*d* elements. Nickel(II), cobalt(II), and copper(II) ions form mainly outer-sphere species of the type $\{[M(H_2O)_6].L\}$, while manganese(II) and iron(III) complexes have a mixed composition. The stability of purely outer-sphere species varies in the majority of systems in accordance with the following series of metals: $Cu^{2+} > Ni^{2+} \geqq Co^{2+} > Mn^{2+} \ll Fe^{3+}$, which constitutes a complete analogy with inner-sphere complex formation and corresponds to the same extent with the energy of stabilisation by the crystal field.

The size of the ligands apparently also plays a definite role in the formation of the ISC. Large polyatomic ions SO_4^{2-}, NO_3^-, ClO_3^-, and SiF_6^- form ISC more rarely than the monatomic ions F^- and Cl^-. The stability series for the OSC with different ligands is as follows:

$$F^- > SO_4^{2-} > ClO_3^- \simeq NO_3^-, \quad Cl^- > Br^-.$$

The ISC and OSC of bivalent manganese, cobalt, nickel, and copper have been studied systematically[71] by NMR on the basis of chemical, paramagnetic, and isotopic shifts, line widths, and spin–spin and hyperfine interaction constants. The ligands were the fluoride and oxide fluoride complexes of a number of metals. These large ions formed mainly OSC. If it is assumed that the assumptions made[67,71] in the calculation of the association constants do not introduce large errors, then the tendency of these ions towards the formation of both ISC and OSC diminishes in the following sequences:

$$MoO_2F_4^{2-} > WO_2F_4^{2-} > TiF_6^{2-} > SnF_6^{2-} > GeF_6^{2-} > SiF_6^{2-} > BF_4^-;$$
$$Fe^{2+} > Mn^{2+} > Co^{2+} > Ni^{2+} > Cu^{2+}.$$

These sequences are determined not only by the charges and dimensions of the ions but also by the nature of the M–F bond and the lability of the hydration shell of the cation.

However, the extremely significant difference between the data for the stabilities of the associated species under consideration is striking. The stability constants of such species are much higher, according to the results of new investigations[71] than those based on the results of earlier studies, although the methods of investigation and conditions were analogous.

It is of interest to note that molybdenyl and tungstyl tetrafluorides interact[71] via the fluoride ions in the *trans*- and *cis*-positions with respect to oxygen, forming equatorial and axial OSC with the cations, the former predominating.

The association of the cation with the perchlorate ions of the supporting salt plays a significant role in outer-sphere complex formation. The dependence of the stability constants on the ionic strength of the solution should be greater than is in reality the case. Nevertheless, despite the competition by the perchlorate ions, the ligand series quoted here confirm the occurrence of a predominantly ionic interaction, as has in fact been suggested for outer-sphere complex formation[7].

A common feature of the OSC is their low thermodynamic stability. When the overall complex formation reactions lead to stable complexes, for example, those of iron(III) with acetate or formate ions, the OSC are not manifested thermodynamically and play only a kinetic role.

Table 4. The stability constants of inner- and outer-sphere 1 : 1 complexes of the aquo-ions of *d* elements with different ligands (at 25.0°).

Ligand	β_{10}, ω_{01} or $\beta_{10}+\omega_{01}$	Ionic strength	Type of complex	Method of determination*	References
		Cu^{2+}(aq.)			
SO_4^{2-}	178	0	OSC	SP	42
SO_4^{2-}	6.0	1.0	OSC	SP	127
SO_4^{2-}	5.0	3.0	OSC	SP	38,39,101
SO_4^{2-}	2.3	3.0	OSC	SP	127
SO_4^{2-}	3.3	4.0	OSC	SP	127
NO_3^-	2.0	0	OSC	SP	45
NO_3^-	1.4	1.0	OSC	KIN	106,128
NO_3^-	0.40	3.0	OSC	SP	45
ClO_3^-	2.2	1.0	OSC	KIN	106,128
F^-	11.4	3.0	ISC,OSC	SP,C	103
Cl^-	0.87	3.0	ISC	SP	39,45
Cl^-	0.80	2.39	ISC	SP	93
Cl^-	0.58	3.0	ISC	SP	127
Cl^-	1.72	0	ISC	SP	42,45
Cl^-	1.63	0	ISC	SP	93
Cl^-	0.95	4.0	ISC	SP	127,1
Br^-	0.28	3.0	ISC,OSC	SP	38,38,101
Br^-	0.25	1.857	ISC,OSC	SP	95
Br^-	0.60	4.0	OSC	SP	127,1
SCN^-	82	3.0	ISC,OSC	SP	38
SiF_6^{2-}	0.8	1.0	ISC	NMR	71
SiF_6^{2-}	5	1.0	OSC	NMR	71
GeF_6^{2-}	0.8	1.0	ISC	NMR	71
GeF_6^{2-}	5	1.0	OSC	NMR	71
SnF_6^{2-}	0.7	1.0	ISC	NMR	71
SnF_6^{2-}	5	1.0	OSC	NMR	71
TiF_6^{2-}	1.0	1.0	ISC	NMR	71
TiF_6^{2-}	7	1.0	OSC	NMR	71
		Ni^{2+}(aq.)			
SO_4^{2-}	120	0	OSC	SP	127
SO_4^{2-}	1.8	3.0	OSC	S,P	38
SO_4^{2-}	3.2	4.0	OSC	SP	127
F^-	5.8	3.0	OSC	C,P	103
Cl^-	1.63	0	OSC	SP	127
Cl^-	0.20	1.0	OSC	SP	129
Cl^-	0.27	3.0	OSC	SP	38
Cl^-	0.50	3.0	OSC	SP	127
Cl^-	0.39	—	OSC	P	94
Br^-	1.04	0	OSC	SP	127
Br^-	0.13	1.0	OSC	SP	129
Br^-	0.15	3.0	OSC	SP	38
SCN^-	21.7	3.0	OSC	SP	38
SCN^-	12	—	ISC	IR	85
SCN^-	3	—	OSC	IR	85
GeF_6^{2-}	15	1.0	OSC	NMR	71
GeF_6^{2-}	1.7	1.0	ISC	NMR	71
SnF_6^{2-}	15	1.0	OSC	NMR	71
SnF_6^{2-}	1.7	1.0	ISC	NMR	71
SiF_6^{2-}	15	1.0	ISC	NMR	71
SiF_6^{2-}	1.7	1.0	ISC	NMR	71
TiF_6^{2-}	17	1.0	OSC	NMR	71
TiF_6^{2-}	1.9	1.0	OSC	NMR	71
NO_3^-	1.02	1.0	OSC	KIN	106, 128
ClO_3^-	2.2	1.0	OSC	KIN	106, 128
		Co^{2+}(aq)			
SO_4^{2-}	102	0	OSC	SP	127
SO_4^{2-}	1.65	1.0	OSC	SP	129
SO_4^{2-}	1.70	3.0	OSC	S,P	38
SO_4^{2-}	3.2	3.0	OSC	SP	127
F^-	4.4	3.0	OSC	C,P	103
Cl^-	2.2	0	OSC	SP	127
Cl^-	0.43	1.0	OSC	SP	129
Cl^-	0.57	3.0	OSC,ISC	SP	38
Cl^-	0.32	—	OSC	P	94
Cl^-	0.43	—	ISC	P	94
Br^-	1.7	0	OSC	SP	127
Br^-	1.17	1.0	OSC	SP	129
Br^-	0.19	3.0	OSC	SP	38
Br^-	0.41	3.0	OSC	SP	127
SCN^-	18.7	3.0	OSC,ISC	SP	38
SiF_6^{2-}	25	1.0	OSC	NMR	71
SiF_6^{2-}	2.0	1.0	ISC	NMR	71
CrF_6^{3-}	25	1.0	OSC	NMR	71
CrF_6^{3-}	2.2	1.0	ISC	NMR	71

Table 4 (Cont'd.)

Ligand	β_{10}, ω_{01} or $\beta_{10}+\omega_{01}$	Ionic strength	Type of complex	Method of determination*	References
		Co^{2+}(aq.)			
TiF_6^{2-}	33	1.0	OSC	NMR	71
TiF_6^{2-}	2.8	1.0	ISC	NMR	71
		Fe^{3+}(aq.)			
SO_4^{2-}	580	4.0	ISC,OSC	SP	130
SO_4^{2-}	5.0	3.0	ISC,OSC	P	132
Cl^-	14.4	4.0	ISC,OSC	S,C	130
Cl^-	3.0	1.0	ISC	KIN	131
Cl^-	2.2	1.0	OSC	KIN	131
Br^-	2.3	4.0	OSC,ISC	SP,S,C	130
SCN^-	155	4.0	ISC	SP,S	130
$HCOO^-$	$3.4\cdot10^3$	4.0	ISC	SP	130
CH_3COO^-	$2.9\cdot10^5$	4.0	ISC	SP	130
		Mn^{2+}(aq.)			
SO_4^{2-}	22.4	0	ISC,OSC	P	127
SO_4^{2-}	3.3	1.0	ISC,OSC	P	127
SO_4^{2-}	1.7	3.0	ISC,OSC	P	107
SO_4^{2-}	1.62	3.0	ISC,OSC	SP	101
Cl^-	2.68	0	ISC,OSC	P	127
Cl^-	1.7	3.0	ISC,OSC	P	62
Cl^-	0.78	3.0	ISC,OSC	P	127
Cl^-	0.22	3.0	OSC	EPR	62
Br^-	1.53	0.0	ISC,OSC	P	127
Br^-	1.34	3.0	ISC,OSC	SP	62
Br^-	0.4	3.0	ISC,OSC	P	127
Br^-	0.17	3.0	OSC	EPR	62
$S_2O_4^{2-}$	18	—	OSC	EPR	63
$S_2O_4^{2-}$	4	—	ISC	EPR	63
SCN^-	9.4	3.0	ISC,OSC	SP	130

* Notation: SP = spectrophotometry; KIN = kinetic method; C = calorimetry; S = solubility; P = potentiometry.

It is noteworthy that the thermodynamics of the formation of OSC change fundamentally[15] on passing from "hydrophilic" to "hydrophobic" complex cations. The thermodynamic parameters examined above, which indicate the structure of the associated species, are valid only when the outer-sphere ligands interact with "hydrophilic" complex cations.

Analysis of data on the stability of the OSC of 3d metals shows that the order in which the stabilities vary for a series of metals depends little on the nature of the anion in the outer sphere. This indicates a major role of the central atom in the outer-sphere bond, the latter being subjected to its influence owing to the alteration of the properties of the coordinated inner-sphere ligand.

IV. OUTER-SPHERE COMPLEXES OF NON-TRANSITION (*s*,*p*), LANTHANIDE, AND ACTINIDE ELEMENTS (*f* METALS)

Metals whose valence is determined solely by *s* and *p* electrons exist in aqueous solution as singly- and doubly-charged ions. These are, in particular, alkali and alkaline earth metals. The stability of the hydration shells of these ions is high and increases with decrease of their atomic weight.

Aqueous solutions of the majority of salts of these metals with singly charged anions contain only outer-sphere associated species at concentrations below the total hydration limit. The stability of these species usually increases with decrease of the stability of the solvation shell from lithium to caesium and from beryllium to barium[28,29]. The tendency towards association with hydroxide, fluoride, acetate, and lactate, and similar ions varies in the opposite direction, indicating the dominant influence of the inner sphere interaction.

The 1–2- and 2–2-valent electrolytes based on these metals frequently exist in dilute aqueous solutions in the form of outer-sphere associated species. The contribution of the inner-sphere interactions in such solutions increases sharply, becoming dominant on passing from 1–2- to 2–2-valent electrolytes, on replacement of weakly polarisable anions by highly polarisable anions with a high electron-donating capacity, and with increase of the concentration of the solutions. The validity of the above postulates is confirmed by the satisfactory agreement between the results obtained using different experimental techniques[28,29].

Fairly extensive information about the thermodynamics of associated species formed by complex anions with alkali and alkaline earth metal cations has been examined by Mironov[2,3]. It shows unambiguously that complex anions are in many respects analogous to simple anions as regards their capacity for addition to the outer-spheres of alkali and alkaline earth metal aquo-cations. However, the outer-sphere association of unstable complex anions with cations usually leads to the additional incorporation of simple anionic ligands in the inner sphere of the complex anion as a result of the decrease of the negative charge of the entire associated species owing to the interaction of the complex anions with the alkali or alkaline earth metal cation[2]:

$$K^+ + [PbCl_3(H_2O)]^- \rightarrow K^+ \ldots [PbCl_3(H_2O)]^- \xrightarrow{+Cl^-} K^+ \ldots [PbCl_4]^{2-} + H_2O\,.$$

The interaction of triply and quadruply charged anions with alkali and alkaline earth metal cations is determined by the nature of the anions. In these systems the anions are usually incorporated in the inner coordination sphere, displacing water, and forming mixtures of ISC and OSC only occasionally in a small number of systems[2,3]. Judging from the infrared spectra of solutions, a good example of such OSC[86] is provided by magnesium and calcium compounds with certain doubly, triply, and quadruply charged ligands of the type of $CH_3PO_4^{2-}$, $CH_3P_2O_7^{3-}$, and $AP_3O_{10}^{4-}$, where A is adenosine. It is of interest to note that these ligands also form mainly OSC with doubly charged manganese, cobalt, and nickel ions, but are incorporated in the inner spheres of copper(II) and zinc(II).[86] In our view the validity of these postulates requires confirmation.

On the other hand, the interactions of alkali and alkaline earth cations (as well as cations of *p* and *f* metals even with singly charged anions at fairly high concentrations of aqueous solutions lower the symmetry of complex ligands. Thus Raman spectra demonstrate unambiguously[90] the decrease of the symmetry of the nitrate ion to C_{2v}. This effect weakens in the following sequence of cations:

$$Th^{4+} > In^{3+} > Cu^{2+} > Hg^{2+} > Ce^{3+} > Ca^{2+} > Zn^{2+} > Al^{3+} > Ag^+ > Na^+ \simeq K^+ \simeq NH_4^+\,.$$

It is believed[90] that the decrease of the symmetry is the result of the formation of ion pairs. Raman bands corresponding to the M–O bond have not been observed, but, bearing in mind the low sensitivity of Raman spectra, the presence of covalent bonds cannot be fully ruled out in all the systems investigated. One may assert[135] that only OSC are formed in solutions of alkali metal nitrates, but, judging from a comparison of the Raman and infrared spectra, the nitrate ion is partly incorporated in the inner spheres of zinc(II), copper(II), mercury(II), calcium, indium(III), and cerium(III) cations[136,137].

The decrease of the symmetry of the ligand cannot be always regarded as a criterion of the occurrence of the ISC or OSC interaction, since the tetrahedral structure of the sulphate and perchlorate ions is not distorted[135] by certain cations. In dilute solutions the sulphate ion, for example, does not in fact enter into the inner spheres of many cations, but, with increase of concentration, the main bulk of the OSC are converted into ISC. This has been observed[83] for the sulphate complexes of aluminium and certain other metals[138,139].

It has been shown[140,141] that *s* and *p* metals in perchlorate solutions bind and polarise outer sphere water and induce structure formation in the latter more vigorously than *d* elements, which are more likely to have a structure breaking effect on the outer-sphere water. Consequently the formation of OSC by *s* and *p* metals should be more accurately regarded as substitution or displacement of outer-sphere water molecules. Studies[53,142–144] of the association of beryllium(II) with sulphate ions, which have been discussed in detail[143], are of interest from this point of view. As an illustration, Table 5 presents the thermodynamic functions for the outer-sphere complex $[Be(H_2O)_4].SO_4$ and for its conversion into the inner-sphere complex $[Be(SO_4)(H_2O)_3]$ obtained from measurements of the relaxation time of the pressure jump[144] and by an iterative procedure[52–54,142].

Table 5. Thermodynamic constants for the formation of $[Be(H_2O)_4].SO_4$ and for its conversion into $[Be(SO_4)(H_2O)_3]$ at 25 °C and zero ionic strength of the solution[143].

Complex and equilibrium	ω_{01} ($K_П$)	ΔH°, kcal mol^{-1}	ΔS°, e.u.	ΔV°, cm^3 mol^{-1}
$[Be(H_2O)_4]\cdot SO_4 \rightleftarrows [Be(SO_4)(H_2O)_3]$	100±20 (0.65±0.1)	1.4±0.8 (0.9±0.3)	14.0±0.3(2.2±1.5)	10±3 (3±2)

The data in Table 5 show that OSC predominate in the system of beryllium sulphate complexes, being formed with increase of entropy and molar volume. These OSC consist of $Be(H_2O)_4^{2+}$ tetrahedra and sulphate ions in contact with three water molecules of tetraaquoberyllium[143]. The entropy of formation of OSC by tetrahedral aquo-complexes is the same as that of the formation of "hydrophilic" OSC having an octahedral structure[15,30].

Aluminium and gallium sulphate complexes have been investigated by the analogous method involving the measurement of the pressure jump[145]. The predominance of OSC has been observed to an even greater extent for these compounds in solutions at ionic strengths of 0.1 than for beryllium. Here the equilibrium constant for the transformation of the OSC into the ISC is in the range 10^{-2}–10^{-1}.

Comparison of aluminium(III), gallium(III), and indium(III) monosulphate complexes shows that in this series the contribution of the inner-sphere interaction to the overall complex formation increases from aluminium(III) to indium(III). The considerable contribution or complete dominance of the OSC of metals with singly charged anions in aqueous salt solutions has been pointed out in many studies[134,146–166]. An increase of the degree of formation of OSC is observed with increase of the concentration of the supporting salt. The decrease of the activity of water under these conditions, of the kind which occurs after the introduction of non-aqueous solvents, has a particularly marked influence on the nature of the complexes of the light lanthanides[162]. This is associated with the greater stability of the aquo-complexes of the yttrium group compared with the cerium group[156].

The influence of non-aqueous solvents on the formation of the OSC of the lanthanides is determined mainly by the dielectric constant of the medium, while the formation of ISC is greatly influenced by the electron-donating properties of solvent molecules[163]. However, doubtful claims have been

made[156] that erbium(III) does not form ISC in methanol; certain objections have been made to this claim[165]. There has also been disagreement in the estimates for the formation of OSC by lanthanides, for example as regards the linkage of the perchlorate ion in the inner sphere[162,165] and the purely inner-sphere nature of fluoride and iodate associated species[155]. The cause of the presence of a covalent bond between lanthanide and nitrate ions in aqueous solutions[167] and of the absence of such a bond in tributyl phosphate solutions[147] has not been elucidated.

The attempts to solve the problem concerning the inner- and outer-sphere nature of the complexes of lanthanides with singly charged anions on the basis of the enthalpies and entropies of formation yielded doubtful results. This is because the above functions are small and are usually determined from the temperature variation of the equilibrium constants[28,29]. This can be seen in relation to the complexes with SO_4^{2-} and $Fe(CN)_6^{3-}$; on passing to doubly and triply charged anions, the contribution of lanthanide ISC increases[168-172].

The OSC of the actinide ions have been investigated in less detail than those of lanthanide ions. The chloride, thiocyanate, and polyaminocarboxylate complexes of tervalent actinides have been thoroughly investigated. Inner-sphere polyaminocarboxylate complexes of the actinides are more stable than those of the lanthanides[173-176]. The stability constants of the chloride complexes in 1–4 M solutions in LiCl are almost identical for tervalent actinides and lanthanides with the same ionic radii[150,177]. Only OSC are formed under the conditions indicated[150]. In solutions 10 M in LiCl the actinides (III) form mainly ISC,[178] like the lanthanides, the actinide complexes being more stable than the lanthanide complexes. An analogous situation has been observed[151,174,179-183] also on comparing the stability constants of lanthanide and actinide nitrate and thiocyanate complexes. In view of the similarity of the stability constants, it is possible to determine the type of coordination (in the inner or outer sphere) by analysing the enthalpies and entropies of formation[151,174,180].

Appreciable differences have been observed in the behaviour of the OSC of the actinides relative to the corresponding lanthanide complexes. In aqueous solutions of lanthanide chlorides and perchlorates without added ligands only OSC are formed[184], as in dilute solutions of the nitrates. Judging from the heats of dilution of solutions of these salts, their behaviour is determined by a two-group effect[184], i.e. by the influence of the properties of the cerium and yttrium group. The apparent molal enthalpies of aqueous solutions of these salts increase with increasing radius of the cations (as is shown particularly clearly for the chlorides), which is associated with the presence of hydration shells in the cations. A similar effect has not been observed for the actinide complexes.

Actinide(III) sulphate complexes probably involve the same contribution of the outer-sphere interaction as their lanthanide analogues, i.e. approximately 10%.[169,185] The formation of OSC on interaction of thorium(IV) and neptunium(IV) with sulphate ions[10,186] does not produce a notable effect.

The principal causes responsible for the contributions of different types of forces to the formation of OSC and ISC have been discussed[187]. Analogous but more general attempts had been made also in earlier studies[1-10,188].

V. CERTAIN FEATURES OF THE OUTER-SPHERE INTERACTION OF LABILE OUTER-SPHERE COMPLEXES

The above postulates and certain literature data quoted below make it possible to formulate a number of features of the outer-sphere interaction.

In the majority of systems of labile complexes the coordination "centres" forming the outer (second) coordination sphere are, as for the inert complexes, coordination-saturated cations and to a lesser extent anions. Complex cations with a labile first coordination sphere as well as those with an inert first coordination sphere interact consecutively with the ligands in the second sphere, which are located at definite points in space determined by the inner-sphere ligands. This has been satisfactorily confirmed[18-23,189,190] by the study of inert and, especially, labile OSC in which the strength of the bonds in the second sphere is as a rule much smaller than in the first. The forces of such interaction are predominantly electrostatic: $[ML_6]^{n\pm}...A^{m\pm}$.

At the same time numerous experimental data on the equilibria involving inert and labile[3-5,14,15] compounds, particularly neutral species[16], based on structural data obtained by NMR[18-23,67-80], EPR[27,62-65], and X-ray diffraction[112] as well as the influence of non-aqueous additives[45,47,95,198,199] confirm the important role of the inner-sphere ligand[5,143,199] in outer-sphere interactions. The donor–acceptor interaction of the outer-sphere ligand with the active centres of the inner sphere is outstanding in this respect. This type of interaction includes also hydrogen bonding[138]. The interaction can be represented schematically by $[M(L_6\text{-}l)]...A$, where $(L_6\text{-}l)$ are ligands containing free electron-donating or electron-accepting atoms l.

The coordination number, structure, nature of the bond, and the influence of OSC on the inner sphere are determined by the type of the $l \leftrightharpoons A$ interaction. The concept of the outer-sphere complex becomes much broader in this approach.

The thermodynamic properties of the OSC are determined by the contributions of the electrostatic and donor–acceptor interactions. In many systems the thermodynamic strengths of the binding of the ligands in the first and second coordination spheres are comparable[2]. In such cases it is usually impossible to observe a stepwise outer-sphere interaction. The first ligand, having become attached to the outer-sphere, then passes to the inner sphere. For example, anionic ligands[43-45,127] behave in this way in relation to solvated cations. In the systems indicated the effect of the outer-sphere interaction is manifested most clearly after the addition of the first ligand and then diminishes sharply[82] when the first ligand has been incorporated in the inner sphere.

The features examined above refer to the addition of the first ligand to the outer sphere. As in the stepwise interaction in the second sphere, this ligand adds to energetically favourable positions, determined by geometrical factors, within the complex cation with a saturated inner sphere[18-23]. The systems considered can be divided into three groups: (a) systems in which the formation of OSC greatly predominates; (b) systems with comparable amounts of OSC and ISC; (c) systems in which the formation of ISC greatly predominates. Systems of the first and third types can be studied by the usual methods, neglecting the formation of ISC or OSC. The majority of systems are of this kind.

The principal complications arise in the presence of comparable amounts of OSC and ISC. The formation of OSC and ISC is greatly influenced by the ionic strength of the solution and non-aqueous additives[45,127,189,191]. An increase of ionic strength and of the fraction of the non-aqueous additive reduces the contribution of the OSC and increases that of the ISC. A fairly considerable decrease of ionic strength can lead to the formation of OSC alone, while an increase of the amount of the non-aqueous additive, which lowers the dielectric constant of the medium, can lead to the formation of ISC only. These factors can be used in estimating the contributions of the OSC and ISC in systems where their amounts are comparable.

If the complex formation proceeds via the mechanism initial ions ⇋ OSC ⇋ ISC [see equilibrium (1)], then the overall equilibrium constant K_1 can be formulated thus: $K_1 = \omega_{0,1} + \beta_{10} = \omega_{0,1}(1 + K_\Pi)$.

We shall consider the influence of certain factors on $K_1, \omega_{0,1}$, and K_Π when ionic bonds predominate. For a series of identically charged cations, a number of changes occur when their radii increase[188].

1. The M–L attraction diminishes with increase of the distance between M and L. This effect entails a decrease of $\omega_{0,1}$ and K_Π.

2. The extent of local hydrolysis diminishes owing to the depolarisation of the inner-sphere water, which leads to a decrease of $\omega_{0,1}$.

3. (a) The degree of hydration of the cation diminishes, i.e. there is a partial displacement of water, which facilitates the entry of the anion into the coordination sphere;

(b) the degree of hydration of the cation decreases without the displacement of water from its first coordination sphere, which facilitates the incorporation of L into the first coordination sphere of M. Both these effects increase K_Π.

4. The energy of the stabilisation of the aquo-cation, arising as a result of the polarity of the water in the second sphere, progressively diminishes as L approaches M, which leads to a decrease of $\omega_{0,1}$ and K_Π.

Sometimes when M and L have electrostatic properties similar to those of the dipolar water molecules, the increase of K_Π by the third and fourth factors can be selective in relation to the enhancement of the M–L interaction or the increase of the dipole moment of water.

Using the above factors, it is possible to explain the characteristic features of the changes in many formation constants of OSC and ISC.

In the vast majority of the OSC examined the bond between solvated M and L is predominantly ionic, being complicated by the operation of dispersion and van der Waals forces as well as the contributions of the hydrogen bonds and charge transfer in accordance with the scheme M ← L.[194–197] As a rule the charges (or the charge and the dipole moment of L) as well as the radii of M and L determine the stability of the OSC formed. The contribution of the energy of stabilisation by the crystal field or the covalence of the M–L bond can increase K_Π and the sum $\beta_{10} + \omega_{0,1}$. From these standpoints, it is possible to account for the increase of the stability of the OSC with increasing charges on M and L, but the fraction of the OSC relative to the sum of the complexes then diminishes.

Analysis of the thermodynamics of the formation of the ISC and OSC leads to a thermodynamic criterion, which determines the type of complex predominant in the system. New thermodynamic results require correction for the conditions under which the criterion is applied: it is applicable only to "hydrophilic" cations and partly to "soft" anions, in terms of Pearson's terminology, which form OSC with a predominantly ionic bond.

The available literature data[28,29] for the OSC in systems of labile OSC refer mainly to acceptors M of class *a*, i.e. "hard" ions. For these acceptors, the overall stability of the halide complexes diminishes in the sequence of the anions $F^- \gg Cl^- > Br^- > I^-$. The contribution of the OSC to the overall effect of the interaction usually increases in the opposite sequence (from I^- to F^-), although frequently large, for example, complex anions with identical charges, form compounds with M, in which there is an increased contribution of the OSC.[2,3]

For copper(II) complexes, an increased tendency for ligands to enter the inner sphere compared with nickel(II) and cobalt(II) has been observed[38,45,127,133]. This property can probably be accounted for by the anisotropy[197] of the copper(II) ISC formed due to the Jahn–Teller effect.

Regardless of their composition, structure, and charge, all the "hydrophilic" complex cations form monoligand OSC on interaction with doubly charged anions, for which $\Delta S^\circ \cong 15$ e.u. in solutions at zero ionic strength[15]. This constancy of ΔS°, which so far is not altogether explicable, has been observed mainly for inert complexes and, if it is confirmed for labile systems, the problem of the identification of OSC will be solved.

Data for the variation of the stability of OSC and of their contribution to the overall complex formation effect as a function of the nature of the central ion are contradictory, although a correlation with the number of *d* electrons has been sometimes noted[127,192]. However, it is clear that the series of central ions corresponding to the variation of the stability of OSC and ISC are different[127]. These differences increase with increasing degree of covalence of the M–L bond in the first coordination sphere and with increase of the complexity of the interaction of the inner- and outer-sphere ligands.

Outer-sphere coordination entails a change in the length of the inner-sphere bond[198,199] in consequence of the enhancement of the polarisation of ligands. This induces a far-reaching rearrangement of the inner sphere, which is manifested by the enhancement of the acid properties of the metal aquo-ion[199], a change of the structure of the inner-sphere complex in the melt[200] and in the crystal[201], a change in the stretching vibration frequencies of the bonds[202,203], and ultimately a change in the reactivity of the compound[203]. All these phenomena, which fit within the framework of the fundamental concept of the mutual influence of ligands, have the specific features of an individual property of outer-sphere complexes, and can be referred to as the outer-sphere effect.

However, the insufficiency of data on the thermodynamics, structure, and kinetic properties of the OSC greatly hinders the extension of the generalisations. In order to be able to reach deeper conclusions, a considerable increase of the amount of information in this field is necessary.

REFERENCES

1. M.T.Beck, "The Chemistry of Complex Formation Equilibria" (Translated into Russian), Izd.Mir, Moscow, 1973, p.324.
2. V.E.Mironov, Doctoral Thesis, Lensovet Leningrad Technological Institute, Leningrad, 1963.
3. V.E.Mironov, Uspekhi Khim., **35**, 1102 (1966) [Russ.Chem.Rev., No.6 (1966)].
4. V.E.Mironov, Uspekhi Khim., **39**, 702 (1970) [Russ.Chem.Rev., No.4 (1970)].
5. Yu.A.Makashev and V.E.Mironov, Symposium "Termodinamika i Struktura Kompleksnykh i Sverkhkompleksnykh Soedinenii" (Thermodynamics and Structure of Complex and Ultracomplex Compounds), Uch.Zap.LGPI im.A.I.Gertsena, **385**, 4 (1969).
6. M.T.Beck, Coordin.Chem.Rev., **3**, 91 (1968).
7. J.Bjerrum, Adv.Chem.Ser., **62**, 178 (1967).
8. J.Bjerrum, "Proceedings of IIIrd Symposium on Coordination Chemistry (Debrecen, 1970)", Budapest, 1971, Vol.2, p.9.
9. S.Ahrland, "Proceedings of IIIrd Symposium on Coordination Chemistry (Debrecen, 1970)", Budapest, 1971, Vol.1, p.13.
10. S.Ahrland, Coordin.Chem.Rev., **8**, 21 (1972).
11. L.A.Ryazantseva, P.G.Antonov, and V.E.Mironov, Zhur.Neorg.Khim., **14**, 3211 (1969) [Russ.J.Inorg. Chem., No.12 (1969)].

12. I.N.Marov (Editor), "Metody i Dostizheniya Bioneorganicheskoi Khimii" (Methods and Achievements of Bioinorganic Chemistry), Izd.Mir, Moscow, 1978.
13. L.A.Ryazantseva, P.G.Antonov, and V.E.Mironov, Elektrokhimiya, **5**, 933 (1969).
14. V.M.Fadeev, Candidate's Thesis, Lensovet Leningrad Technological Institute, 1972.
15. A.K.Pyartman, Candidate's Thesis, Lensovet Leningrad Technological Institute, 1977.
16. A.V.Komarova, Candidate's Thesis, Lensovet Leningrad Technological Institute, 1971.
17. O.I.Koifman, T.A.Koroleva, and B.D.Berezin, Trudy Ivanovsk.Khim.-Tekhnol.Inst., No.20, 78(1976).
18. D.R.Eaton, Canad.J.Chem., **47**, 2645 (1969).
19. D.R.Eaton, H.O.Ogorodnykh, and L.Seville, Canad.J.Chem., **49**, 1218 (1971).
20. D.R.Eaton, Congr.on Bioinorganic Chemistry USA and Canada, Adv.Chem.Ser., **100**, 174 (1971).
21. D.R.Eaton, L.Seville, and J.P.Jesson, Canad.J. Chem., **49**, 2751 (1971).
22. D.R.Eaton and K.L.Chua, Canad.J.Chem., **51**, 4137 (1973).
23. A.M.Shchupik, V.M.Novikov, and K.I.Zamaraev, Dokl.Akad.Nauk SSSR, **214**, 629 (1974).
24. P.Hemmes, Chem. and Biol.Appl.Relaxat., NATO Adv.Study Inst. (Salford, 1974), Dordrecht–Boston, 1975, p.291.
25. M.Stadnikova, J.Smola, and P.Precehtel, Coll. Czech.Chem.Comm., **41**, 548 (1976).
26. J.Narbutt and S.J.Siekierski, J.Inorg.Nuclear Chem., **38**, 305 (1976).
27. V.I.Ermakov, V.V.Orlov, E.S.Shapiro, and P.A.Zagorets, Trudy Moskov.Khim.-Tekhnol. Inst.im.Mendeleeva, No.67, 124 (1970).
28. L.G.Sillén and A.E.Martell, "Stability Constants", Supplement No.1, Chem.Soc., London, 1971.
29. R.M.Smith and A.E.Martell, "Critical Stability Constants", Vol.4, Inorganic Complexes, Plenum Press, New York–London, 1976.
30. M.A.Chugunnikova, Candidate's Thesis, Lensovet Leningrad Technological Institute, 1976.
31. F.Posey and H.Taube, J.Amer.Chem.Soc., **75**, 1463 (1953).
32. F.Posey and H.Taube, J.Amer.Chem.Soc., **78**, 15 (1956).
33. W.M.Smithon and J.P.Williams, J.Amer.Chem.Soc., **80**, 457 (1958) [sic][This may be a reference to W.M.Smithson and R.J.P.Williams, J.Chem.Soc., 457 (1958)(Ed. of Translation)].
34. L.E.Orgel, "Introduction to Transition-Metal Chemistry–Ligand–Field Theory" (Translated into Russian), Izd.Mir, Moscow, 1964.
35. F.Basolo and R.G.Pearson, "Mechanisms of Inorganic Reactions" (Translated into Russian), Izd.Mir, Moscow, 1971, p.39.
36. E.Wendling, O.Buali-Bactich, and G.Yaker, Rev. Chim.Miner., **8**, 559 (1971).
37. C.K.Jørgensen, "Proceedings of the Symposium on Coordination Chemistry, Budapest, 1965", p.11.
38. V.E.Mironov, Yu.A.Makashev, I.Ya.Mavrina, and M.M.Kryzhanovskii, Zhur.Neorg.Khim., **15**, 1301 (1970) [Russ.J.Inorg.Chem., No.5 (1970)].
39. Yu.A.Makashev, M.I.Shalaevskaya, V.V.Blokhin, and V.E.Mironov, Zhur.Fiz.Khim., **38**, 2066 (1974) [Russ.J.Phys.Chem., No.8 (1974)].
40. Yu.A.Makashev, M.I.Shalaevskaya, V.V.Blokhin, and V.E.Mironov, Zhur.Fiz.Khim., **39**, 837 (1975) [Russ.J.Phys.Chem., No.4 (1975)].
41. V.E.Mironov, Yu.A.Makashev, I.Ya.Mavrina, and D.M.Markhaeva, Zhur.Fiz.Khim., **32**, 2987 (1968) [Russ.J.Phys.Chem., No.11 (1968)].
42. Yu.A.Makashev, F.Ya.Kul'ba, M.I.Agaf, Yu.A.Volokhov, and V.E.Mironov, Zhur.Fiz.Khim., **45**, 735 (1971) [Russ.J.Phys.Chem., No.3 (1971)].
43. V.E.Mironov, Yu.A.Makashev, and I.Ya.Mavrina, Zhur.Neorg.Khim., **14**, 1424 (1969) [Russ.J.Inorg. Chem., No.5 (1969)].
44. I.Ya.Mavrina, V.E.Mironov, and Yu.A.Makashev, See Ref.5, p.153.
45. M.I.Shalaevskaya, Candidate's Thesis, Gertsen Leningrad State Pedagogic Institute, 1975.
46. L.Johansson, Acta Chem.Scand., **25**, 3569 (1971).
47. F.Ya.Kul'ba, Yu.A.Makashev, and M.I.Shalaevskaya, "XXVIII Gertsenovskie Chteniya, Khimiya" (The XXVIIIth Gertsen Lectures, Chemistry), LGPI, im. A.I.Gertsena, Leningrad, 1976, p.30.
48. F.J.C.Rossotti and H.S.Rossotti, "Determination of Stability Constants and Other Equilibrium Constants in Solutions" (Translated into Russian), Izd.Mir, Moscow, 1965, p.330.
49. M.Eigen, Discuss.Faraday Soc., 17, 194 (1954).
50. M.Eigen and K.Tamm, Z.Elektrochem., **66**, 107 (1962).
51. I.Petrucci, "Ionic Interactions", Acad.Press, New York–London, 1971, Vol.2, p.39.
52. G.Köhler and H.Wendt, Ber Buns.Geselsch.Phys. Chem., **70**, 676 (1966).
53. P.Brumm and U.Rüppel, Ber.Buns.Geselsch.Phys. Chem., **75**, No.2, 102 (1971).
54. C.Kalidas, W.Knoche, and D.Papadopulos, Ber.Buns. Geselsch.Phys.Chem., **75**, No.2, 106 (1971).
55. A.Carrington and A.D.McLachlan, "Introduction to Magnetic Resonance; With Applications to Chemistry and Chemical Physics" (Translated into Russian), Izd.Mir, Moscow, 1970.
56. I.B.Bersuker, "Elektronnoe Stroenie i Svoistva Koordinatsionnykh Soedinenii" (The Electronic Structure and Properties of Coordination Compounds), Izd.Khimiya, Leningrad, 1976.
57. V.V.Blokhin, G.K.Ragulin, V.A.Anufrienko, Yu.A.Makashev, and V.E.Mironov, Zhur.Fiz.Khim., **44**, 2654 (1970) [Russ.J.Phys.Chem., No.10 (1970)].
58. V.V.Blokhin, V.F.Anufrienko, Yu.A.Makashev, and V.E.Mironov, Zhur.Fiz.Khim., **45**, 1960 (1971) [Russ.J.Phys.Chem., No.8 (1971)].
59. N.A.Kostromina, Symposium, "Voprosy Kinetiki i Kataliza" (Problems of Kinetics and Catalysis), Ivanovo, 1974, No.2, p.85.
60. R.G.Hayes and R.J.Myers, J.Chem.Phys., **40**, 877 (1964).
61. D.C.McCain and R.J.Myers, J.Phys.Chem., **72**, 4115 (1968).
62. V.B.Blokhin, L.I.Razmyslova, Yu.A.Makashev, and V.E.Mironov, "Nauchno-Tekhnicheskaya Konferentsiya LTI im.Lensoveta, Kratkie Soobshcheniya" (The Science and Engineering Conference of the Lensovet Leningrad Technological Institute. Brief Communications), Leningrad, 1972, p.51.
63. R.Burlamacchi and E.Tiezzi, J.Molec.Struct., **2**, 261 (1968).
64. R.Burlamacchi and E.Tiezzi, J.Phys.Chem., **73**, 1588 (1969).
65. R.Burlamacchi, E.Tiezzi, and G.Martini, J.Phys. Chem., **74**, 8, 1809 (1970).
66. O.Benali-Baitich and E.Wendling, Canad.J.Chem., **54**, 878 (1976).

67. R.Haque and N.Cyr, Trans.Faraday Soc., **66**, 1848 (1970).
68. G.Gordon and W.Melvin, "Proceedings of the IIIrd Symposium on Coordination Chemistry (Debrecen, 1970)", Budapest, Vol.1, p.45.
69. M.Alei, Inorg.Chem., **3**, 44 (1964).
70. T.R.Strengle and C.H.Langford, J.Phys.Chem., **69**, 3299 (1965).
71. B.N.Chernyshev, Candidate's Thesis, Institute of Chemistry, USSR Academy of Sciences, Vladivostok, 1973.
72. V.A.Shcherbakov, Symposium "Spektroskopicheskie Metody v Khimii Kompleksnykh Soedinenii" (Spectroscopic Methods in the Chemistry of Complex Compounds), Izd.Khimiya, Moscow–Leningrad, 1964, p.203.
73. V.A.Shcherbakov, Candidate's Thesis, Leningrad, 1967.
74. V.A.Shcherbakov, B.N.Chernishov, and R.L.Davidovich, Spectr.Letters, **5**, 213 (1972).
75. V.A.Shcherbakov, B.N.Chernishov, and R.L.Davidovich, Spectr.Letters, 5, 421 (1972).
76. V.A.Shcherbakov, B.N.Chernishov, and R.L.Davidovich, Spectr.Letters, **6**, 115 (1973).
77. V.I.Chizhik, Symposium "Termodinamika i Stroenie Rastvorov" (Thermodynamics and the Structure of Solutions), Ivanovo, 1976, No.5, p.11.
78. J.W.Akitt, N.N.Greenwood, and B.L.Khandewal, Dalton J.Chem.Soc., 1226 (1972).
79. V.M.Vdovenko, V.A.Shcherbakov, A.P.Gulya, and A.V.Ablov, Zhur.Neorg.Khim., 18, 843 (1973) [Russ. J.Inorg.Chem., No.3 (1973)].
80. A.J.Leffler, J.Phys.Chem., **74**, 2910 (1970).
81. V.A.Glebov and T.M.Nikitina, Koord.Khim., 1, 1106 (1975).
82. R.Larsson, Acta Chem.Scand., **18**, 1923 (1964).
83. Yu.A.Volokhov, N.I.Eremin, and V.E.Mironov, Symposium, "Issledovaniya v Oblasti Neorganicheskoi Tekhnologii" (Studies in Inorganic Technology), Izd.Nauka, Leningrad, 1972, p.258.
84. Yu.A.Volokhov, Candidate's Thesis, Lensovet Leningrad Technological Institute, 1971.
85. S.Froneus and R.Larsson, Acta Chem.Scand., **16**, 1433 (1965).
86. H.Brintsinger, Helv.Chim.Acta, **48**, 47 (1965).
87. S.Froneus and R.Larsson, "Proceedings of the VIIIth International Congress on Coordination Chemistry", Vienna–New York, 1964, p.383.
88. R.E.Hester, R.A.Plane, and G.E.Walrafen, Chem. Phys., **38**, 249 (1963).
89. R.E.Hester, R.A.Plane, and G.E.Walrafen, Chem. Phys., **40**, 411 (1964).
90. R.E.Hester, R.A.Plane, and G.E.Walrafen, Inorg. Chem., **3**, 768 (1964).
91. R.E.Hester, R.A.Plane, and G.E.Walrafen, Inorg. Chem., **3**, 769 (1964).
92. A.R.Devis and C.Chong, Inorg.Chem., 11, 1891 (1972).
93. Z.Libus, Inorg.Chem., **12**, 2972 (1973).
94. Z.Libus and H.Tailowska, J.Solut.Chem., **4**, 1011 (1975).
95. Z.Libus and W.Maciejewski, Roczniki Chem., **50**, 1661 (1976).
96. K.B.Yatsimirskii, Symposium, "Termodinamika i Struktura Rastvorov" (Thermodynamics and the Structure of Solutions), Izd.Akad.Nauk SSSR, Moscow, 1959, p.133.
97. V.P.Vasil'ev, Zhur.Neorg.Khim., 7, 555 (1962) [Russ.J.Inorg.Chem., No.3 (1962)].
98. V.P.Vasil'ev et al., Zhur.Fiz.Khim., **37**, 1089 (1963) [Russ.J.Phys.Chem., No.5 (1963)].
99. V.P.Vasil'ev and N.K.Grechina, Zhur.Neorg.Khim., 9, 641 (1964) [Russ.J.Inorg.Chem., No.3 (1964)].
100. V.P.Vasil'ev et al., Izv.Vys.Ucheb.Zaved., Khim.i Khim.Tekhnol., 339 (1963).
101. V.V.Blokhin, L.I.Razmyslova, Yu.A.Makashev, and V.E.Mironov, Zhur.Fiz.Khim., **48**, 151 (1974) [Russ. J.Phys.Chem., No.1 (1974)].
102. V.E.Mironov, Yu.A.Makashev, and V.V.Blokhin, Zhur.Fiz.Khim., **45**, 772 (1971) [Russ.J.Phys.Chem., No.4 (1971)].
103. L.A.Kul'vinova, V.V.Blokhin, and V.E.Mironov, Zhur.Fiz.Khim., **50**, 1287 (1976) [Russ.J.Phys. Chem., No.5 (1976)].
104. V.P.Vasil'ev, Trudy Ivanovsk.Khim.-Tekhnol.Inst., No.10, 17 (1968).
105. R.Aruga, J.Nuclear Inorg.Chem., **36**, 3779 (1974).
106. R.Aruga, J.Chem.Soc., Dalton Trans., 2534 (1975).
107. J.W.Larsson, J.Phys.Chem., **74**, 3392 (1970).
108. F.H.Fisher, J.Phys.Chem., **69**, 695 (1965).
109. F.H.Fisher, J.Phys.Chem., **69**, 8, 2595 (1965).
110. V.A.Latysheva, Zhur.Obshch.Khim., **41**, 1889 (1971).
111. T.S.Spiro, A.Revers, and J.Lee, J.Amer.Chem. Soc., **90**, 4000 (1968).
112. A.K.Dorosh, Dokl.Akad.Nauk Ukrain.SSR, B, 7, 612 (1976).
113. D.L.Wertz and J.L.Tyvoll, J.Inorg.Nuclear Chem., **36**, 3713 (1974).
114. M.L.Steele and D.L.Wertz, J.Amer.Chem.Soc., **98**, 4424 (1976).
115. O.Ya.Samoilov, "Struktura Vodnykh Rastvorov Elektrolitov i Gidratatsiya Ionov" (The Structure of Aqueous Electrolyte Solutions and Ion Hydration), Izd.Akad.Nauk SSSR, Moscow, 1957.
116. K.P.Mishchenko and G.M.Poltoratskii, "Voprosy Termodinamiki i Stroeniya Vodnykh i Nevodnykh Rastvorov Elektrolitov" (Problems of the Thermodynamics and Structure of Aqueous and Non-Aqueous Electrolyte Solutions), Izd.Khimiya, Leningrad, 1968.
117. G.A.Krestov, "Termodinamika Ionnykh Protsessov v Rastvorakh" (Thermodynamics of Ionic Processes in Solutions), Izd.Khimiya, Leningrad, 1973.
118. R.J.P.Williams, J.Phys.Chem., **58**, 121 (1954).
119. K.Schug and E.L.King, J.Amer.Chem.Soc., 80, 1089 (1958).
120. D.F.C.Morris and S.D.Hammond, Electrochem.Acta, **13**, 545 (1968).
121. N.C.Naic and R.K.Namda, J.Inorg.Chem., 36, 3793 (1974).
122. V.A.Fedorova, V.E.Mironov, and F.Ya.Kul'ba, Zhur.Neorg.Khim., 7, 2529 (1962) [Russ.J.Inorg. Chem., No.11 (1962)].
123. J.M.Christiansen and R.M.Izatt, "Handbook of Metal Ligand Heats and Related Thermodynamic Quantities", Dekker, New York, 1970.
124. S.A.Shukarev, L.S.Lilich, and V.A.Latysheva, Zhur.Neorg.Khim., 36 (1956).
125. V.E.Mironov, N.P.Kolobov, and M.A.Chugunnikova, "Doklady XII Vsesoyuznogo Chugaevskogo Soveshchaniya po Khimii Koordinatsionnykh Soedinenii, Novosibirsk, 1975" (Reports at the XIIth All-Union Chugaev Conference on the Chemistry of Coordination Compounds, Novosibirsk, 1975), p.22.
126. V.E.Mironov, A.K.Pyartman, and N.P.Kolobov, Zhur.Fiz.Khim., **50**, 7 (1976) [Russ.J.Phys.Chem., No.1 (1976)].

127. T.N.Koneva, Candidate's Thesis, Kirov Kazakh State University, Alma-Ata, 1975.
128. M.H.Hutchinson and W.C.E.Higginson, J.Chem. Soc., Dalton Trans., 1247 (1973).
129. L.I.Razmyslova, Candidate's Thesis, Lensovet Leningrad Technological Institute, 1973.
130. A.A.Anashkina, Candidate's Thesis, Gertsen Leningrad State Pedagogic Institute, Leningrad, 1972.
131. H.A.Schwartz and R.W.Dodson, J.Phys.Chem., **80**, 2801 (1976).
132. M.M.Kryzhanovskii, Candidate's Thesis, Leningrad, 1969.
133. V.V.Blokhin, Candidate's Thesis, Leningrad, 1970.
134. N.K.Davidenko, Doctoral Thesis, Institute of Physical Chemistry, Academy of Sciences of Ukrainian SSR, Kiev, 1971.
135. P.I.Protsenko, O.N.Shokina, and N.P.Chekhunova, Zhur.Fiz.Khim., **38**, 1857 (1964) [Russ.J.Phys. Chem., No.7 (1964)].
136. R.E.Hester and R.A.Plane, J.Chem.Phys., **45**, 4588 (1966).
137. R.E.Hester and W.E.L.Grossman, Spectrochim.Acta, **A23**, 1945 (1967).
138. J.E.Prue, "Essays in Coordination Chemistry", New York, 1964, p.157.
139. I.D.Isaev, Candidate's Thesis, Institute of Inorganic Chemistry, USSR Academy of Sciences, Novosibirsk, 1974.
140. N.Babakulov, Candidate's Thesis, Leningrad State University, Leningrad, 1975.
141. E.G.Grigor'eva, Candidate's Thesis, Leningrad State University, Leningrad, 1975.
142. H.Strehlow and W.Knoche, Ber.Buns.Geselsch. phys.Chem., **73**, 427 (1969).
143. W.Knoche, Chem.and Biol.Appl.Relax.Spectrometry, Proc.NATO Adv.Study Inst., Salford, 1974; Dordrecht–Boston, 1975, p.265.
144. W.Knoche, C.A.Firth, and D.Hess, Adv.Molec. Relax.Proc., 6, 1 (1974).
145. B.Behr and H.Wendt, Z.Elektrochem., **66**, 223 (1962).
146. J.Brady, Chem.Phys., **33**, 1079 (1960).
147. G.R.Choppin and W.F.Strazik, Inorg.Chem., 4, 1250 (1965).
148. J.C.Barnes, J.Chem.Soc., 3880 (1964).
149. G.R.Choppin and A.J.Graffeo, Inorg.Chem., 4, 1254 (1965).
150. G.R.Choppin and P.J.Unrein, J.Inorg.Nuclear Chem., **25**, 387 (1963).
151. G.R.Choppin and J.J.Ketels, J.Inorg.Nuclear Chem., 27, 1335 (1965).
152. N.A.Goward and R.W.Kiser, J.Phys.Chem., **70**, 213 (1966).
153. G.R.Choppin, D.E.Henrie, and K.Buys, Inorg. Chem., 5, 1743 (1966).
154. G.R.Choppin, Pure Appl.Chem., **27**, 23 (1971).
155. G.R.Choppin and S.Z.Bertha, J.Inorg.Nuclear Chem., **35**, 1309 (1973).
156. N.N.Kozachenko, N.A.Panteleeva, V.V.Netsveteeva, and I.M.Batyaev, Zhur.Neorg.Khim., **18**, 1776 (1973) [Russ.J.Inorg.Chem., No.7 (1973)].
157. I.Abrahamer and Y.Marcus, Inorg.Chem., **6**, 2103 (1967).
158. B.Voleisiene and E.Jaronis, Nauch.Trudy.Vys. Ucheb.Zaved.Lit.SSR ("Ul'trazvuk"), No.6, 33 (1974).
159. H.B.Silber, J.Phys.Chem., **78**, 1940 (1974).
160. N.N.Kozachenko and I.M.Batyaev, Zhur.Neorg.Khim., 16, 125 (1971) [Russ.J.Inorg.Chem., No.1 (1971)].
161. N.N.Kozachenko, I.M.Batyaev, and V.E.Mironov, Zhur.Neorg.Khim., **15**, 888 (1970) [Russ.J.Inorg. Chem., No.3 (1970)].
162. H.B.Silber and A.Pezzica, J.Inorg.Nuclear Chem., **38**, 2053 (1976).
163. B.M.Antipenko, I.M.Batyaev, and T.A.Privalova, Zhur.Neorg.Khim., **20**, 12 (1975) [Russ.J.Inorg. Chem., No.1 (1975)].
164. G.A.Shutova, K.B.Yatsimirskii, and T.A.Mal'kova, Zhur.Neorg.Khim., **13**, 2708 (1968) [Russ.J.Inorg. Chem., No.10 (1968)].
165. J.Reidler and H.J.Silber, J.Phys.Chem., **78**, 424 (1974).
166. K.P.Khopkar and J.N.Mathur, J.Inorg.Nuclear Chem., **36**, 3819 (1974).
167. L.I.Katzin and M.L.Barnet, J.Phys.Chem., **68**, 3779 (1964).
168. A.V.Stepanov, Zhur.Neorg.Khim., **18**, 371 (1973) [Russ.J.Inorg.Chem., No.2 (1973)].
169. R.G.Carvalho and G.R.Choppin, J.Inorg.Nuclear Chem., **29**, 737 (1967).
170. A.Bellomo, A.Casale, and D.De Marco, Talanta, **20**, 338, 355 (1973).
171. R.Stampfli and G.R.Choppin, J.Inorg.Nuclear Chem., **34**, 205 (1972).
172. A.Bellomo, D.De Marco, and A.Easale, Ann.Chim., **63**, 477 (1973).
173. G.Schwarzenbach, R.Gut, and G.Anderegg, Helv. Chim.Acta, **37**, 936 (1954).
174. G.Füger and B.B.Cunnigham, J.Inorg.Nuclear Chem., **27**, 1079 (1965).
175. R.D.Baybarz, J.Inorg.Nuclear Chem., **21**, 1837 (1965).
176. H.Brandau, Inorg.Nuclear Chem.Letters, 7, 1177 (1971).
177. D.F.Peppard, G.W.Mason, and I.Huchar, J.Inorg. Nuclear Chem., 33, 495 (1971).
178. M.Shiloh and Y.Marcus, J.Inorg.Nuclear Chem., **28**, 2725 (1966).
179. H.D.Harmon, J.R.Petterson, W.J.McDowell, and C.F.Coleman, J.Inorg.Nuclear Chem., **34**, 1381 (1972).
180. P.K.Khopkar and J.N.Mathur, J.Inorg.Nuclear Chem., **36**, 3819 (1974).
181. A.D.Jones and G.R.Choppin, Actin.Rev., 1, 311 (1969).
182. B.M.Antipenko, V.M.Ermolaev, and T.A.Privalova, Zhur.Neorg.Khim., 17, 651 (1972) [Russ.J.Inorg. Chem., No.3 (1972)].
183. C.L.Rao, C.J.Shahani, and K.A.Mathew, Inorg. Nuclear Chem.Letters, **4**, 655 (1968).
184. F.H.Spedding, C.W.De Kock, G.W.Pepple, and A.Habeschuss, J.Chem.Eng.Data, **22**, 58 (1977).
185. D.P.Fay, D.Litchinsky, and N.Puride, J.Phys. Chem., **73**, 544 (1965).
186. S.Ahrland, Struct.Bonding (Berlin), 5, 118 (1968).
187. B.Gruenewald, W.Knoche, and N.M.Rees, J.Chem. Soc.Dalton Trans., 2338 (1976).
188. D.R.Rosseinsky, J.Chem.Soc., 787 (1962).
189. J.F.Coetzee, Pure Appl.Chem., **49**, 27 (1977).
190. V.V.Trofimov and B.S.Krumgal'z, Zhur.Fiz.Khim., **50**, 146 (1976) [Russ.J.Phys.Chem., No.1 (1976)].
191. T.N.Koneva, Symposium, "Fizicheskaya Khimiya" (Physical Chemistry), Krasnoyarsk, 1975, No.2, p.84.
192. T.N.Koneva, V.A.Fedorov, and G.L.Trofimov, Zhur.Fiz.Khim., **51**, 793 (1977) [Russ.J.Phys.Chem., No.4 (1977)].

193. T.N.Koneva and V.A.Fedorov, Symposium, "Fizicheskaya Khimiya" (Physical Chemistry), Krasnoyarsk, 1975, No.2, p.92.
194. L.S.Frankel, J.Phys.Chem., **73**, 3897 (1969).
195. U.Mayer, Coord.Chem.Rev., **21**, 159 (1976).
196. P.L.Huyskens, "Symposium on Ions and Ion-Pairs Non Aqueous Media, Leuven, 1976", p.145.
197. N.N.Knyazeva, Candidate's Thesis, Lensovet Leningrad Technological Institute, Leningrad, 1974.
198. V.Gutmann and R.Schmidt, Coord.Chem.Rev., **12**, 263 (1974).
199. V.Gutmann, Chimia (Switz.), **31**, 1 (1977).
200. S.V.Volkov and N.I.Buryak, Zhur.Neorg.Khim., **22**, 150 (1977) [Russ.J.Inorg.Chem., No.1 (1977)].
201. Yu.Ya.Kharitonov and G.B.Seifer, Zhur.Neorg.Khim., 11, 1973 (1966) [Russ.J.Inorg.Chem., No.8 (1966)].
202. S.P.Gabuda and S.V.Zemskov, "YaMR v Kompleksnykh Soedineniyakh" (NMR in Complexes), Izd.Nauka, Novosibirsk, 1976.
203. A.B.Nikol'skii, Doctoral Thesis, Leningrad State University, Leningrad, 1977.

Lensovet Leningrad
Technological Institute

Translated from *Uspekhi Khimii*, 49, 1214-1233 (1980) U.D.C. 547.1'13

Diastereotopy in Transition Metal Complexes

G.B.Shul'pin

Cases of diastereotopy—the stereochemical non-equivalence of atoms or groups within a single molecule—in transition metal complexes are examined. The application of the concept of diastereotopy, introduced into stereochemistry several years ago, makes it possible to interpret correctly complex nuclear magnetic resonance spectra and to reach on their basis conclusions about the fine structure of the molecule. Instances of the diastereotopy of the atoms of coordinated ligands and other groups in π-complexes are classified.
The bibliography includes 63 references.

CONTENTS

I. Introduction 645
II. Diastereotopy in cyclic ligands linked to an asymmetric atom 647
III. Diastereotopy induced by planar chirality 650
IV. Diastereotopy in achiral molecules 651
V. Diastereotopy in α-metallocenyl-substituted carbonium ions 651
VI. Certain other cases of diastereotopy 653
VII. Chemical non-equivalence of diastereotopic atoms 653

I. INTRODUCTION

In the middle of the 1960's enormous factual NMR data required a detailed analysis of the stereochemistry of molecules containing seemingly equivalent atoms or groups of atoms, which, however, are manifested in the spectra by different signals. Such generalisations were made by Mislow and Raban[1]

It was found that sometimes atoms or groups, which are at first sight identical, are in fact in different steric environments. Structurally identical atoms or groups have been divided into three categories in accordance with the stereochemical characteristics of the environment. Atoms or groups capable of being interchanged by simple rotation of the molecule about an n-fold axis are called equivalent. As an example, one may quote the hydrogen atoms in methyl chloride (rotation about the threefold axis passing through the carbon and chlorine atoms), the geminal hydrogen atoms in ethylene, the methyl groups in acetone (in both cases the atoms or groups are interchangeable on rotation about the twofold axis passing along the double bond). It the atoms or groups are not interchangeable on rotation but each occupies the site of the other on reflection in a mirror plane (in the more general case when they are linked by a rotation-reflection axis S_n), then such atoms are referred to as enantiotopic (by analogy with the relations between molecules linked by mirror symmetry, which are known as enantiomers). An example of enantiotopic atoms is provided by the two protons in bromochloromethane.

Equivalent and enantiotopic atoms and groups are subject to identical magnetic shielding and hence are manifested in NMR spectra by signals having equal, equivalent chemical shifts. One should note that in the majority of molecules two stereochemically equivalent or enantiotopic nuclei respond differently to other nuclei in the molecule as regards spin–spin interaction. Thus the equivalent hydrogen atoms in the molecule of 1,1-difluoroethylene should have spin–spin coupling constants with two fluorine atoms (for each hydrogen nucleus, one of the fluorine nuclei is in the *cis*-position and the other is in the *trans*-position). Such hydrogen nuclei are referred to as magnetically non-equivalent (as regards the spin–spin coupling). Two nuclei with identical chemical shifts are magnetically equivalent as regards spin–spin coupling only when they are disposed symmetrically relative to any "trial" nucleus within the limits of the given group of magnetically interacting nuclei. Magnetically equivalent nuclei should be interchangeable on reflection in a plane perpendicular to the line connecting these nuclei and passing through the "trial" nucleus[2]. In *p*-chloronitrobenzene the stereochemically equivalent *ortho*-protons have the same chemical shift. However, two such protons interact differently with one of the *meta*-protons and are therefore non-equivalent as regards spin–spin coupling. The four protons of *p*-chloronitrobenzene form the AA'XX' system.

Cases are possible in which structurally identical atoms or groups within the limits of a single molecule are in diastereoisomeric environments and cannot change places whatever the symmetry operation. Such atoms or groups have been called diastereotopic (by analogy with diastereoisomeric relations between molecules). The hydrogen atoms of the methylene groups of chlorocyclobutane (two pairs of diastereotopic atoms) and of bromodichloroethane $ClCH_2$–$CHClBr$ are diastereotopic; in the second molecule the methylene group is linked to an asymmetric tetrahedral carbon atom. However, it must be emphasised that the presence of a chiral centre in the molecule is not an obligatory condition for the occurrence of diastereotopy. Thus the chlorocyclobutane molecule is achiral†. Another important example is the diastereotopy of the geminal protons in achiral monosubstituted ethylene. Since the diastereotopic atoms are in somewhat different steric environments, their magnetic shielding should differ (for example, the hydrogen atoms in the chlorocyclobutane molecule in the *trans*-position with respect to chlorine are influenced by the halogen atom less than the *cis*-atoms) and in the general case diastereotopic atoms should be manifested in the NMR spectra in the form of signals with different chemical shifts (it is said that such atoms are anisochronous). Naturally the resolving power of a specific NMR apparatus can be insufficient to detect different signals for diastereotopic nuclei: diastereotopic nuclei remain isochronous.

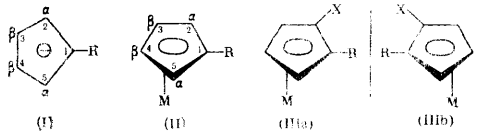
The groups $-CH_2R(R \neq H)$ and $-C(CH_3)_2R(R \neq CH_3)$ proved to be convenient and fairly sensitive indicators reflecting the stereochemistry of the molecule. In most cases these groups are enantiotopic and hence isochronous. When a

† The molecule is called chiral, if it cannot be made to coincide with its image in a planar mirror[3].

chiral centre is introduced into the molecule the H atoms or CH_3 group become diastereotopic, which is reflected in the splitting of the corresponding signals in the NMR spectra. We may note that the carbon atoms linked to H or CH_3 in these groups are prochiral centres, since the replacement of one of the hydrogen atoms or one of the methyl groups by some other atom or group makes the carbon atoms chiral.

Potentially diastereotopic organometallic groups have been recently attracting increasing attention. In the monosubstituted cyclopentadienyl anion (I) the α-atoms (as well as β-atoms) of carbon and hydrogen are stereochemically equivalent, since they are linked by a twofold axis of rotation passing through the substituent and the nodal $C_{(1)}$ atom. The coordination of the cyclopentadienyl anion to a metal atom as in formula (II) makes the two sides ("above" and "below") of the plane of the cyclic ligand non-equivalent and the atoms in the α-position with respect to the substituent become enantiotopic, because they can be interchanged only on reflection in the mirror plane passing through the substituent, the $C_{(1)}$ atoms linked to it, and the metal atom; the same applies also to the β-atoms. At the same time the protons in the 2- and 5- (or 3- and 4-) positions in a monosubstituted cyclopentadienyl anion (stereochemically equivalent) and ferrocene (enantiotopic) are magnetically non-equivalent as regards spin–spin coupling. Indeed the 2- and 5-nuclei are disposed asymmetrically relative to the 3-nucleus and interact with the latter in different ways. The system of four magnetically interacting protons in a monosubstituted metallocene can be described as AA'BB'.

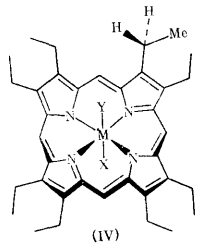
We may note that the replacement of one of the hydrogen atoms of the substituted cyclopentadienyl (CPD) by a group X gives rise to chirality in the molecule, the so called planar chirality. Two enantiomers (IIIa) and (IIIb) are therefore possible:



(I) (II) (IIIa) (IIIb)

Thus the monosubstituted CPD ligand coordinated to a metal atom is a group with enantiotopic carbon and hydrogen atoms within the 2/5 and 3/4 pairs; under certain conditions, these atoms can be converted into diastereotopic atoms. The present review is devoted to the discussion of various cases of the diastereotopy of atoms in this and similar indicator groups.

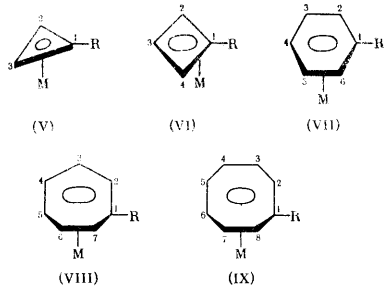
The study of the diastereotopy of atoms and groups is important for several reasons. Such analysis permits an exact interpretation of the NMR spectra of the compounds synthesised and is therefore essential for the determination of their structures. Enantiotopic and diastereotopic relations between atoms within a single molecule are linked directly to the stereochemical (enantiomeric and diastereoisomeric) relations between molecules. For example, the diastereotopy of indicator groups makes it possible to establish in many instances the presence of chirality in the molecule (either its appearance or disappearance). Thus the appearance of diastereotopy in the $-Sn(CH_3)_2R$ indicator group when the migration of this fragment in the cyclopentadiene ring is retarded, has been used to determine the energetics of the metallotropic process[4]. The observation of diastereotopy makes it possible to establish the fine features of the molecular structure. Thus the diastereotopy of the protons of the methylene groups in derivatives of metal octaethylporphyrinates (IV)[5] indicates either the coordination of two different ligands X and Y to the metal atom or the displacement of the metal atom from the plane of the porphyrin ring.



(IV)

In both cases the diastereotopy is due to the non-equivalence of the two sides of the porphyrin ring arising under these conditions (consequently the difference between the chemical shifts is not related to the hindered rotation of the ethyl groups). Finally, diastereotopic atoms have somewhat different reactivities, which must be taken into account, in particular, in the study of reaction mechanisms. Analysis of the stereochemical relations of the atoms and groups within the limits of a single molecule makes it possible to predict the direction of the reaction. It is not therefore surprising that such analysis is beginning to be formulated as a special branch of stereochemistry. We may note several reviews devoted to the theory of diastereotopy[1,2,8] (see also Sokolov[6] and Shul'pin[7]). The diastereotopy of the nuclei in transition metal complexes has not been considered in special reviews.

A coordinated monosubstituted CPD ligand is one of the most convenient organometallic indicator groups which have been investigated in comparative detail. However, the coordination of other cyclic ligands to transition metal atoms should also lead to the appearance of the enantiotopy of the atoms in these ligands and under certain conditions should also lead to diastereotopy. In a coordinated cyclopropenylium cation (V) this refers to the 2/3 pair of atoms. In the cyclobutadiene ligand (VI) and 2/4 nuclei are enantiotopic (and can become diastereotopic). In the coordinated substituted benzene (VII) there are two pairs of enantiotopic atoms (2/6 and 3.5), as in CPD. In the cycloheptatrienyl ligand (VIII) there are three such pairs: 2/7, 3/6, and 4.5. In the cyclooctatetraenyl groups (IX) there are also three such pairs: 2/8, 3/7, and 4/6. The observation of the diastereotopy of the nuclei in some of these systems is a task for the future.



(V) (VI) (VII)

(VIII) (IX)

As already pointed out, the diastereotopy of atoms is not always manifested in NMR spectra, i.e. such atoms are not necessarily anisochronous. Whether or not diastereotopy is detected in the spectra depends on many factors. The account below will make it clear that the diastereotopy of a coordinated substituted CPD ligand has been observed much more frequently in ^{13}C NMR spectra than in proton resonance spectra. It is therefore understandable why the phenomenon of the diastereotopy in metallocenes has attracted the attention of investigators only recently when ^{13}C NMR has begun to be used widely. The manifestation of diastereotopy in the spectra is influenced greatly by the solvent. The overall signal of the diastereotopic atoms is sometimes split on

passing to a more polar solvent. We may note that in the general case enantiotopic atoms can become anisochronous in an enantiomeric solvent[1].

Certain cases of the diastereotopy of the atoms in a substituted coordinated cyclopentadienyl group and other cyclic ligands, caused by the stereochemical features of the metallocene molecules, are examined below. The diastereotopy of other indicator groups, indiced by the chirality of the metallocenyl fragment linked to them and the chemical non-equivalence of the diastereotopic nuclei in ferrocene derivatives, are discussed in the last sections of the review.

II. DIASTEREOTOPY IN CYCLIC LIGANDS LINKED TO AN ASYMMETRIC ATOM

1. The Classical Asymmetric Carbon Atom

The ^{1}H NMR spectrum of a coordinated monosubstituted CPD ligand depends greatly on the electron-donating or electron-accepting capacity of the substituent. In the spectra of monosubstituted ferrocenes and other metallocenes with electron-accepting substituents (for example, with the acetyl group) the protons of the substituted ring are manifested by two pseudotriplets in the range $\delta = 4-5$ p.p.m. relative to tetramethylsilane (TMS). The unsubstituted ring gives rise to a singlet with a chemical shift of ~4 p.p.m. In the spectra of alkyl derivatives of metallocenes the protons of the substituted ring usually give rise to a narrow multiplet and are frequently manifested actually in the form of a singlet signal. Thus the ^{1}H NMR spectrum of 1,1'-di-(2-cyanoethyl)ferrocene has a single fairly narrow unresolved multiplet centred at 4.09 p.p.m. In the calculated spectrum the chemical shift of the α-protons is assumed equal to -1.1 Hz and that of the β-protons is assumed to be +1.1 Hz from the centre of the multiplet (in $CHCl_3$ at a frequency of 90 MHz).[9] It is not therefore surprising that for a long time it was impossible to observe the effect of the stereochemistry of the substituent in the ^{1}H NMR spectra of metallocenes.

Table 1. The chemical shifts of the protons of the substituted CPD ring in the ^{1}H NMR spectra of cymantrenes containing an asymmetric carbon atom in the substituent [in $CHCl_3$, δ(p.p.m.) relative to TMS].[11,12]

Substituent	$H_{(2,5)}$	$H_{(3,4)}$	References
—CH (OH) CH_3	4.78	4.61	11
—CH (OH) CF_3	4.87; 5.03	4.68	11
—CH (OH) C_6H_5	4.63; 4.86	4.58	11
—C (CH_3) (OH) P (O) (OC_2H_5)$_2$	4.90; 5.20	4.51; 4.70	11
—C (CH_3) (OH) P (O) (OC_4H_9)$_2$ CH_3	4.91; 5.23	4.53; 4.72	11
—C (OH) (CH_3) C_6H_5	4.76; 4.94	4.61	12
—C (OH) (CH_3) C_6H_5	4.82; 4.89	4.51	12
—C (OH) (C_6H_5) $C_6H_4OCH_3$-*p*	4.84	4.64	12

The stereochemical non-equivalence of the α-protons of the CPD ring was first observed in 1971 in the ^{1}H NMR spectra of 1,1,1-trifluoro-2-hydroxyethylcymantrene[10]. The α-protons were manifested in the spectrum in the form of two signals (Table 1). The splitting of the signals of both α- and β-protons was observed in the spectra of cymantrenes containing some cumbersome asymmetric substituents with a phosphorus atom[11]. On the other hand, the influence of the asymmetry of a substituent such as the α-hydroxyethyl group was insufficient to split the signals even in the case of α-protons.

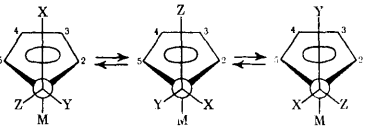


Figure 1. Certain conformations of a metallocene containing a substituent with an asymmetric carbon atom: M = $Mn(CO)_3$, FeC_5H_5, etc.

Fig.1 shows that, in the presence of the classical asymmetric carbon atom, linked directly to the CPD ligand of the metallocene, the 2- and 5-atoms (or 3- and 4-atoms) are subjected to different shielding in any possible conformation. The presence of the asymmetric centre leads to the appearance of two enantiomers. However, the spectra of the two enantiomers are identical. The 2-nucleus in the molecule of one of the enantiomers has the same shielding as the nucleus designated by the same number in the molecule in the second enantiomer (Fig.2). This also applies to the remaining nuclei in these molecules.

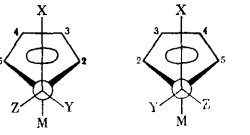


Figure 2. Enantiomers of a metallocene with an assymetric carbon atom.

Whereas the diastereotopy of the 2/5 and 3/4 nuclei of the CPD ring has been observed in the ^{1}H NMR spectra only for certain cymantrenes containing an asymmetric carbon atom in the substituent, following the introduction of ^{13}C NMR it was possible to distinguish the diastereotopic nuclei in the ferrocene analogue, ruthenocene, and other metallocene derivatives as well as derivatives of benzenechromium tricarbonyl and cyclobutadieneiron tricarbonyl. The splitting of the 2/5 and 3/4 signals was first observed in the spectra of α-hydroxyethyl- and α-hydroxybenzylferrocenes[13], although it was not explained #. Fairly numerous examples of the diastereotopy of the nuclei of a monosubstituted CPD ligand, with an asymmetric carbon, in different transition metal complexes have been found in recent years, (Table 2).

Bridged metallocenes constitute a special case[25], because the substitution of one hydrogen atom in the bridge of such compounds can lead to the appearance of an asymmetric carbon atom, which induces in its turn the diastereotopy of the

See also the study of Sokolov et al.[53], which is discussed in Section V.

nuclei of two ligands at once. It a ferrocenophane drivative[3] (X) one of the CPD rings (*A*) adjoins directly an asymmetric carbon atom, while the *B* ring is separated from it by a chain of two carbon atoms. The signals of the 2/5 and 3/4 atoms of both rings were found to be split in the ^{13}C NMR spectrum of this compound[19] (seven peaks: 67.2, 71.1, 71.8, 68.6, 69.5, 68.0, and 72.2 p.p.m.). In the molecule of the isomeric ferrocenophane (XI) the asymmetric carbon atom is separated by equal distances from the ligands. In the carbon resonance spectrum of compound (XI) the 2-, 3-, 4-, and 5-atoms of the CPD rings give rise to eight signals (*A* ring: 69.6, 70.1, 68.0, and 72.0 p.p.m.; *B* ring: 73.2, 72.0, 72.4, and 66.4 p.p.m.). It is of interest that in compounds (X) and (XI) the protons in the two rings are also spectroscopically distinguishable. In the ^{1}H NMR spectrum of compound (X) the protons of the *A* ring give signals at $\delta = 4.64$, 4.05, 3.94, 4.46 p.p.m. The *B* ring also gives rise to four signals: 4.87, 4.33, 4.29, and 4.70 p.p.m. The spectrum of compound (XI) consists of eight signals (*A* ring: 4.68, 4.07, 3.90, and 4.39 p.p. m.; *B* ring: 5.02, 4.36, 4.28, and 4.61 p.p.m.). In the ^{13}C NMR spectrum of the bridged cyclopentadienyl derivative of titanium (XII) the 2-, 3-, 4-, and 5-carbon atoms in the two rings give seven signals: 115.4, 116.8, 121.3, 121.6, 123.5, 123.7, and 123.9 p.p.m. [19]

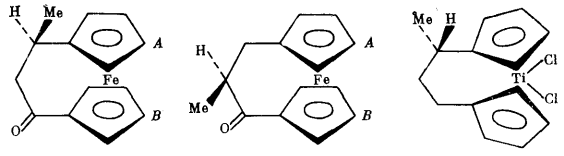


Table 2. Chemical shifts of the signals due to the carbon nuclei of the substituted CPD ring in the ^{13}C NMR spectra of certain derivatives of π-complexes [δ (p.p.m.) relative to TMS].

Substituent	$C_{(1)}$	$C_{(2,5)}$	$C_{(3,4)}$	Refs.
	Ferrocene			
—CH (OH) CH_3	94.1	65.4; 66.0	67.4; 67.5	14
—CH (OH) C_6H_5	93.9	65.3; 67.0	67.7; 67.8	14
—CH (OH) CH_2CN	90.0	65.5; 66.2	68.1; 68.2	14
—CH (CH_3) C_6H_5	94.2	65.9; 66.7	67.3; 67.7	15
—C (OH) (CH_3) C_6H_5	100.3	65.6; 67.1	67.6; 68.0	15
—CH (OH) CH $(CH_3)_2$	92.6	68.5; 64.5	67.4; 67.1	16
—CH (OH) C $(CH_3)_3$	91.4	69.4; 65.2	67.3; 67.2	16
—C (OH) (CH_3) CH $(CH_3)_2$	99.3	65.3; 68.4	67.4; 67.7	17,18
—C (OH) (CH_3) C $(CH_3)_3$	98.4	66.8; 69.3	66.7; 67.3	17,18
—CH (CH_3) CH_2COOH	93.7	65.8; 66.3	67.1	19
—CH_2CH (CH_3) COOH	85.2	67.3	69.2	19
	Ruthenocene			
—CH (OH) CH $(CH_3)_2$	98.9	73.9; 69.9	72.3; 68.8	20
	Cymantrene			
—CH (OH) CH_3	110.4	82.1; 81.6	81.4; 80.8	21
—CH (OH) CF_3	97.1	84.1; 83.2	82.0; 81.6	21
—C (OH) (CH_3) P (O) $(OCH_2CH_3)_2$	106.7	85.8; 83.8	82.0; 78.0	21
—CH (OH) C_6H_5	108.2	82.1; 82.5	80.0; 81.2	22
—C (OH) (CH_3) C_6H_5	114.1	83.3; 82.5	80.7; 78.7	22
—C (OH) (CH_3) C_6H_5	114.0	84.4; 83.7	81.2; 79.4	22
—C (OH) (C_6H_5) $C_6H_4OCH_3$-*p*	112.1	89.7	80.1; 79.9	22
—CH (OH) $C_5H_4Mn(CO)_2P(C_6H_5)_3$*	107.8	80.2; 81.6; 85.5	80.9; 83.3; 87.9	23
—CH (OH) $C_5H_4FeC_5H_5$	108.7	81.0; 82.7	81.6	23
	Cyclopentadienyltriphenylphosphinemanganese dicarbonyl			
—CH (OH) C_6H_5	107.0	84.9; 83.1	84.2; 80.0	24
—C (OH) (CH_3) C_6H_5	112.6	85.2; 82.8	81.5	24
	Dicyclopentadienyltitanium dichloride			
—CH (CH_3) C_6H_5	115.4	117.9; 122.0	119.2	19

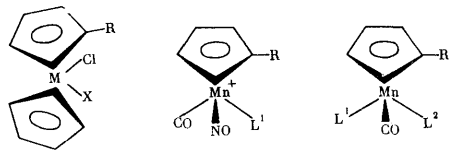
*The $C_{(2,3,4,5)}$ signals of both CPD ligands.

The diastereotopy of the 2/6 and 3/5 nuclei was observed in the ^{13}C NMR spectra of benzenechromium tricarbonyl derivatives [VII, $M = Cr(CO)_3$] containing an asymmetric carbon atom in the substituent. Thus, for $R = CH(OH)C_6H_5$, the unsubstituted carbon atoms of the benzene ring give rise to four signals: 90.1, 91.7, 91.9, and 92.1 p.p.m. The diastereotopy of both pairs is reflected in the spectrum of the analogous derivative with $R = C(OH)(CH_3)C_6H_5$: $\delta = 90.0$, 90.6, 92.8, 93.1, and 94.1 p.p.m.[26] The splitting of the signal due to the 2/4 nuclei was also discovered in the ^{13}C NMR spectra of carbinols of the cyclobutadieneiron tricarbonyl series [VI, $M = Fe(CO)_3$]: $\delta = 62.6$ and 62.7 p.p.m. for $R = CH(OH)CH_3$ and $\delta = 63.4$ and 63.6 p.p.m. for $R = CH.(OH)C_6H_5$.[27]

The splitting of the signal of the 2/5 and 3/4 carbon atoms in the cyclopentadienyl complexes containing a substituent with an asymmetric carbon atom in the ring was used to determine the nature of the bond in the cyclopentadienyl complexes of thallium[15].

2. The Asymmetric Transiton Metal Atom

The diastereotopy of the atoms in a substituted cyclic π-ligand arises also when the chiral centre of the molecule consists of the transition metal atom itself. In compound [XIII, M = Ti, $R = CH_3$, $X = OC_6H_3(CH_3)_2$-*o*,*o*] the titanium atom is linked to four different substituents. Four signals due to the 2-, 3-, 4-, and 5-atoms of the substituted CPD ring were found in the ^{13}C NMR spectrum of this complex with the chemical shifts $\delta = 109.6$, 115.6, 121.1, and 121.8 p.p.m.[19]



Cymantrene gives rise to extensive possibilities in this sense. The diastereotopy of the 2/5 and 3/4 nuclei was observed for two types of complexes. The first type (XIV) is formed when one of the CO ligands in the monosubstituted cymantrene is replaced by NO and the other arises when it is substituted by an *n*-donor (phosphine, arsine). In this case the complex has a positive charge. The second type of compound with a chiral manganese atom (XV) has been obtained on replacement of two carbonyl ligands by different *n*-donors (phosphine and phosphite). The NMR data for complexes of both types are listed in Table 3. It is of interest that the slight difference between triethyl phosphite and trimethyl phosphite is not reflected in the spectrum—diastereotopy is not manifested for these ligands.

3. The Asymmetric Carbon Atoms

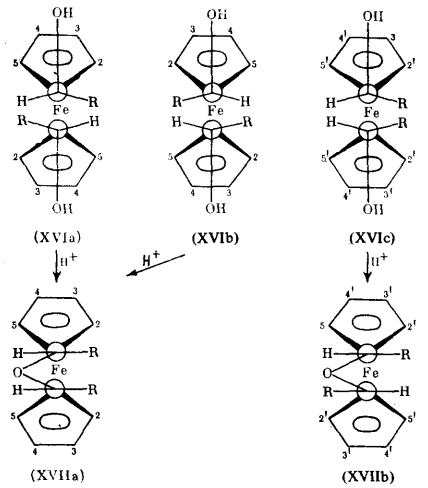
Numerous ferrocene derivatives containing two identical asymmetric carbon atoms in two different rings are known. Such compounds are usually obtained on reduction of heteroannular diacylferrocenes. The presence of two asymmetric centres leads to the appearance of two diasteroisomers. For identical centres, these consist of a pair of enantiomers [for example, (XVI, a and b)] and the *meso*-form (XVIc). Naturally the diasteroisomers should give rise to different NMR spectra and in the spectrum of each diastereoisomer one should be able to observe the diastereotopy of the 2/5 and 3/4 nuclei of each CPD ring.

In the ^{13}C NMR spectrum of a mixture of diastereoisomers of 1,1'-di-(1-hydroxyethyl)ferrocene (XVI, *a,b*, and *c*, R = CH_3) (in CH_2Cl_2) nine signals were found in the range δ = 60–70 p.p.m.[30]: 65.2, 65.5, 65.7, 66.1, 66.3, 66.7, 67.5, and 67.7 (with a double intensity), and 68.0 p.p.m. Two of these peaks correspond to the carbon atoms linked to the hydroxy-group and the remaining seven signals indicate the non-equivalence of the 2/5, 3/4, 2'/5', and 3'/4' atoms (two signals are accidentally superimposed). The signals with δ = 25.3 and 26.0 p.p.m. correspond to the methyl groups of different diastereoisomers. In the spectrum of the mixture of the diastereoisomers of 1,1'-di-(1-hydroxybenzyl)ferrocene (XVI, a, b, and c; R = C_6H_5) (in CH_2Cl_2) ten signals were found[30] for the 2/5, 3/4, and 2'/5', 3'/4', and C–OH atoms: 66.3, 66.7, 66.9, 67.3, 68.0, 68.2, 68.4, 68.5, 71.9, and 72.8 p.p.m. The signals with δ = 94.0 and 94.5 p.p.m. refer to the 1- and 1'-atoms of the two diastereoisomers [in the spectrum of (XVI, a, b, and c; R = CH_3) the key 1- and 1'-atoms give rise to a single peak at 95.3 p.p.m.].

Table 3. Chemical shifts in the ^1H and ^{13}C NMR spectra of cymantrene derivatives [δ (p.p.m.) relative to TMS].

Compound	R	L^1	L^2	H(2,5)	H(3,4)	C(2,5)	C(3,4)	Refs.
(XIV)	CH_2CH_3	$P(C_6H_5)_3$		5.10; 5.23	5.63	91.6; 94.0	93.5; 97.5	28
(XIV)	CH_2CH_3	$As(C_6H_5)_3$		5.65; 5.75	5.38	90.8; 92.8	92.4 95.9	28
(XIV)	CH_2CH_3	$P(CH_2C_6H_5)_3$		4.80; 5.35	5.10	90.7; 93.4	91.4 95.7	28
(XV)	$CO(CH_2)CO_2{\cdot}CH_3$	$P(OCH_3)_3$	$P(C_6H_5)_3$	4.76; 4.96	3.76; 4.01	—	—	29
		$P(OCH_3)_3$	$P(OC_6H_5)_3$	4.93	4.41	—	—	29

On treatment with acid, the isomers are converted stereoselectively into oxygen-containing ferrocenophanes[31]: the racemate of the enantiomers (XVI, a and b) gives rise to the *cis*-isomer (XVIIa) and the *meso*-form (XVIc) is converted into the *trans*-isomer (XVIIc). Eight signals, two of which are due to the C–OH atoms and the remainder are associated with the 2-, 3-, 4-, 5-, 2'-, 3'-, 4'-, and 5'-carbon atoms in the ring, were observed in the spectrum of ferrocenophane (XVII) obtained from (XVI, R = CH): δ (in CH_2Cl_2) = 62.6, 65.3, 67.5, 68.3, 69.4, 70.2, 71.4, and 72.1 p.p.m.[30] Presumably only the signals of the 2/5 and 2'/5' pairs are split. In addition, two signals for each of the 1- and 1'-atoms (89.2 and 90.9 p.p.m.) and for the methyl groups (19.3 and 22.3 p.p.m.) were found in the spectrum.



Only two signals due to the peak $C_{(1)}$ atoms, corresponding to two different types of ferrocene fragments (mono- and di-substituted ferrocene rings), were found in the ^{13}C NMR spectrum of 1,1'-di-[2-ferrocenyl-4-methoxycarbonyl)butyl]-ferrocene containing two identical asymmetric centres §. In the region of the signals due to the 2-, 3-, 4-, and 5-nuclei six peaks were observed, which indicates the diastereotopic anisochronicity of only the 2/5 atoms in each type of ferrocene fragment[32].

Two asymmetric carbons can be linked to the same π-ligand. In this case three isomers are possible for compounds with two identical asymmetric centres: the racemate of the two enantiomers (XVIII, a and b) and the two *meso*-forms (XVIIIc) and (XVIIId).

In the benzenechromium tricarbonyl compounds (XVIIIc) and (XVIIId) there is a plane of symmetry, by virtue of which the atoms within the 3'/6' and 4'/5' pairs in the first compound and the 3''/6'' and 4''/5'' pairs in the second are enantiotopic. Indeed, two overall signals were observed in the ^{13}C NMR spectrum of each compound for these atoms: 90.2 and 93.3 p.p.m. in the spectrum of (XVIIIc) and 91.5 and 93.5 p.p.m. in the spectrum of (XVIIId). The carbon atoms linked to the substituents in the two compounds are isochronous [118.2 p.p.m. for (XVIIIc) and 114.4 p.p.m. for (XVIIId)].

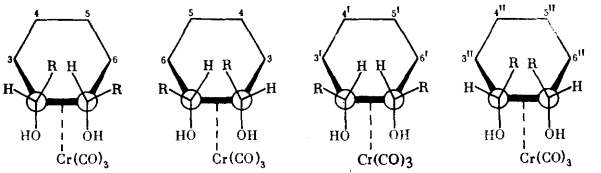


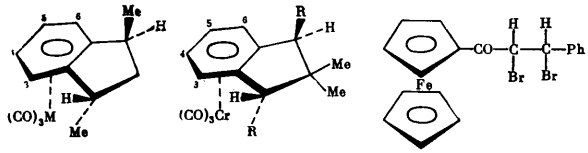
Table 4. ^1H NMR spectra of arenechromium tricarbonyl and arenemolybdenum tricarbonyl derivatives [δ (p.p.m.) relative to TMS].[33]

Compound	H(3)	H(4)	H(5)	H(6)
(XIX), M=Cr	5.12	5.36	5.00	5.43
(XIX), M=Mo	5.52	5.66	5.35	5.73
(XX), R=$OCOCH_3$	5.36	5.36	5.20	5.50

In either of the two enantiomers (XVIIIa) and (XVIIIb) the 3/6 and 4/5 atoms are diastereotopic, which is manifested in the carbon resonance spectra (89.7, 92.6, 92.5, and 94.5 p.p.m.) and in ^1H NMR (5.78, 5.56, 5.51, and 5.76 p.p.m.). The atoms of the benzene ring carrying substituents are also anisochronous (113.1 and 120.1 p.p.m.).[26] The non-equivalence of the 3/6 and 4/5 atoms was observed as early as 1969 in the ^1H NMR spectra of compounds (XIX) and (XX), which exist in the form of two enantiomers[33]. The chemical shifts are listed in Table 4.

§ The stereochemistry of ferrocene derivatives containing two identical or different asymmetric centres has been discussed[63].

Two signals of the 2/5 protons were observed in the ^1H NMR spectrum of the substituted ferrocene (XXI) ($\delta = 4.90$ and 4.66 p.p.m.).[34] However, one should note that the splitting of the signal of the α-protons can be induced both by the diastereotopy of the 2/5 atoms and by the non-equivalence of the α-protons in the two diastereoisomers of compound (XXI) containing two asymmetric carbon atoms in the side chain.

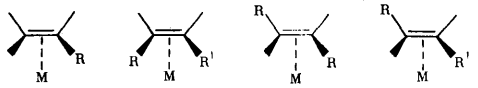


(XIX) (XX) (XXI)

III. DIASTEREOTOPY INDUCED BY PLANAR CHIRALITY

The coordination of a planar cyclic (cyclopentadienyl, benzene) or non-cyclic (monoolefin, diene) π-ligand to a transition metal atom makes the hitherto equivalent sides of the ligand non-equivalent. If two different substituents are linked to a cyclic ligand, then, after coordination, there is a possibility of two different dispositions of these substituents [see structures (IIIa) and (IIIb)] and two enantiomers appear. Such planar chirality (induced by the non-equivalence of the sides of planar ligands) is most typical for organometallic complexes of transition metals, although one can imagine cyclophane, triquinacene, and corannulene molecules containing two different substituents in the ring and exhibiting planar chirality. Chiral cyclophanes have been obtained in an optically active form.

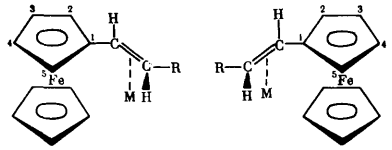
One of the important instances of the manifestation of planar chirality is the existence of the enantiomers of mono-olefins coordinated to organometallic groups. The enantiomers can be obtained for a monosubstituted olefin (XXII), a disubstituted olefin with different substituents in the *cis*-positions (XXIII) and also with identical [compound (XXIV)] or different [compound XXV] substituents in the *trans*-positions.



(XXII) (XXIII) (XXIV) (XXV)

1. Planar Chirality of the Substituent

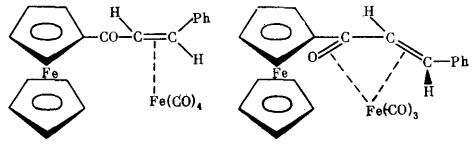
When rotation about the C^1–CH= bonds is possible in the vinylferrocene molecule, the 2/5 and 3/4 atoms of the CPD ligand are enantiotopic. The coordination of the double bond to the organometallic group leads to diastereotopy of these nuclei. In the resulting enantiomers (XXVIa) and (XXVIb) the nuclei having identical environments are designated by identical numbers ¶.



(XXVIa) (XXVIb)

¶ The molecules of the enantiomers (XXVIa) and (XXVIb) have a planar chiral fragment (a double bond coordinated to the metal atom) and a planar prochiral fragment FeC_5H_4X.

The diastereotopy of the 2/5 and 3/4 nuclei of the CPD ligand, induced by the presence of a chiral fragment in the substituent—a coordinated double bond—was observed for the complexes of certain vinylferrocenes with iron tetracarbonyl and iron tricarbonyl groups and also with the cyclopentadienylmanganese dicarbonyl group (Table 5).[35-37] Two features may be noted. Diastereotopy was not manifested in the ^{13}C NMR spectrum of the complex of cinnamoylferrocene with the iron tetracarbonyl group (XXVII) using CH_2Cl_2 as the solvent. In the more polar solvents acetone and nitromethane it was possible to observe the splitting of the signals due to the 2/5 and 3/4 nuclei. In the ^1H NMR spectra the anisochronicity of the nuclei of the CPD ring of ferrocene was not observed with the exception of the complex of cinnamoylferrocene with iron tricarbonyl (XXVIII). In this case the presence of a very cumbersome chiral group led to the splitting of the H 2/5 signal (4.64 and 4.99 p.p.m. in $CHCl_3$).

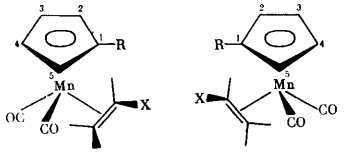


(XXVII) (XXVIII)

Table 5. Chemical shifts in the ^{13}C NMR spectra of certain derivatives of vinylferrocenes [δ(p.p.m.) relative to TMS].

Compound	M	R	Solvent	$C_{(2,5)}$	$C_{(3,4)}$	Refs.
(XXVI)	$Fe(CO)_4$	COC_6H_5	CH_2Cl_2	62.4; 68.0	70.0; 70.4	35,36
(XXVII)	$Fe(CO)_4$	—	CH_2Cl_2	68.7	72.5	35,36
(XXVII)	$Fe(CO)_4$	—	$(CH_3)_2CO$	69.1; 71.2	72.6; 72.9	35,36
(XXVII)	$Fe(CO)_4$	—	CH_3NO_2	69.8; 71.8	73.2; 73.6	35,36
(XXVIII)	—	—	CH_2Cl_2	67.8; 71.2	71.5; 72.8	35,36
(XXVI)	$Mn(CO)_2C_5H_5$	H	CH_2Cl_2	67.4; 68.1	68.6	37
(XXVI)	$Mn(CO)_2C_5H_5$	COC_6H_5	CH_2Cl_2	62.4; 68.1	68.6	37

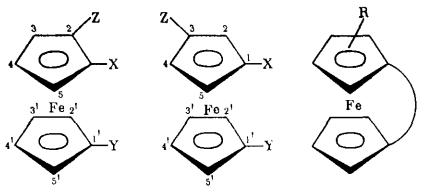
The diastereotopy of the 2/5 and 3/4 nuclei of the monosubstituted CPD ring can be expected in the NMR spectra of the complex of cyclopentadienylmanganese dicarbonyl with a monosubstituted olefin. In this case there is a possibility of two enantiomers (XXIXa) and (XXIXb).



(XXIXa) (XXIXb)

2. The Planar Chirality of the Metallocene Molecule

In chiral trisubstituted ferrocenes (XXX, a and b; $X \neq Y \neq Z \neq H$ or $X = Y \neq Z \neq H$) the 2'/5' and 3'/4' atoms of the monosubstituted ring are diastereotopic. The possibility of the anisochronicity of these nuclei is most evident in the case of monosubstituted ferrocenophanes (XXXI, R = acetyl, for example).



(XXXa) (XXXb) (XXXI)

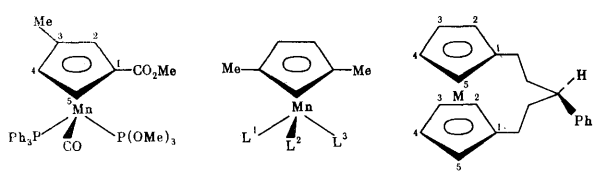
Indeed it is seen from literature data[38-40] that the α-protons (as well as the β-protons) of the monosubstituted ring in the spectra of compounds (XXXI) in general give rise to different signals. It is more difficult to observe the anisochronicity of the protons of the monosubstituted ring in the spectra of non-bridged derivatives (XXX). However, on comparing the results of a whole series of investigations[41-45], one may conclude that the appearance of a multiplet structure in the signal of the monosubstituted ring protons (a CPD ring linked to a single alkyl substituent usually gives rise to a narrow singlet) is associated precisely with the diastereotopy of the 2′/5′ and 3′/4′ protons. It is of interest that the anisochronicity of the monosubstituted ring protons is more distinct when two different substituents in the second ring occupy the 1- and 3-positions. Thus, whereas in the spectra of compounds (XXXa, $X = Y = C_2H_5$, $Z = CH_2^+$ [43] or $X = Y = CH_2C_6H_5$, $Z = COCH_3$ or COC_6H_5) [45] the signal due to the protons in the ring with the substituent Y consists of a narrow singlet, in the spectra of the corresponding derivatives (XXXb) the monosubstituted ring is manifested by a fairly broad multiplet.

The splitting of the signal due to the 2′/5′ and 3′/4′ nuclei in the ^{13}C NMR spectra has been observed for compounds [XXXb, $X = Y = CH_3$, $Z = C(OH)(CH_3)_2$ [18] and $X = Y = CH_2C_6H_5$, $Z = COC_6H_5$ [45]]. As in the case of proton resonance, the signals of the 2′/5′ and 3′/4′ atoms in the ^{13}C NMR spectrum of the 1,2-isomer of (XXXa, $X = Y = CH_2C_6H_5$, $Z = COC_6H_5$) are not split[45].

3. Combination of an Asymmetric Atom and Planar Chirality

The presence in one ring of a metallocene molecule of two different substituents, one of which contains a chiral centre, leads to the appearance of two diastereoisomers [a more complex case, involving two chiral substituents in a single ring, was analysed above in relation to compound (XVIII)]. Such diastereoisomers of the 1,2-isomers of [XXXa, $X = Y = CH_3$, $Z = CH(OH)CH_3$ [46-48] or $X = Y = CH_2C_6H_5$, $Z = CH(OH)CH_3$ [45]] can be separated chromatographically. They give rise to readily distinguishable ^1H NMR spectra. It is of interest that in the case of compounds [XXXa, $X = Y = CH_2C_6H_5$, $Z = CH(OH)CH_3$] the diastereotopy of the protons in the methylene group is observed for only one isomer[45].

An example of the combination in one molecule of planar chirality and a chiral transition metal atom is known. Since the manganese derivative (XXXII) exists in the form of two diastereoisomers, the ^1H NMR spectrum of their mixture was found to contain four signals associated with the 2/5 atoms and two signals associated with the 4-atom[29].



(XXXII) (XXXIII) (XXXIV)

The two methyl groups in the CPD ring of the complex with a chiral manganese atom are diastereotopic. They give rise to two signals in the proton resonance spectra ($\delta = 1.86$ and 1.93 p.p.m.) for compound [XXXIII, $L^1 = P(OMe)_3$, $L^2 = PPh_3$, $L^3 = CO$]. [29] If the methyl groups are in the 1- and 3-positions, then the hydrogen and carbon atoms in the 4/5 positions are also diastereotopic. When the methyl groups are in vicinal positions, the 3/5 atoms of the CPD ring are diastereotopic.

IV. DIASTEREOTOPY IN ACHIRAL MOLECULES

An achiral molecule can also contain diastereotopic atoms and groups. In the series of metallocenes such a compound is, for example, the phenyl derivative of [5] ferrocenophane (XXXIV, M = Fe). In contrast to the unsubstituted [5] ferrocenophane, whose molecule is divided by a plane of symmetry passing through the iron atom and through all the carbon atoms of the bridge and $C_{(1)}$ and in which the 2/5 and 3/4 atoms of both rings are enantiotopic, in the phenyl derivative there is no plane of symmetry. As a result, the 2/5 and 3/4 atoms in the molecule of compound (XXXIV) become diastereotopic in each ring. It is of interest that the atoms in different rings, designated by identical numbers, form enantiotopic pairs, since they are linked by a mirror plane. In order to account for the non-equivalence of the 2/5 and 3/4 nuclei in compounds resembling (XXXIV), one can also employ a different, more traditional approach. The point is that the above nuclei are involved in *syn/anti (cis/trans)* relations with the phenyl substituent.

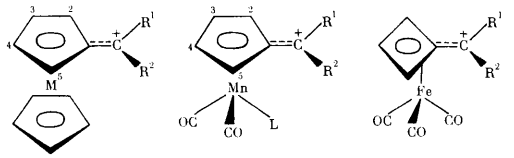
As was to be expected, two common signals for the 2/5 and 3/4 atoms of both rings are observed in the ^{13}C NMR spectrum of [5] ferrocenophane[49] ($\delta = 68.4$ and 66.9 p.p.m. in CH_2Cl_2 at 15 °C). In the spectrum of the γ-phenyl derivative of (XXXIV, M = Fe), the 2-, 3-, 4-, and 5-carbon atoms of the CPD rings give rise to four signals ($\delta = 66.0$, 66.9, 67.8, and 68.9 p.p.m. in CH_2ClCH_2Cl at 30 °C). [50] Analogous splitting has been observed in the spectrum of the γ-phenyl derivative of [5] ruthenocenophane (XXXIV, M = Ru): 68.0, 68.8, 71.1, 72.6 p.p.m. [51] We may note that in both cases the 2/5 and 3/4 carbon atoms of the CPD rings are sensitive to the introduction of a substituent in the γ-position in the bridge, separated from the ring by 2–3 atoms. For comparison, we may point out that the diastereotopy of the 2/5 and 3/4 atoms could not be observed when the asymmetric carbon atom was separated from the ring by one methylene group [the compound $C_5H_5FeC_5H_4CH_2CH(CH_3)COOH$; see Table 2]. Naturally, the fact that in the above compound the γ-methylene group with the methyl substituent is in spatial proximity to the ferrocene ring has an effect in the case of ferrocenophane.

In contrast to compounds (XXXIV), the molecules of the bridged metallocenes (X), (XI), and (XII) are no longer achiral, because the carbon atom in the bridge, linked to the substituent, is also linked to four different groups and in this case one can assume that the diastereotopy of the 2/5 and 3/4 nuclei is induced by the presence of an asymmetric carbon atom in the bridge.

V. DIASTEREOTOPY IN α-METALLOCENYL-SUBSTITUTED CARBONIUM IONS

When carbinols, containing metallocenyl (ferrocenyl, ruthenocenyl, osmocenyl, cymantrenyl, and cyclobutadiene-iron tricarbonyl) fragments in the α-position are dissolved in acids, unusually stable carbonium ions are formed[52]. The

signals of the 2/5 and 3/4 atoms of the CPD ligand are found to be split in both ^1H and ^{13}C NMR spectra of such ions containing two different substituents at the carbonium centre in addition to the metallocenyl fragment. This served as a basis for the hypothesis that the rotation about the $\overset{+}{C}-C_{(1)}$ bond is hindered, because such a bond has partial double bond character. The ^1H and ^{13}C NMR data for certain metallocenes having a single carbonium centre as a substituent are compiled in Tables 6 and 7. More complex carbonium ions, particularly those of the ferrocenophane series, have been discussed in the literature[41-44,47,48,57].

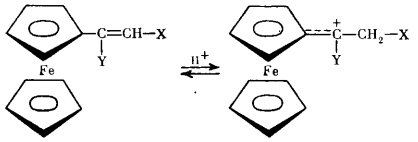


(XXXV) (XXXVI) (XXXVII)

Table 6. Chemical shifts in the ^1H NMR spectra of α-metallocenylcarbonium ions [δ(p.p.m.) relative to TMS].

Compound	R^1	R^2	H(2,5)H(3,4)	Refs.
(XXXV), M=Fe	H	$CH(CH_3)_2$	6.45 5.18 4.58	20
(XXXV), M=Fe	H	CH_3	5.03 6.36 4.49 6.21	54
(XXXV), M=Fe	H	C_6H_5	5.52 6.45 4.77 6.24	54
(XXXV), M=Ru	H	$CH(CH_3)_2$	6.19 6.07 5.11	20
(XXXV), M=Os	H	$CH(CH_3)_2$	6.26 5.23	20
(XXXVI), L=CO	CH_3	C_2H_5	5.70 6.25 7.78	12
(XXXVI), L=CO	H	C_6H_5	5.91 6.12 5.45	12
(XXXVI), L=CO	CH_3	C_6H_5	5.73 5.91 6.16	12
(XXXVI), L=CO	C_6H_5	p-$C_6H_4OCH_3$	5.72 6.34 5.88	12
(XXXVI), L=$P(C_6H_5)_3$	H	C_6H_5	5.00 5.45 5.82	24

The splitting of the signals due to the 2/5 and 3/4 carbon atoms in the spectra of α-ferrocenylcarbonium ions was first noted by Sokolov et al.[53]. Subsequently the ^{13}C NMR spectra of metallocenylcarbonium ions were discussed frequently[16-18, 20,22-24,27,55,56]. The exact assignment of the signals to the 2/5 and 3/4 atoms was made by Koridze et al.[16] Nesmeyanov et al.[55] observed for the first time the splitting of the signals of the 2/5 and 3/4 carbon atoms in the spectra of the carbonium ion (XXXIX) formed on protonation of the double bond in the vinylferrocenes [XXXVIII, X = C_6H_5, Y = H(a); X = $CO_2C_2H_5$, Y = CH_3(b)]. However, it was given an incorrect explanation. The cation (XXXIXb) was investigated in greater detail in another study by Nesmeyanov et al.[56]



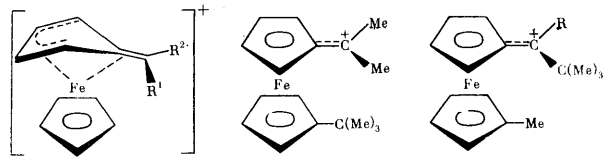
(XXXVIIIa and b) (XXXIXa and b)

The spectra of the derivative (XXXVII) show that the 2- and 4-carbon atoms are also anisochronous [δ(2/4) = 78.8 and 80.4 p.p.m. for R^1 = H and R^2 = CH_3], but, for R^1 = H and R^2 = C_6H_5, the chemical shifts of the 2- and 4-atoms fortuitously coincide and a common signal with δ = 80.0 p.p.m. is observed[27].

Table 7. Chemical shifts in the ^{13}C NMR spectra of certain α-metallocenylcarbonium ions [δ(p.p.m.) relative to TMS].

Compound	R^1	R^2	C(2,5)	C(3,4)	Refs.
(XXXV), M=Fe	H	CH_3	80.9; 80.0	93.3; 93.0	16
(XXXV), M=Fe	H	$CH(CH_3)_2$	79.7; 78.9	93.2; 92.6	16
(XXXV), M=Fe	H	$C(CH_3)_3$	81.4; 80.2	93.8; 93.6	16
(XXXV), M=Fe	CH_3	$CH(CH_3)_2$	76.9; 77.9	94.5; 94.9	18
(XXXV), M=Fe	CH_3	$C(CH_3)_3$	79.2; 80.3	95.1; 95.3	18
(XXXV), M=Fe	H	$CH_2COC_6H_5$	80.9; 82.8	96.2; 96.5	55
(XXXV), M=Fe	CH_3	$CH_2CO_2CH_3$	78.0; 78.6	94.4; 94.8	56
(XXXVI), L=CO	H	C_6H_5	92.8; 100.2	97.6; 98.3	22
(XXXVI), L=CO	CH_3	C_6H_5	93.3; 94.4	94.6; 98.3	22
(XXXVI), L=$P(C_6H_5)_3$	H	C_6H_5	103.9; 103.6	96.3; 92.3	24
(XXXVI), L=$P(C_6H_5)$	CH_3	C_6H_5	104.2; 103.4	92.1; 91.6	24

The diastereotopy of the 2/5 nuclei in metallocenylcarbonium cations shows some similarity with the diastereotopy of the geminal protons in monosubstituted olefins. Even if the carbonium ion has the non-planar structure (XL), as was assumed, the diastereotopy of the 2/5 and 3/4 nuclei should persist for $R^1 \neq R^2$.



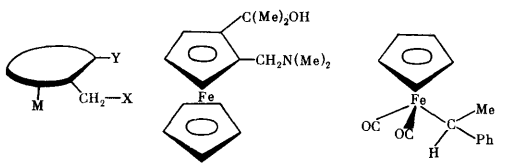
(XL) (XLI) (XLII)

An attempt has been made[44,48] to demonstrate the deviation of the carbonium fragment from the planar configuration. A comparison was made of the ^1H NMR spectra of the two isomeric carbonium ions (XLI) and (XLII, R = CH_3) or (XLIIa). The spectrum of compound (XLI), due to the protons of the ring to which the t-butyl group is attached, is manifested by a slightly broadened singlet. Hence it follows that the differences in the shielding of the 2'-, 3'-, 4'-, and 5'-protons are small. In the spectrum of the cation (XLIIa) the protons of the ring linked to the methyl group give rise to two well resolved multiplets. The authors[44,48] concluded that the mutual rotation of the rings in this compound is hindered, which leads to a time-averaged non-equivalence of the α- and β-protons of the methyl-substituted ring. Since the rotation is not hindered in the first isomer, it is concluded that in compound (XLIIa) rotation is hindered by the mutual repulsion of the $C(CH_3)_3$ and CH_3 groups, arising in connection with the deformation illustrated in structure (XL). However, an alternative explanation is also possible[45]. The hydrogen atoms in the ring without a cationic centre (2'/5' and 3'/4') are enantiotopic in compound (XLIIa), while in compound (XLIIa) they are diastereotopic (this is a special case of diastereotopy associated with the planar chirality of the molecule discussed above) and can be anisochronous. However, one cannot rule out the possibility that the anisochronicity of the diastereotopic 2'/5' and 3'/4' nuclei is manifested solely by virtue of the deformation postulated by the authors[44,48]. An unambiguous choice in favour of one of the explanations could be made by measuring the spectrum of

compound [XLII, R = $C(CH_3)_3$]. In this molecule the 2'/5' and 3'/4' atoms again become enantiotopic, but the postulated hindered rotation persists.

VI. CERTAIN OTHER CASES OF DIASTEREOTOPY

The diastereotopy of different groups in the molecules of π-complexes of transiton metals may not be associated with the specific features of the geometry of the metallocene (it can be caused, for example, by the presence of an asymmetric carbon atom in the side chain), but it is possible to quote examples where the structure of the metallocene sandwich does in fact induce diastereotopy. Thus, if one of the substituents in the homoannular disubstituted metallocene contains a methylene group, then its protons will be diastereotopic [see compound (XLIII)]. This phenomenon was observed for the first time in the spectra of the substituted ferrocene (XLIV) (the methyl groups in the neighbouring substituent are also diastereotopic).[58] Similarly the diastereotopy of the protons of the CH_2 groups was noted in a derivative of benzenechromium tricarbonyl[59]. It is of interest that in the ^1H NMR spectra of acetyl-1,1'-dibenzylferrocenes the diastereotopic anisochronicity could be observed only for the protons of the benzyl group in the disubstituted ring and only when the acetyl group was located in the α-position relative to this group[45].

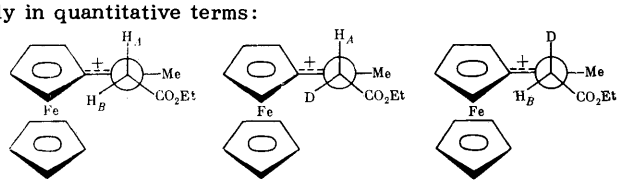


(XLIII) (XLIV) (XLV)

The diastereotopic anisochronicity of the carbonyl groups (δ = 217.1 and 217.5 p.p.m.), due to the presence of the asymmetric carbon atom, has been observed in the ^{13}C NMR spectrum of compound (XLV).[60] The magnetic non-equivalence of phosphorus atoms has been noted in cationic phosphine complexes of a cymantrene derivative[61]. The non-equivalence of the methyl groups has been observed in derivatives of dicyclopentadienyl compounds of zirconium and hafnium containing asymmetric metal atoms[62].

VII. CHEMICAL NON-EQUIVALENCE OF DIASTEREOTOPIC ATOMS

The observation of the chemical non-equivalence of diastereotopic atoms is an important and interesting task. Naturally, diastereotopic atoms have different chemical properties only in quantitative terms:



(XXXIXb) (XLVIa) (XLVIb)

In the carbonium ion (XXXIXb) the hydrogen atoms of the methylene group are diastereotopic. They are manifested in the ^1H NMR spectrum by an *AB* quartet [δ = 3.53 and 3.87 p.p.m.; $J(AB)$ = 16 Hz].[56] It was found that these protons undergo deuterium exchange at different rates. The more rapid exchange was observed for the H_A proton whose signal is at a higher field. Evidently the H_A proton, sterically less shielded than the H_B proton, should in fact be more reactive. The diastereoisomer (XLVIb) is formed more rapidly as a result of the exchange[56].

REFERENCES

1. K.Mislow and M.Raban, in "Topics in Stereochemistry", (Edited by N.Allinger and E.L.Eliel), Interscience, New York, 1967, Vol.1, p.1.
2. R.M.Silverstein, G.C.Bassler, and T.C.Morrill, "Spectrometric Identification of Organic Compounds" (Translated into Russian), Izd.Mir, Moscow, 1977, p.322.
3. W.Prelog, Uspekhi Khim., 38, 952 (1969)[Russ.Chem. Rev., No.5 (1969)].
4. A.Davison and P.E.Rakita, J.Organometal.Chem., 23, 407 (1970).
5. C.A.Busby and D.Dolphin, J.Magn.Res., 23, 211 (1976).
6. V.I.Sokolov, "Novoe v Stereokhimii" (Advances in Stereochemistry), Izd.Znanie, Moscow, 1975.
7. G.B.Shul'pin, Khimiya i Zhizn', No.10, 20 (1978).
8. V.I.Sokolov, "Vvedenie v Teoreticheskuyu Stereokhimiya" (Introduction to Theoretical Stereochemistry), Izd.Nauka, Moscow, 1979.
9. G.B.Shul'pin, A.A.Koridze, A.A.Pogrebnyak, M.I.Rybinskaya, and A.N.Nesmeyanov, Synth.Inorg. Metal Org.Chem., 3, 83 (1973).
10. D.N.Kursanov, Z.N.Parnes, and N.M.Loim, "Tezisy Dokladov V Mezhdunarodnogo Kongressa po Metalloorganicheskoi Khimii" (Abstracts of Reports at the Vth International Congress on Organometallic Chemistry), Moscow, 1971, Vol.2, p.262.
11. D.N.Kursanov, Z.N.Parnes, N.M.Loim, N.E.Kolobova, I.B.Zlotina, P.V.Petrovskii, and E.I.Fedin, J.Organometal.Chem., 44, C15 (1972).
12. N.M.Loim, L.A.Malutschenko, Z.N.Parnes, and D.N.Kursanov, J.Organometal Chem., 108, 363 (1976).
13. A.N.Nesmeyanov, P.V.Petrovskii, L.A.Fedorov, V.I.Robas, and E.I.Fedin, Zhur.Strukt.Khim., 14, 49 (1973).
14. A.A.Koridze, P.V.Petrovskii, A.A.Mokhov, and A.I.Lutsenko, J.Organometal.Chem.. 136, 57 (1977).
15. A.A.Koridze, N.A.Ogorodnikova, and P.V.Petrovskii, J.Organometal.Chem., 157, 145 (1978).
16. A.A.Koridze, P.V.Petrovskii, S.P.Gubin, V.I.Sokolov, and A.A.Mokhov, J.Organometal.Chem., 136, 65 (1977).
17. S.Braun and W.E.Watts, J.Organometal.Chem., 84, C33 (1975).
18. S.Braun, T.S.Abram, and W.E.Watts, J.Organometal. Chem., 97, 429 (1975).
19. M.L.Martin, J.Tirouflet, and B.Gautheron, J.Organometal.Chem., 97, 261 (1975).
20. V.I.Sokolov, P.V.Petrovskii, A.A.Koridze, and O.A.Reutov, J.Organometal.Chem., 76, C15 (1974).
21. N.M.Loim, D.N.Kursanov, Z.N.Parnes, N.N.Sul'dina, and E.I.Fedin, J.Organometal.Chem., 52, C33 (1973).
22. N.M.Loim, P.V.Petrovskii, V.I.Robas, Z.N.Parnes, and D.N.Kursanov, J.Organometal Chem., 117, 265 (1976).
23. A.G.Ginzburg, V.N.Setkina, Sh.G.Kasumov, G.A.Panosyan, P.V.Petrovskii, and D.N.Kurzanov, Dokl.Akad.Nauk SSSR, 228, 1368 (1976).

24. A.G.Ginzburg, V.N.Setkina, P.V.Petrovskii, Sh.G.Kasumov, G.A.Panosyan, and D.N.Kursanov, J.Organometal.Chem., 121, 381 (1976).
25. G.B.Shul'pin and M.I.Rybinskaya, Uspekhi Khim., 43, 1524 (1974)[Russ.Chem.Rev., No.8 (1974)].
26. J.Tirouflet, J.Besancon, and F.Mabon, Org.Magn. Resonance, 8, 444 (1976).
27. C.S.Eschbach, D.Seyferth, and P.C.Reeves, J. Organometal.Chem., 104, 363 (1976).
28. A.G.Ginzburg, V.N.Setkina, P.V.Petrovskii, V.I.Robas, and D.N.Kurzanov, Koord.Khim., 1, 1542 (1975).
29. M.Le Plouzennec, F.Le Moigne, and R.Dabard, J. Organometal.Chem., 132, 409 (1977).
30. G.B.Shul'pin, Candidate's Thesis, Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow, 1975.
31. K.Yamakawa and M.Hisatome, J.Organometal.Chem., 52, 407 (1973).
32. A.T.Nielsen and W.P.Norris, J.Org.Chem., 41, 655 (1976).
33. D.E.F.Gracey, W.R.Jackson, W.B.Jennings, S.C.Rennison, and R.Spratt, J.Chem.Soc., (B), 1210 (1969),
34. S.Toma, M.Sališová, and E.Solčániová, J.Organometal.Chem., 90, 335 (1975).
35. A.N.Nesmeyanov, G.B.Shul'pin, L.A.Fedorov, P.V.Petrovskii, and M.I.Rybinskaya, J.Organometal. Chem., 69, 429 (1974).
36. A.N.Nesmeyanov, G.B.Shul'pin, L.V.Rybin, N.T.Gubenko, M.I.Rybinskaya, P.V.Petrovskii, and V.I.Robas, Zhur.Obshch.Khim., 44, 2032 (1974).
37. A.N.Nesmeyanov, G.B.Shul'pin, L.M.Korneva, and M.I.Rybinskaya, Dokl.Akad.Nauk SSSR, 217, 1091 (1974).
38. K.L.Rinehart, D.E.Bublitz, and D.H.Gustafson, J.Amer.Chem.Soc., 85, 970 (1963).
39. M.I.Levenberg and J.H.Richards, J.Amer.Chem.Soc., 86, 2634 (1964).
40. T.H.Barr, E.S.Bolton, H.L.Lentzner, and W.E.Watts, Tetrahedron, 25, 5245 (1969).
41. J.Feinberg and M.Rosenblum, J.Amer.Chem.Soc., 91, 4324 (1969).
42. M.Hisatome and K.Yamakawa, Tetrahedron Letters, 3533 (1971).
43. R.G.Sutherland, J.R.Sutton, and W.M.Horspool, Tetrahedron Letters, 328 (1973).
44. T.D.Turbitt and W.E.Watts, J.Organometal.Chem., 49, C30 (1973).
45. G.B.Shul'pin and A.N.Kitaigorodskii, Izv.Akad. Nauk SSSR, Ser.Khim., No.1, 168 (1980).
46. E.A.Hill and J.H.Richards, J.Amer.Chem.Soc., 83, 4216 (1961).
47. N.M.D.Brown, T.D.Turbitt, and W.E.Watts, J. Organometal.Chem., 46, C19 (1972).
48. T.D.Turbitt and W.E.Watts, J.Chem.Soc., Perkin Trans.II, 177 (1974).
49. A.N.Nesmeyanov, G.B.Shul'pin, P.V.Petrovskii, V.I.Robas, and M.I.Rybinskaya, Dokl.Akad.Nauk SSSR, 215, 865 (1974).
50. A.N.Nesmeyanov, G.B.Shul'pin, and M.I.Rybinskaya, Dokl.Akad.Nauk SSSR, 218, 1107 (1974).
51. A.N.Nesmeyanov, G.B.Shul'pin, D.V.Zagorevskii, and M.I.Rybinskaya, Dokl.Akad.Nauk SSSR, 229, 881 (1976).
52. M.Cais, Organometal.Chem.Rev., 1, 435 (1966).
53. V.I.Sokolov, P.V.Petrovskii, and O.A.Reutov, J. Organometal.Chem., 59, C27 (1973).
54. M.Hisatome and K.Yamakawa, Tetrahedron, 27, 2101 (1971).
55. A.N.Nesmeyanov, G.B.Shul'pin, M.I.Rybinskaya, and P.V.Petrovskii, Dokl.Akad.Nauk SSSR, 215, 599 (1974).
56. A.N.Nesmeyanov, B.A.Surkov, I.F.Leshcheva, and V.A.Sazonova, Dokl.Akad.Nauk SSSR, 222, 848 (1975).
57. A.Ratajczak, B.Czech, B.Misterkiewicz, A.Piorko, and H.Zyzik, Bull.Acad.Polon.Sci., Ser.Sci.Chim., 24, 775 (1976).
58. P.Smith, J.J.McLeskey, and D.W.Slocum, J.Org. Chem., 30, 4356 (1965).
59. W.R.Jackson and W.B.Jennings, J.Chem.Soc., B, 1221 (1969).
60. T.Yu.Orlova, P.V.Petrovskii, V.N.Setkina, and D.N.Kursanov, J.Organometal.Chem., 67, C23 (1974).
61. A.G.Ginzburg, V.N.Setkina, and D.N.Kursanov, J.Organometal.Chem., 77, C27 (1974).
62. P.Renaut, G.Tainturier, and B.Gautheron, J. Organometal.Chem., 148, 43 (1978).
63. S.I.Goldberg, W.D.Bailey, and M.L.McGregor, J.Org.Chem., 36, 761 (1971).

Institute of Chemical Physics,
USSR Academy of Sciences,
Moscow

Translated from *Uspekhi Khimii*, **49**, 1234 - 1259 (1980) U.D.C. 541.49 : 541.63

Stereochemistry of Four-coordinate Chelate Compounds of Schiff Bases and Their Analogues

G.V.Panova, N.K.Vikulova, and V.M.Potapov

The problem of the configuration of the chelate group and the metal ring in chelates of transition metals with Schiff bases and their analogues is discussed, and the influence of various factors analysed, in particular the nature of the central metal atom and the steric and electronic effects of the ligands. Various types of conformational changes in conjugated metal rings in bicyclic and tricyclic chelates are surveyed, and factors influencing these changes are noted. The conformation of the non-conjugated metal rings in tricyclic chelates is discussed. A list of 188 references is included.

CONTENTS

I. Introduction 655
II. Configuration of chelate group in four-coordinate compounds 655
III. Conformation of chelates of Schiff bases and their analogues 660

I. INTRODUCTION

A fundamental aspect of the chemistry of chelate compounds is their spatial and electronic structure, not only of theoretical interest but also very important for the practical application of chelates. The geometrical structure is related to the arrangement of energy levels in the molecule, which in turn determines the luminescent and phosphorescent properties. Stereochemical and electronic factors largely govern the reactivity and the stability of chelate compounds[1-3], as well as the possibility of using the ligands as analytical reagents[4].

Undervaluation of the structure of reagents and chelates has been a serious defect in theoretical and practical work on the extraction of chelate compounds[5]. The sterochemistry and the electronic structure of chelates determine also their redox properties[4], reactivity[6], and ability to form adducts[7-10], which is quite important for an understanding of many catalytic processes[11] and phenomena occurring in living organisms[12].

Chelate compounds containing a bis(oxa,aza)-chelate group form one of the most common and important classes of chelates. They are model analogues of certain metal enzymes and group-B vitamins[13,14]. Furthermore, these chelates develop considerable fungicidal and antimicrobial activity[15,16]. Therefore many investigations have been published on chelates of this type.

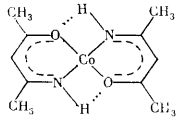
Chelate compounds obtained from Schiff bases and enaminoketones are convenient for the study of chelate structure, since varying the substituents in the metal rings permits variation in the three-dimensional structure of the molecule within wide limits. Some of the sterochemical results for such chelates have been summarised in reviews[17-22]. In the present Review, therefore, attention is directed mainly at work done during recent years, with the chief aim not of describing sterochemical features of individual chelates[18,21] but of examining the factors influencing their spatial structure.

II. CONFIGURATION OF CHELATE GROUP IN FOUR-COORDINATE COMPOUNDS

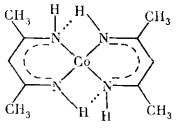
1. Effect of Nature of Metal Atom on Configuration of Chelate Group

The configuration of the chelate group in four-coordinate compounds may be square planar (with *cis* or *trans* arrangement of donor atoms around the central metal atom), tetrahedral, distorted tetrahedral, or distorted pyramidal with the metal atom at the apex. The configuration depends primarily on the nature of the metal atom, but also on the magnitude and symmetry of the ligand field. It is affected significantly also by steric hindrance in the molecule resulting from the interaction of non-bonded atoms and functional groups. Crystal packing effects must also be taken into account when the stereochemistry of a chelate in the solid state is being considered.

We can usefully consider each of these factors in greater detail on the basis of published information on the configuration of the chelate group formed by Schiff bases and enaminoketones, as summarised in Tables 1–4. These show that almost all cobalt(II) chelates, independently of the structure of the ligands, contain a chelate group of tetrahedral configuration, the most advantageous for such compounds[123]. Exceptions are bicyclic chelates of acetylacetone-mono- and di-imines[124,96] and tricyclic chelates in which 1,2-diamines serve as amino-components in the ligands[14,125-127]. However, in the first case the structure of the chelate is probably stabilised by intramolecular hydrogen bonding



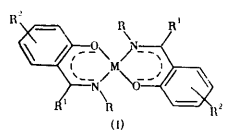
(V)



(VI)

and in the second case the structure is rigidly fixed by the shortness of the ethylene bridge.

Table 1. Configuration of the chelate group in the chelates.

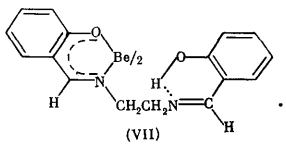


(I)

M	R^2	R^1	R	Configuration of chelate group* in solid**	Configuration of chelate group* in non-donor solvents	Ref.
Cu	H	H	H	sqpl	sqpl	23,24
Cu	H	H	CH_3	sqpl	sqpl	24,25,26
Cu	H	H	C_2H_5	distetr (35.6°)	sqpl	26,27,28
Cu	H	H	n-C_3H_7	sqpl	sqpl	29—31
Cu	H	H	n-C_4H_9	sqpl	sqpl	28,32,33
Cu	H	H	n-C_6H_{11}	sqpl	sqpl	34
Cu	H	H	iso-C_3H_7	distetr (59.7°)	distetr	28,30,33,35
Cu	H	H	t-C_4H_9	distetr (53.6°)	distetr	30,31,36
Cu	5,6-benzo	H	CH_3	sqpl	distetr	37
Cu	H	H	C_6H_5	sqpl	sqpl	38,39,40
Cu	5-Me, 3-CHO	H	C_6H_5	sqpl	—	41
Cu	H	H	C_2H_4OH	sqpl	sqpl	42,43
Cu	H	CH_3	H	sqpl	sqpl	44,45
Cu	H	CH_3	CH_3	sqpl	—	46
Cu	H	CH_3	iso-C_4H_9	sqpl	—	46
Cu	H	CH_3	n-C_6H_{13}	sqpl	—	47
Cu	H	CH_3	n-C_8H_{17}	sqpl	—	46
Cu	H	CH_3	n-$C_{10}H_{19}$	sqpl	—	48
Cu	H	CH_3	$C_6H_5CH_2$	distetr (29°)	—	46
Cu	H	CH_3	$C_6H_5CH(CH_3)$	distetr (26°)	—	49
Cu	H	H	$C_6H_5CH(CH_3)$	distetr (36°)	—	49
Cu	H	H	p-C_6H_4—CH_3	sqpl	—	50
Ni	H	H	H	sqpl	sqpl	26,51,52
Ni	H	H	CH_3	sqpl	octass	53,54
Ni	H	H	C_2H_5	sqpl	octass	54,55
Ni	H	H	n-C_4H_9	sqpl	octass	54,56
Ni	H	H	n-C_6H_{13}	sqpl	—	57
Ni	H	H	n-C_7H_7	sqpl	sqpl	58
Ni	H	H	C_6H_5	sqpl	—	59
Ni	H	H	iso-C_3H_7	distetr	eqmixt (49%)	60—62
Ni	3-CH_3	H	iso-C_3H_7	sqpl	eqmixt	62,63
Ni	3-C_2H_5	H	iso-C_3H_7	distetr (85°)	eqmixt	62,63
Ni	H	H	t-C_4H_9	—	eqmixt (95%)	64,65
Ni	3-OCH_3	H	p-C_6H_4-OCH_3	—	tetr	66
Ni	5,6-benzo	H	s-C_4H_9	—	eqmixt (57%)	67
Ni	3,4-benzo	H	s-C_4H_9	—	eqmixt (75%)	67
Ni	3-OCH_3	H	iso-C_3H_7	distetr (79°)	—	68
Co	H	H	n-C_4H_9	tetr	tetr	69,70
Co	H	H	s-C_4H_9	—	tetr	64
Co	H	H	iso-C_3H_7	tetr	tetr	71,72
Co	3-OCH_3	H	iso-C_3H_7	tetr	—	68
Co	H	H	C_6H_5	tetr	tetr	73—75
Co	H	H	m-C_6H_4-OCH_3	tetr	—	76
Zn	H	H	n-C_4H_9	tetr	tetr	69,77,78
Zn	H	H	iso-C_4H_9	—	tetr	77,79
Zn	H	H	s-C_4H_9	—	tetr	77,79
Zn	H	H	t-C_4H_9	—	tetr	77—79
Zn	H	H	iso-C_3H_7	tetr	tetr	71,79,80
Be	H	H	CH_3	—	tetr	81
Be	H	H	n-C_3H_7	—	tetr	81
Be	H	H	iso-C_3H_7	—	tetr	81
Pd	H	H	CH_3	sqpl	sqpl	82,83
Pd	H	H	C_2H_5	sqpl	sqpl	83,84
Pd	H	H	n-C_3H_9	sqpl	sqpl	83,85
Pd	H	H	iso-C_3H_7	sqpl	sqpl	83,86
Pd	3-CH_3	H	iso-C_3H_7	sqpl	sqpl	87
Pd	3-C_2H_5	H	iso-C_3H_7	sqpl	—	87
Pd	H	H	t-C_4H_9	sqpl	sqpl	83,88
Pd	H	H	C_2H_4OH	sqpl	sqpl	43

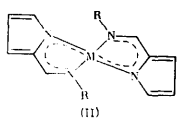
* Abbreviations: sqpl = square[sic]planar; distetr = distorted tetrahedral (relative angle of two metal rings); tetr = tetrahedral; eqmixt = equilibrium mixture of planar and tetrahedral forms of chelates (content of tetrahedral form);; octass = octahedral association complexes.
** From results of X-ray structural analysis.

In almost all chelates of bivalent zinc, mercury, and beryllium, like those of cobalt, a tetrahedral structure is energetically most advantageous independently of the structure of the ligand. The energy of stabilisation of tetrahedral chelates by the crystal field is greatest in the case of beryllium. As a consequence, this metal differs from cobalt and zinc in not forming a planar tricyclic chelate with ethylenebis-*N*-salicylideneimine, but gives the tetrahedral bicyclic chelate[81]



(VII)

Table 2. Configuration of chelate group in the chelates.



(II)

M	R	Configuration of chelate group* in solid**	Configuration of chelate group* in solution	Ref.
Cu	H	sqpl	sqpl	89,90
Cu	s-C_4H_9	—	sqpl	91
Cu	n-C_4H_9	—	sqpl	90
Cu	iso-C_3H_7	—	sqpl	90
Cu	t-C_4H_9	distetr (61°)	distetr	90,92
Cu	C_6H_5	—	sqpl	90
Ni	C_2H_5	—	sqpl	93
Ni	n-C_3H_7	—	sqpl	93
Ni	iso-C_3H_7	—	eqmixt	93
Ni	s-C_4H_9	—	eqmixt	93
Ni	t-C_4H_9	distetr (84°)	tetr	92,93
Co	t-C_4H_9	tetr	tetr	93,94
Zn	t-C_4H_9	tetr	tetr	92,93
Zn	iso-C_3H_7	—	tetr	93,95
Hg	CH_3	—	tetr	95
Hg	t-C_4H_9	—	tetr	95
Pd	CH_3	—	sqpl	93,95
Pd	iso-C_3H_7	—	sqpl	93,95

* Abbreviations as in Table 1.
** Results of X-ray structural analysis.

Chelates of bivalent palladium and platinum are mostly characterised by a square planar configuration[123]. The tendency of these metals to form such chelates is so great that this configuration appears even under exceptionally unfavourable steric conditions. Thus the chelate of palladium(II) with *N*-t-butylsalicylideneimine retains a planar structure[88] despite strong steric interactions of the t-butyl group with the azomethine hydrogen atom and with the oxygen atom of the adjacent ligand molecule.

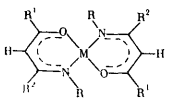
Besides the above extreme cases there exist many chelate compounds for which planar and tetrahedral structures differ little in energy of stabilisation by the crystal field. This applies especially to chelates of bivalent nickel and copper, whose stereochemistry is determined mainly by three-dimensional and electronic structural features of the ligands.

2. Effect of Structure of Ligands on Configuration of Chelate Group

(a) Steric effect of ligands

We must first consider briefly the structure of nickel and copper chelates. X-Ray results show (Tables 1 and 2) that in the solid state the chelate groups possess either a planar or a variously distorted tetrahedral configuration depending on the structure of the ligands. In solution the situation is more complicated: measurements of magnetic and dipole moments, proton magnetic resonance spectra, and electronic absorption spectra suggested[21] that an equilibrium is established between planar and tetrahedral forms of nickel(II) chelates of Schiff bases and enamino-ketones, whose position depends on the structure of the ligand and the temperature. However, other workers[128–130] are very doubtful about the establishment of such an equilibrium. Nevertheless, such studies are few and, in spite of some ambiguity in the treatment of several experimental facts, the hypothesis that an equilibrium is established between planar square and tetrahedron is generally accepted in discussion of the configuration of nickel(II) chelates in solution[131].

Table 3. Configuration of chelate group in the chelates.



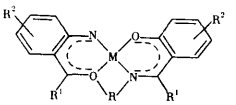
(III)

M	R¹	R²	R	Configuration of chelate group in non-donor solvents*	Ref.
Co	CH_3	CH_3	H	eqmixt (76%)	96, 97
Co	t-C_4H_9	CH_3	H	eqmixt (29%)	96, 97
Co	CH_3	CH_3	CH_3	tetr	96
Co	CH_3	CH_3	iso-C_3H_7	tetr	96
Co	CH_3	CH_3	C_6H_5	tetr	96
Ni	CH_3	CH_3	iso-C_4H_9	eqmixt (3%)	98
Ni	C_6H_5	H	s-C_4H_9	eqmixt (86%)	98
Ni	C_6H_5	CH_3	n-C_3H_7	eqmixt (23%)	98
Ni	CH_3	CH_3	iso-C_3H_7	tetr	98
Ni	C_6H_5	H	C_6H_5	eqmixt (6%)	98
Cr	C_6H_5	CH_3	H	sqpl	99
Cr	C_6H_5	CH_3	iso-C_3H_7	sqpl	99
Fe	C_6H_5	CH_3	H	tetr	99
Fe	C_6H_5	CH_3	CH_3	tetr	99
Fe	C_6H_5	CH_3	iso-C_3H_7	tetr	99
Cu	CH_3	CH_3	H	sqpl	100
Cu	C_6H_5	CH_3	iso-C_3H_7	distetr	99
Cu	C_6H_5	H	$CH(CH_3)C_6H_5$	distetr	101
Cu	p-CH_3-C_6H_4	H	$CH(CH_3)C_6H_5$	distetr	101
Cu	p-OCH_3-C_6H_4	H	$CH(CH_3)C_6H_5$	distetr	101
Cu	p-Br-C_6H_4	H	$CH(CH_3)C_6H_5$	distret	101
Pd	C_6H_5	H	CH_3	sqpl	102
Pd	C_6H_5	H	iso-C_3H_7	sqpl	102

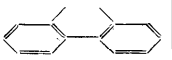
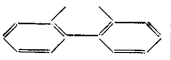
* Abbreviations as in Table 1.

There is no generally accepted view on the structure of copper(II) chelates in solution. From measurements of dipole moments Soviet workers[39,132–134] suggested that an equilibrium between planar and tetrahedral forms was established in solutions of certain such chelates. However, this hypothesis is inconsistent with the electronic absorption spectra of copper(II) chelates, which differ from those of nickel(II) chelates in being almost identical for solid specimens and for solutions[30,31,135,136] and furthermore hardly change with temperature. This indicates that only one form of the chelate is present in solution, with either a planar or a distorted tetrahedral configuration of the chelate group depending on the structure of the ligand.

Table 4. Configuration of chelate group in the chelates.



(IV)

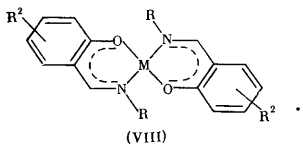
M	R²	R¹	R	Configuration of chelate group in solid and in solution*	Ref.
Mg	H	H	$(CH_2)_2$	sqpl	103
Pd	H	H	$(CH_2)_3$	sqpl	104
Cd	H	H	$(CH_2)_2$	sqpl	104
Co	H	H	$(CH_2)_2$	sqpl	14, 105
Ni	5-Cl	C_6H_5	$(CH_2)_2$	sqpl	106
Cu	H	CH_3	$(CH_2)_3$	distetr (34.4°)	107
Zn	H	H	$(CH_2)_5$	distetr	108
Ni	5-Cl	C_6H_5	$(CH_2)_3$	sqpl	106
Co	3-iso-C_3H_7	H	$(CH_2)_3$	distetr	109
Cu	H	H	$(CH_2)_4$	distetr	110—112
Zn	H	H	$(CH_2)_4$	tetr	106
Be	H	H	$(CH_2)_4$	tetr	106
Co	H	H	$(CH_2)_{4-10}$	tetr	113—115
Co	3-iso-C_3H_7	H	$(CH_2)_{4-7}$	tetr	109
Co	3-t-C_4H_9	H	$(CH_2)CHCH(CH_3)$	distetr	116
Ni	H	H	$(CH_2)_{2-5}$	sqpl	111, 117
Cu	H	H		sqpl	118
Cu	H	H		distetr (41°)	118, 119
Co	H	H		distetr (67°)	120
Co	H	H		sqpl	121
Pd	H	H		sqpl	122

* Abbrevations as in Table 1.

A similar conclusion has been reached[33] from a structural study by electron spin resonance of bicyclic copper(II) chelates of salicylideneimines *N*-substituted by n-butyl, isopropyl, or t-butyl. It was demonstrated unambiguously that these chelates exist in only one form either in the solid state or in solution, with the *g*-factor varying in parallel with the angle between the two metal rings. This view is probably more soundly based, and we shall adhere to it in describing the stereochemistry of copper(II) chelates in solutions.

It can be concluded from Tables 1–4 that all copper(II) chelates and most of the nickel chelates obtained from sterically inactive ligands have a planar chelate group. If to the nitrogen atom of the ligand are attached bulky radicals capable of interacting sterically with a radical on a neighbouring carbon atom and with the oxygen atom of the second ligand, the chelate group becomes tetrahedrally distorted in the case of copper(II) complexes, but either a tetrahedral form appears or its content increases siginificantly in the case of nickel(II) chelates. The degree of distortion and the percentage of the tetrahedral form increase with the volume of the radical attached to the nitrogen atom.

Steric stresses may increase not only with change in the *N*-substituent but also on the introduction of various substituents R^2 into the salicylaldehyde ring:



(VIII)

The greatest effect will obviously be exerted by radicals present at position 3 in the aromatic ring. Indeed, Japanese workers have found[138] that the chelate group in copper(II) complexes from 3-t-butyl- and 3-cyclohexylsalicylaldehydes is more distorted than in chelates of the unsubstituted aldehyde. Similarly, the content of the tetrahedral form in the nickel(II) chelate of *N*-isopropyl-3,4-benzosalicylideneimine ($R = iso\text{-}C_3H_7$, $R^2 = 3,4$-benzo) has increased to 68% from the 50% in *N*-isopropylsalicylideneimine ($R = iso\text{-}C_3H_7$, $R^2 = H$),[65] which is due to the steric effect of the bulky 3,4-benzo-group. The tetrahedral structure of the nickel chelate of 3-methoxy-*N*-*p*-methoxyphenylsalicylideneimine ($R = p\text{-}CH_3O.C_6H_4$, $R^2 = 3\text{-}CH_3O$)[66] is probably also a consequence of steric effects of the 3-methoxy-group.

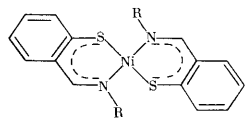
(b) Electronic effect of ligands

Ring substituents in salicylaldehyde are able to exert not only a steric but also an electronic effect on the configuration of the chelate group, with the latter effect quite often opposing the former. Such an electronic influence is most clearly evident when the steric demands made by the nature of the *N*-substituent require a minimal difference in energies of stabilisation of planar and tetrahedral forms by the crystal field.

This principle is illustrated by the stereochemical investigation[30,31,61,64,65,139] of chelates (I: M = Cu, Ni; $R = n\text{-}C_3H_7$, $iso\text{-}C_3H_7$, $t\text{-}C_4H_9$; and $R^2 = 3,4$- or 5,6-benzo, 3- or 5-Cl, 3- or 5-NO_2), showing that, independently of the nature of R^2, all the chelates with $R = n\text{-}C_3H_7$ have a planar chelate group, but those with $R = t\text{-}C_4H_9$ have a tetrahedral or distorted tetrahedral structure. Yet the configuration of the chelate group when $R = iso\text{-}C_3H_7$ depends significantly on R^2. In the solid state the structure is distorted tetrahedrally when $R^2 = H$, 3,4-benzo, and planar when $R^2 = 5,6$-benzo, 3- or 5-Cl, 3- or 5-NO_2. The nickel(II) chelate containing 5,6-benzo retains a planar structure even in solution, whereas the corresponding chelate with $R^2 = H$ contains 50% of the tetrahedral form in solution. The electronic influence of chlorine atoms, which tends to flatten the chelate group as with a 5,6-benzo-substituent, can be traced in nickel(II) chelates by comparing the square–tetrahedron equilibrium free energies: for chelates with $R^2 = H$, 3-Cl, 5-Cl, ΔF has the respective values −0.52, 0.35, and 0.15 kcal $mole^{-1}$ at 120 °C.

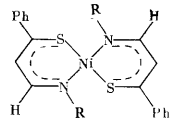
In connection with the effect of isosteric ligands on the configuration of nickel(II) chelates considerable interest attaches to a comparison[140] of chelates from amino-derivatives of 3-hydroxymethylenecamphor with analogous chelates from enamino-ketones of pentane-2,4-dione (III: M = Ni and $R^1 = R^2 = CH_3$), 1-phenylbutane-1,3-dione (III: M = Ni, $R^1 = C_6H_5$, and $R^2 = CH_3$), and Schiff bases of salicylaldehyde (I) and pyrrole-2-aldehyde(II). An attempt was made[140] to assess qualitatively the tendency of different isosteric ligands, containing the same *N*-substituents, to form tetrahedral chelate groups. The results showed this tendency to be greatest for chelates from amino-derivatives of 3-hydroxymethylenecamphor, and least for chelates of Schiff bases of pyrrole-2-aldehyde. These differences are most probably a consequence of different ligand field strengths in these chelates. Schiff bases of pyrrole-2-aldehyde are ligands having a strong field, and therefore tend to form planar chelate groups. But steric features of the five-membered camphor ring lead to a weak ligand field, so that they give chelates with a maximum content of the tetrahedral form.

The ligand field strength depends not only on the substituents in the metal ring but also on the nature of the donor atoms. Such an effect is clearly demonstrated by an investigation of the nickel(II) chelates with certain sulphur analogues of Schiff bases and enamino-ketones[98,141,142]



(IX)

R = CH_3, C_2H_5, $iso\text{-}C_3H_7$, $s\text{-}C_4H_9$, $t\text{-}C_4H_9$



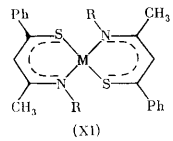
(X)

R = $(C_2H_5)_2CH$, $iso\text{-}C_4H_9$, $iso\text{-}C_5H_{11}$, C_6H_5

Almost all chelate groups formed by *N*-alkyl-*o*-mercaptobenzylideneimines have a square planar structure[141]. The only exception has $R = t\text{-}C_4H_9$, whose strong steric effect prevails over the electronic effect of the sulphur atom. Flattening of the chelate group on the replacement of oxygen by sulphur is indicated also by the fact that the content of the tetrahedral form in solutions of chelates of enamino-thiones is little more than half that for the corresponding enamino-ketones[98].

3. Competitive Effects of Nature of Metal and Ligand on Configuration of Chelates

When considering the effect of various factors on the configuration of a chelate group, we must bear in mind that in many cases one such factor is dominant, while the remainder operate only on the background of this main effect. For example, the electronic effect of the sulphur atom in zinc and cadmium chelates of enamino-thiones is insufficient to balance the tendency of these metals to form tetrahedral chelates, so that the compounds



(XI)

M = Zn, Cd;
R = $iso\text{-}C_3H_7$, $C_6H_5{-}CH_2$, $C_6H_5{-}CH(CH_3)$

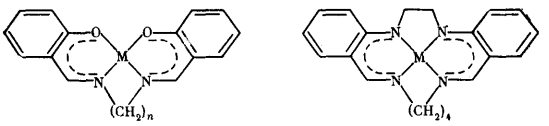
have a tetrahedral structure[143]. The absolute configuration of the chelate group in them may be either Δ or Λ: because of the absence of factors stabilising either absolute configuration, the proton magnetic resonance spectra for these chelates indicate rapid inversion $\Delta \rightleftharpoons \Lambda$, with intermediate formation of a planar chelate. This inversion occurs far more rapidly in chelates from enamino-thiones than in corresponding chelates from enamino-ketones. The difference is attributed[143] to the "flattening effect" of the sulphur atom discussed above.

Another example is provided by the stereochemistry[144] of nickel(II) and zinc(II) chelates with (−)-propylenebis-*N*-salicylideneimine. The steric demands of the ligand are

such that the chelate group in these compounds should be planar. However, this configuration is realised only in the nickel chelate, whereas the zinc chelate is non-planar owing to the tendency of this metal ion to form a tetrahedral configuration.

It is generally difficult to predict which of the factors will predominate, and hence the structure of the resulting chelate. The only exceptions are found when the factors act in the same direction, as e.g. in cobalt(II) and zinc(II) chelates in which bulky branched amines have been used in the ligand. The tetrahedral structure of these chelates is due both to steric features of the ligands and to the energy requirements of the metal ion. If, however, the different factors do not act in parallel, the structure of the chelate group will be determined by competition between them. Thus comparison of results for the three-dimensional structure of bivalent palladium, copper, and nickel chelates with ligands containing isopropylamine[86,35,60] shows that the tendency of the palladium ion to form planar complexes prevails over the steric requirements of the ligands, and the chelate has a square planar structure. In the nickel and copper chelates, however, the steric effect of the ligand predominates over the tendency of these metal ions to form planar chelates, so that the resulting compounds have a distorted configuration.

Another example is provided by investigations[145–153] on the tricyclic chelates

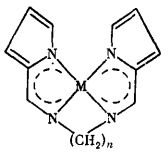


(XII)

M = Co, Ni, Cu; n = 2–4

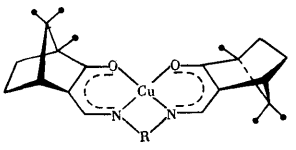
(XIII)

M = Co, Ni, Cu



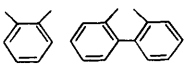
(XIV)

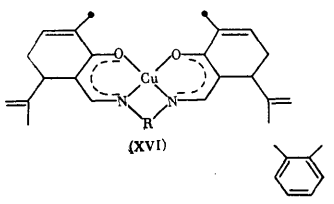
M = Cu, Ni; n = 2–5



(XV)

R = $(CH_2)_n$, where n = 2–6, 8;



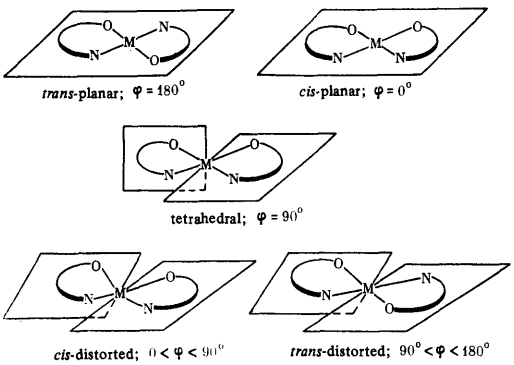


(XVI)

$R = (CH_2)_n$, where n = 2—6,8,10;

(see also Table 4). Inspection of geometric models of these chelates shows that lengthening the polymethylene bridge should cause distortion of the planar configuraiton of the chelate group owing to diminished interaction of non-bonded atoms in the distorted structures. However, this distortion is readily and completely realised only in cobalt(II) chelates, and is completely absent from nickel(II) chelates.

The structure of tricyclic copper(II) chelates is most interesting. Various structures can be realised when the planes of the metal rings undergo mutual rotation through an angle ϕ:



trans-planar; $\varphi = 180^\circ$

cis-planar; $\varphi = 0^\circ$

tetrahedral; $\varphi = 90^\circ$

cis-distorted; $0 < \varphi < 90^\circ$

trans-distorted; $90^\circ < \varphi < 180^\circ$

Electron spin resonance and spectropolarimetric studies[150–153] on such chelates obtained from enamino-ketones of oxymethylene-camphor and -carvone have shown that chelates containing a polymethylene bridge with $n = 2$ have a planar *cis* structure, whereas those with $n = 8$, 10 have a *trans* structure with a planar arrangement of the chelate group. The *trans*-planar configuration of the latter is probably a consequence of the considerable length of the octa- and decamethylene bridges, which enables the chelate molecule to assume the energetically most favourable *trans*-planar configuration. Owing to the greater length of the trimethylene bridge, chelates with $n = 3$ are somewhat distorted relative to a planar structure.

The e.s.r. spectra of solid chelates with $n = 4–6$ indicate that they are individual compounds existing in the same form with distortion of the chelate group to ensure denser packing. Yet the e.s.r. spectra of these chelates in low-temperature toluene glasses indicated[150–152] that solutions of each of the chelates contain three isomeric complexes, α, β, and γ with chelate groups differing in stereochemistry and distinguished by the angle of rotation ϕ of the planes of the two metal rings.

The current absence of the exact dependence of the g-factor on the angle ϕ prevented these workers from estimating the latter for each isomer. However, comparison of the e.s.r. parameters of these chelates with those of related compounds of known stereochemical structure indicated that all the γ-isomers were *trans*, with the chelate group most distorted tetrahedral in the presence of a tetramethylene bridge ($n = 4$). On the other hand, the α and β-isomers have a distorted tetrahedral configuration of the coordination sphere with a *cis* arrangement of the donor atoms; the latter isomers are considerably more distorted than the former. In the β-isomers, as in the γ-isomers, the degree of distortion of the chelate group diminishes as the polymethylene bridge becomes longer. The initial proportions of rotational isomers appearing after dissolution do not remain constant[150–152], but change with time, with a gradual increase in the concentration of the α-isomer, whose chelate group is least distorted relative to a planar *cis* structure.

To summarise, it can be concluded that the tendency of the planar configuration of the chelate group to be distorted increases as the chelating metal changes in the sequence

$$Pd<Cr<Cu\approx Ni<Co<Fe<Zn<Cd<Be.$$

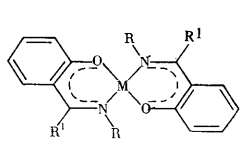
The tendency of the metal ion to form chelates having a tetrahedral configuration varies in the same sequence, provided that the ligand favours such a configuration. The chelate group in compounds of the same metal with isosteric ligands will be more "flattened" the more intense the ligand field in the chelate.

III. CONFORMATION OF CHELATES OF SCHIFF BASES AND THEIR ANALOGUES

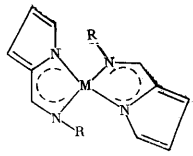
Comparatively few papers have appeared on the conformations of chelates, although this problem is of no less interest than the configuration of the chelate group. This is probably due to the complexity involved in investigating the structure of chelate molecules, since the great majority of physicochemical methods used to study chelate compounds are incapable of registering conformational changes. X-Ray structural analysis is the most accurate method for determining the conformation of a metal ring in the solid state. Proton magnetic resonance and spectropolarimetry are used to study the conformational structure of chelates in solution.

1. Conformation of Conjugated Metal Rings

X-Ray examination of four-coordinate chelates has shown that flat molecules with a completely coplanar arrangement of all the atoms are atypical. The only examples[51,89] of planar chelates are



(XVII)



(XVIII)

with M = Ni and R = R¹ = H in (XVII), and M = Cu and R = H in (XVIII), in both of which no atom departs significantly from the plane. Far more often chelates are met in which the general coplanarity of the molecule is disturbed by folding of the conjugated metal rings along the O....N line, so that the molecule as a whole has the form of a step:

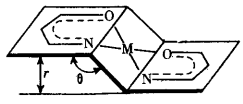
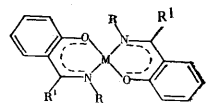


Table 5 summarises published data on the step distortion of metal rings in chelate compounds of several metals with Schiff bases.

The cause of step distortion in chelates obtained from Schiff bases is steric interaction of substituents in the metal ring, the distance between which is significantly less[46] than the sum of the van der Waals radii. Such distortion disturbs the coplanarity of the system and hence diminishes the degree of delocalisation of electron density in the quasi-aromatic metal ring, which is disadvantageous energetically. However, this is balanced by the increased distance between non-bonded atoms resulting in all cases from step distortion along the O...N lines, which lessens steric stresses in the molecule and also lowers its total energy.

Table 5. Data on the conformational structure of the chelates.



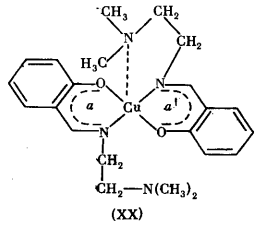
(XIX)

M	R¹	R	r, Å	Ref.
Cu	H	H	0.29	23
Cu	H	C_6H_5	0.24	27
Cu	H	n-C_3H_7	0.32	29
Cu	H	iso-C_3H_7	0.34	35
Cu	H	n-C_4H_9	0.74	32
Cu	H	t-C_4H_9	0.67	36
Cu	H	C_6H_5	0.89	38
Cu	H	p-CH_3-C_6H_4	0.90	50
Cu	H	OH	0.13	154
Cu	CH_3	H	0.48	44
Cu	CH_3	CH_3	1.91	46
Cu	CH_3	iso-C_3H_9	2.24	155
Cu	CH_3	n-C_8H_{17}	2.66	46
Cu	CH_3	n-$C_{10}H_{21}$	2.34	48
Cu	CH_3	C_6H_5—CH_2	1.68	46
Cu	CH_3	$C_6H_5CH(CH_3)$	1.22	46
Ni	H	C_6H_5	1.78	55
Ni	H	C_6H_{13}	0.65	57
Pd	H	iso-C_3H_7	0.42	86
Pd	H	t-C_4H_9	1.72	89

It must therefore be expected that the magnitude of the distortion will depend on the volumes of the substituents R and R¹ in the metal ring and on the related steric stresses within the molecule. Indeed, it is readily seen from Table 5 that r is significantly greater for chelates of Schiff bases obtained from o-hydroxyacetophenone ($R^1 = CH_3$) than for corresponding chelates based on salicylaldehyde ($R^1 = H$). In the former case attachement of methyl to the azomethine carbon atom enhances significantly the steric stresses within the molecule, with a consequent increase in step distortion of the metal rings.

Simple relations between the volume of the radical R and the distance r have not yet been found. The probable reason is that variation in R leads to change not only in the relative arrangement of the metal rings but also in the configuration of the chelate group and the length of the carbon–nitrogen bonds.

Steric stresses in a chelate molecule and the associated step distortion of the metal rings can be caused not only by interaction of juxtaposed atoms and groups but also by certain other structural features of the ligands. An example is provided by X-ray results[156] for the chelate



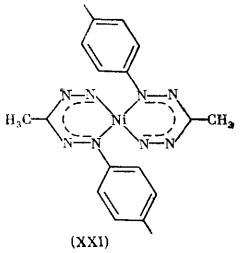
(XX)

in which one molecule of the Schiff base is terdentate, whereas the other is bidentate. Coordination of the ligand through three donor atoms increases the stress in this moiety, leading to conformational non-equivalence of the metal rings *a* and *a'*, with *a* almost planar and *a'* having $r = 0.13$ Å.

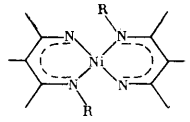
Analogous conformational non-equivalence of the two metal rings has been found in the zinc(II) chelate of *N*-*o*-methoxyphenylsalicylideneimine[157], which has a *cis*-octahedral structure owing to coordination of the zinc atom with the methoxyl-oxygen atom. One of the metal rings is planar, whereas for the other $\theta = 31.5°$. Such non-equivalence of the metal rings is attributed[157] to the difference in the angles of rotation of the anisidino-rings about the two conjugated metal rings.

Steric stresses in a molecule can be eliminated not only by a stepped conformation of the metal rings but also by distortion of the planar configuration of the chelate group to a tetrahedral or distorted tetrahedral configuration. Which path is followed depends primarily on the tendency of a given metal atom to form the energetically most stable configurations Since, as already mentioned, a tetrahedral configuration is the most stable for four-coordinate cobalt(II) chelates, steric stresses are removed from such chelates mostly by the formation of compounds having a tetrahedral chelate group and almost planar metal rings[65,71,73]. However, a stepped structure is formed with all sterically hindered chelates of metal ions that cannot give a tetrahedral configuration. Thus in the palladium(II) chelate of *N*-t-butylsalicylideneimine[88] the chelate remains planar, but the metal rings are strongly deflected from the plane at an angle $\theta = 36°$.

The situation is far more complicated with chelates of metals for whose ions planar and tetrahedral configurations do not differ greatly in energy, as with the nickel(II) chelates



(XXI)



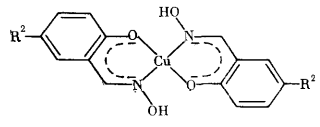
(XXII)

R = Alk, Ar

Thus the diamagnetic chelate (XXI) has a planar chelate group and a strongly step-distorted metal ring ($\theta = 37°$, $r = 1.6$ Å),[158] but in paramagnetic chelates (XXII) steric stresses are removed mainly by distortion of the planar geometry of the chelate group[159].

The magnitude of the step distortion of metal rings depends not only on steric factors but also on electronic structural features of the ligand. The ligand field intensity affects not only the conformation of the chelate group (Section II, 2*b*) but probably also the conformational structure of the metal rings. Thus comparison of X-ray structural data for copper(II) chelates of *N*-t-butylsalicylideneimine[36] (XVII: M = Cu, R = t-C_4H_9, and R^1 = H) and *N*-t-butylpyrrolideneimine[92] (XVIII) M = Cu and R = t-C_4H_9) shows that the latter chelate, in contrast to the former, has an almost planar metal ring. This is probably due to intensification of the ligand field when the donor oxygen atom in (XVII) is replaced by a donor nitrogen in (XVIII).

The effect of the ligand field intensity on the step distortion of the metal ring is confirmed also by X-ray results for the copper chelates of the oximes of salicylaldehyde and its 5-chloro-derivative[154,160]

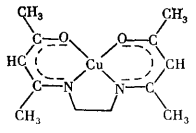


(XXIII)

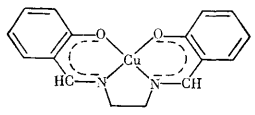
R^2 = H, Cl

Introduction of the chlorine atom weakens the ligand field, which in turn increases considerably the distortion of the metal rings: values of *r* for the chelates obtained from unsubstituted and substituted salicylaldehyde oximes are respectively 0.13 and 0.76 Å.

Interesting information on the effect of ligand field intensity on the general planarity of the molecule has resulted from a structural investigation[161–165] of outer-sphere adducts of *NN'*-ethylenebis(acetylacetoneiminato)copper(II) and *NN'*-ethylenebis(salicylideneiminato)copper(II)



(XXIV)

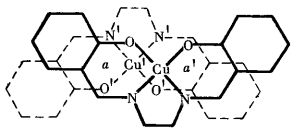


(XXV)

having the compositions (XXIV).$\frac{1}{2}H_2O$, (XXIV).$[CH_3NH_3]^+[ClO_4]^-$, (XXV).$CHCl_3$, and (XXV).*p*-HO.C_6H_4.NO_2. The water, chloroform, and *p*-nitrophenol molecules and the methylammonium ion form hydrogen bonds with the oxygen atom of the metal ring, which tend to increase the π back-bonding of the oxygen atom to the d_π orbitals of the copper atom, i.e. to strengthen the field of the ligands in the chelates. Since water is less capable than methylammonium of forming hydrogen bonds, and chloroform less than *p*-nitrophenol, the ligand field strength will gradually increase on passing from (XXIV) to the hemihydrate and then to the methylammonium adduct, and also on passing from the very weak adduct of (XXV) with chloroform to that with *p*-nitrophenol. X-Ray results for these chelates show that the degree of distortion of the metal rings decreases in the same sequence. Thus, whereas the angle of fold of the metal ring $\theta = 15.5°$ in the chelate (XXIV),[161] it is only 3.5° in the hemihydrate[162], and the metal rings are completely planar in the methylammonium adduct[163]. Similarly, the step distortion of the metal rings $r = 0.55$ and 0.2 Å in the adducts of (XXV) with chloroform and with *p*-nitrophenol respectively. It was concluded[161–165] from these results that the planarity of the molecule can even serve as a criterion for assessing the ligand field strength in a chelate: the greater the general planarity of a molecule the stronger the ligand field in it.

Furthermore, step distortion of metal rings is sometimes a consequence not of the structure of the ligand but of specific intermolecular interactions or lattice effects. Thus a stepped conformation of metal rings has been found in copper(II) chelates of acetylacetone[166], benzoylacetone[167], and salicylaldehyde[168,169], in which there are no steric interactions between the two metal rings and their substituents.

The conformational difference between the two metal rings in the chelate

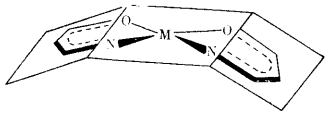


(XXVI)

has also been attributed[165] to intermolecular interactions. The angle of fold of the metal ring *a* is almost double that of *a'*. The greater "flattening" of the latter metal ring is a consequence of intermolecular interaction of the oxygen atom in ring *a* with the copper atom of a second chelate molecule.

Another example is provided by X-ray structural data[170] for the copper chelate of the Schiff base of salicylaldehyde and aminoethanol (XVII: M = Cu, R^1 = H, and R = CH_2CH_2OH). The unit cell contains two independent molecules, the angle of fold of the metal rings in one of which is almost double that in the other. The differences observed in the conformational structure of the metal rings in the two molecules are attributed[170] to effects of their crystalline packing.

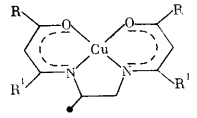
In the above systems distortion of the metal rings yields a stepped molecular structure, with the two metal rings bent in opposite directions relative to the plane of the chelate group CuO_2N_2. Recent work has shown that chelates of Schiff bases may have not only a stepped but also an "umbrella-shaped" structure



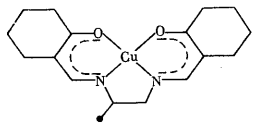
in which the two metal rings are bent in the same direction. Such an "umbrella" structure has been found in particular in the monohydrate of *NN'*-ethylenebis(acetylacetoneiminato) copper (XXIV).H_2O,[171] in which the copper atom is coordinated with the oxygen atom of the water molecule ($\theta = 11.8°$), in *NN'*-ethylenebis(salicylideneiminato)iron(III) chloride[172], in the copper(II) chelate of the Schiff base of *o*-aminobenzaldehyde and propylenediamine[173] (5°), in the dimer of *NN'*-ethylenebis(thiosalicylideneiminato)cobalt(II) (21.4°),[174] and in *NN'*-*o*-phenylenebis(salicylideneiminato)palladium(II).[122] However, the reasons for the appearance of an "umbrella" and not a stepped structure in these cases are not yet clear.

Study of the conformations of conjugated metal rings is quite complicated, since the description of the conformational structure depends on the method of choosing the median plane. Work by Porai-Koshits et al.[175] on the conformations of the metal rings in certain copper(II) and nickel(II) bis-salicylideneiminates suggests that these rings are labile, but the number of possible ways in which they can be distorted is limited. Besides a planar arrangement of all the atoms in a metal ring and folding of the ring along the O....N line, cases have also been examined[175] in which metal and nitrogen atoms are expelled from the plane of the metal ring, or metal and oxygen atoms lie on one side of the median plane, while the nitrogen and attached carbon atom lie on the opposite side.

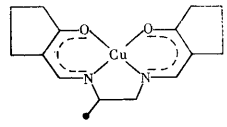
It must again be emphasised that all the structural results for conjugated metal rings considered hitherto have been obtained by X-ray structural analysis and are valid for the conformations of solid chelates. An attempt to assess the conformation of conjugated metal rings in solution involved[176,177] spectropolarimetric examination of the chelates



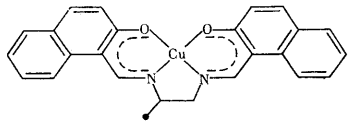
(XXVII)



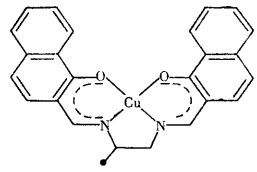
(XXVIII)



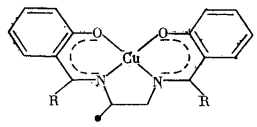
(XXIX)



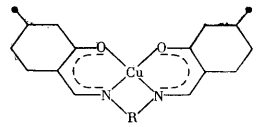
(XXX)



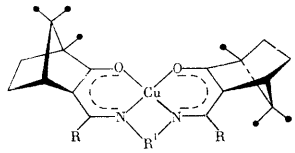
(XXXI)



(XXXII), R = H, CH_3



(XXXIII), R = $(CH_2)_2$,



(XXXIV)

R = H, R^1 = $(CH_2)_2$;

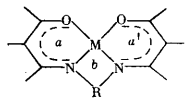
R = CH_3, R^1 = $(CH_2)_2$

The circular dichroism spectra showed a change in sign of the Cotton effect of the $d_{xy} \rightarrow d_{x^2-y^2}$ transition band and a hypsochromic shift in the intraligand $\pi-\pi^*$ transition band on replacement of the azomethine hydrogen atom by a methyl group and on passing from ethylenediamine to *o*-phenylenediamine chelates. Detailed analysis of these spectra indicated that the observed change in sign was due neither to change in conformation of the central non-conjugated metal ring nor to change in configuration of the chelate group but to change in conformation of the conjugated metal rings accompanying change in azomethine *N*- and *C*-substituents capable of steric interaction. It is emphasised[176,177] that, if the change in substituents does not affect the steric stresses in the chelate molecule (as with changes in R), the conformation of the conjugated metal rings remains unchanged.

2. Conformation of Non-conjugated Metal Rings

Besides the chelate compounds having conjugated metal rings already considered there exist a large number of chelates containing also non-conjugated metal rings. They

include primarily tricyclic chelate compounds of the type



(XXXV)

R = $(CH_2)_n$, n = 2-12

formed by quadridentate Schiff bases, in which the non-conjugated polymethylene ring *b* is fused with two conjugated rings. Chelates of this type having $n = 2$, i.e. obtained from 1,2-diamines, have been the most thoroughly studied. Thus in the work already cited[161-165,171,173] investigation of the structure of the conjugated metal rings was accompanied by detailed study of the conformation of the ethylene- and propylene-diamine rings in (XXIV), (XXV), and their adducts, and also in the copper(II) chelate of *NN'*-propylenebis-(*o*-aminobenzylideneimine). X-Ray structural data on the conformations of the non-conjugated metal rings in these chelates (Table 6) show that the most stable form of the five-membered non-conjugated metal ring is the skew conformation

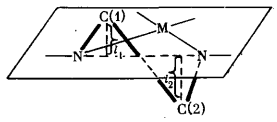


Table 6. Distances l_1 and l_2 of carbon atoms $C_{(1)}$ and $C_{(2)}$ in ethylene bridge from plane of chelate group CuO_2N_2.

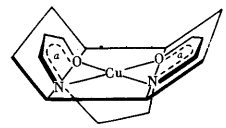
Compound	l_1, Å	l_2, Å	Ref.
(XXIV)	0.44	—0.12	161
(XXIV)·1/2H_2O	0.18	—0.11	162
(XXIV) $[CH_3NH_3]^+$ $(ClO_4)^-$	0.05	0.05	163
(XXIV)·H_2O	—0.11	—0.15	171
(XXV)	0.49	—0.24	178
(XXV)·$CHCl_3$	0.44	—0.12	164
(XXV)·p-HO—C_6H_4—NO_2	0.28	—0.20	165
(XXXVI) *	0.16	—0.14	173
(XXXVII) **	0.44	—0.22	172

* *NN'*-Propylenebis (*o*-aminobenzylideneiminato)copper(II).
** *NN'*-Ethylenebis(salicylideneiminato)iron(III) chloride.

Comparison of Table 6 with the angles of fold of the conjugated metal rings in the same compounds shows that the conformation of the non-conjugated metal ring depends significantly on the structure of the conjugated rings fused with it. It can be concluded firstly that a stepped structure of the chelate molecule as a whole favours a skew conformation of the ethylenediamine ring and secondly that the distance of the carbon atoms $C_{(1)}$ and $C_{(2)}$ of the ethylene bridge from the CuO_2N_2 plane is determined mainly by the magnitude of the step distortion.

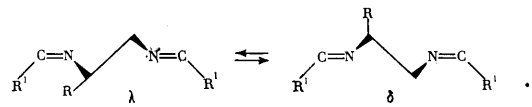
Table 6 shows that these two carbon atoms of the diamine bridge do not usually form an ideally skew conformation, but are situated unsymmetrically with respect to the plane of the chelate group CuO_2N_2. Such lack of symmetry is a consequence of the non-equivalence of the angles of fold of the two conjugated metal rings. From a comparison of the distances l_1 and l_2 of these atoms with the step distortions of the conjugated metal rings it was concluded that the departures of the bridge carbon atoms from the plane of the chelate group diminish with decrease in the angle of fold of the conjugated metal rings. Thus values of l_1 for the chelates (XXIV), (XXIV).$\frac{1}{2}H_2O$, and (XXIV).$[CH_3NH_3]^+[ClO_4]^-$, for which this angle is 13.5°, 3.5°, and 0°, are respectively 0.44, 0.18, and 0.05 Å. Among these compounds the greatest interest attaches to the chelate (XXIV).$[CH_3NH_3]^+[ClO_4]^-$, in which complete coplanarity of the conjugated metal rings leads to formation of the sterically unfavourable completely eclipsed conformation of the ethylene bridge.

The partly eclipsed *cis* conformation of the ethylene bridge (with the two bridge carbon atoms on the same side of the CuO_2N_2 plane) is found in the chelates (XXIV).H_2O and *NN'*-ethylenebis(trifluoroacetylacetoneiminato)nickel(II)[179] with an umbrella structure of the molecule

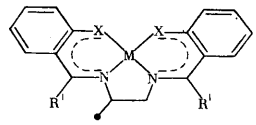


The reason for such an uncharacteristic *cis*-eclipsed conformation of the ethylene bridge is that steric interaction of the bridge carbon atoms with the metal rings *a* is less than for a skew conformation. Yet in *NN'*-propylenebis-(*o*-aminobenzylideneiminato)copper(II) (XXXVI) and in *NN'*-ethylenebis(salicylideneiminato)iron(III) chloride (XXXVII), which like the preceding compounds possess an umbrella structure, the ethylene bridge has an eclipsed conformation. Such a conformation of the non-conjugated metal ring in these chelates is determined mainly not by the way in which the metal rings are folded but by the configuration of the chelate group, which has a distorted tetrahedral structure with a relative angle of rotation of the two metal rings of 9° and 10° respectively.

With a skew conformation the ethylene bridge can have either a λ- or δ-conformation, which are enantiomeric:

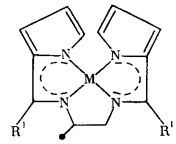


If the substituent R = H, the λ- and δ-conformations of the metal rings are equivalent. With substituted ethylenediamines (e.g. in chelates based on propylenediamine—R = CH_3), however, steric interactions of the radicals R and R^1 should lead to non-equivalence of λ- and δ-conformations, so that one of them will be formed preferentially. Indeed, X-ray results for copper(II) chelates of *NN'*-propylenebis-(*o*-aminobenzylideneimine)[173] and *NN'*-propylenebis(salicylideneimine)[180] show that the propylene bridge has the δ-conformation with an axial methyl group. 1,3-Interaction of R and R^1 is far weaker with an axial than with an equatorial methyl group.



(XXXVIII)

X = O, R^1 = H, CH_3, M = Cu, Ni;
X = N, R^1 = H, M = Cu

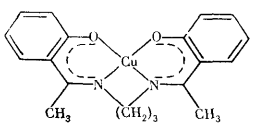


(XXXIX)

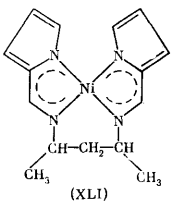
R^1 = H, CH_3

A δ-conformation of the propylene ring in solution was indicated also by a spectropolarimetric investigation[181,182] of the chelates (XXXVIII). The same conclusion has been reached[183,184] for analogous titanium(IV) monoxide and iron(III) chelates, and also in a study[176] of conformational aspects of the chelates (XXVII: R = CH_3, C_6H_5 and R^1 = H, CH_3).

The chelates (XXXIX: R^1 = H) have the propylene ring in the λ-conformation[185], which was explained by weakening the 1,3-equatorial interactions between the methyl group and the azomethine hydrogen atom in chelates (XXXIX) from Schiff bases of pyrrole-2-aldehyde in comparison with chelates (XXXVIII) from Schiff bases of salicylaldehyde. Such weakening is due to the smaller size of the five-membered metal ring in the former case relative to the six-membered ring in the latter. In chelates (XXXIX) of 2-acetylpyrrole ($R^1 = CH_3$), however, the steric stresses in the molecule due to interaction of the two methyl groups are already quite strong, and the central metal ring has the δ-conformation. A 1,2-diaxial conformation of a five-membered metal ring has been found also in the cobalt(II) chelate of the Schiff base of salicylaldehyde and butane-1,2-diamine[186].



(XL)



(XLI)

Very little information has been obtained on the conformation of non-conjugated central metal rings containing more than two carbon atoms. The central metal ring in the chelate (XL), formed by a trimethylene bridge, has a twisted boat conformation[187], but the analogous metal ring in (XLI) possesses a half-chair conformation with both methyl groups in equatorial positions[188]. X-Ray examination of the chelate (XIII) has established[149] that the tetramethylene bridge has a half-boat conformation. It was suggested[149] that the conformation of the central metal rings in chelates obtained from polymethylenediamines as amino-components will probably be determined by the configuration of the chelate group: a planar or slightly distorted planar chelate group should give a boat conformation, but a tetrahedral or nearly tetrahedral group should yield a chair conformation. However, the literature is devoid of results supporting this hypothesis.

* * *

Thus inspection of the literature shows that the conformation of metal rings, like the configuration of the chelate group, depends on the nature of the central metal atom, the spatial and electronic structure of the ligands, and also the character of the intermolecular interactions. Full information on the stereochemistry of chelate compounds can be obtained only by using a combination of diverse physicochemical methods, enabling the structure of chelates to be characterised not only in the solid state but also in solutions.

REFERENCES

1. A.Nakamura, Kagaku no ryoiki (J.Japan Chem.), 30, 665 (1976).
2. V.A.Kogan, N.I.Dorokhova, and O.A.Osipov, Zhur. Neorg.Khim., 16, 179 (1971) [Russ.J.Inorg.Chem., No.1 (1971)].
3. N.I.Dorokhova, V.A.Kogan, and O.A.Osipov, Zhur. Fiz.Khim., 45, 962 (1971) [Russ.J.Phys.Chem., No.4 (1971)].
4. D.D.Perrin, "Organic Analytical Reagents" (Translated into Russian), Mir, Moscow, 1967.
5. Yu.A.Zolotov and I.P.Alimarin, Dokl.Akad.Nauk SSSR, 136, 6 (1961).
6. K.J.Wannowius, H.Voss, and H.Elias, Chem.Ber., 110, 762 (1977).
7. T.S.Kannan and A.Chakravorty, Indian J.Chem., 9, 1153 (1970).
8. P.S.Zacharias and A.Chakravorty, Indian J.Chem., 10, 1148 (1971).
9. J.C.Lockhart and W.J,Mossop, J.Chem.Soc., Dalton Trans., 19 (1973).
10. M.R.Paris and D.Aymes, Bull.Soc.chim.France, 1431 (1976).
11. G.A.Chukhadzhan, E.L.Sarkisyan, and T.S.Elbakyan, Koordinats.Khim., 2, 965 (1976).
12. B.L.Vallee and R.J.P.Williams, Proc.Nat.Acad.Sci. U.S.A., 59, 498 (1968).
13. H.Sigel and D.B.McCormick, Accounts Chem.Res., 3, 201 (1970).
14. A.Bigotto, G.Costa, G.Mestroni, G.Pellizer, A.Puxeddu, E.Relsenhofer, L.Stefani, and G.Tauzher, Inorg.Chim.Acta, Rev., 4, 41 (1970).
15. A.P.Terent'ev, E.A.Viktorova, B.M.Esel'son, A.N. Kost, and V.V.Ershov, Zhur.Obshch.Khim., 30, 2422 (1960).
16. M.D.Aptekar', E.P.Troplina, and I.A.Savich, "Tezisy Dokladov XI Vsesoyuznogo Soveshchaniya po Khimii Kompleksnykh Soedinenii" (Abstracts of Papers at Eleventh All-Union Conference on the Chemistry of Complex Compounds), Alma-Ata, 1973, p.202.
17. S.Yamada, Coordination Chem.Rev., 1, 415 (1966).
18. R.H.Holm, Progr.Inorg.Chem., 7, 83 (1966).
19. E.K.Barefield, D.H.Busch, and S.M.Nelson, Quart. Rev., 22, 457 (1968).
20. L.Sacconi, Transition Metal Chem., 4, 199 (1968).
21. R.H.Holm, and M.J.O'Connor, Progr.Inorg.Chem., 14, 241 (1971).
22. S.Yamada, Kagaku (Chemistry), 30, 477 (1975).
23. E.N.Baker, D.Hall, and T.N.Waters, J.Chem.Soc., (A), 680 (1966).
24. D.Kivelson and R.Neiman, J.Chem.Phys., 35, 149 (1961).
25. E.C.Lingafelter and G.L.Simmons, Acta Cryst., 14, 1222 (1961).
26. K.R.Kumar and R.K.Bhattacharya, Bull.Chem.Soc. Japan, 49, 2872 (1976).
27. C.Panattoni, G.Bombieri, and R.Graziani, Acta Cryst., 23B, 537 (1967).
28. S.Yamada and H.Nishikawa, Bull.Chem.Soc.Japan, 36, 755 (1963).
29. G.Bombieri, C.Panattoni, E.Forsellini, and R.Graziani, Acta Cryst., 25B, 1208 (1969).
30. L.Sacconi and M.Ciampolini, J.Chem.Soc., 276 (1964).
31. L.Sacconi, M.Ciampolini, and G.P.Speroni, J.Amer. Chem.Soc., 87, 3102 (1965).
32. D.Hall, R.H.Sumner, and T.N.Waters, J.Chem.Soc., (A), 420 (1969).
33. G.M.Larin, V.A.Kolosov, G.V.Panova, and N.K. Vikulova, Zhur.Neorg.Khim., 18, 2868 (1973) [Russ. J.Inorg.Chem., No.10 (1973)].

34. E.Frasson, C.Panattoni, and L.Sacconi, Ricerca sci. (IIA), 32, 649 (1962).
35. P.L.Orioli and L.Sacconi, J.Amer.Chem.Soc., 88, 277 (1966).
36. T.P.Cheeseman, D.Hall, and T.N.Waters, J.Chem. Soc.(A), 685 (1966).
37. G.R.Clark, J.M.Waters, and T.N.Waters, J.Inorg. Nuclear Chem., 37, 2455 (1975).
38. L.Wei, R.M.Stogsdill, and E.C.Lingafelter, Acta Cryst., 17, 1058 (1964).
39. V.A.Kogan, O.A.Osipov, V.I.Minkin, and M.I. Gorelov, Dokl.Akad.Nauk SSSR, 153, 594 (1963).
40. M.N.Patel and R.P.Patel, J.Indian Chem.Soc., 52, 1046 (1975).
41. A.N.Shnulin, Yu.T.Struchkov, and Zh.S.Mamedov, Zhur.Strukt.Khim., 17, 866 (1976).
42. I.Kinya and O.Isao, Bull.Chem.Soc.Japan, 43, 1040 (1970).
43. S.N.Podar and K.Dey, J.Indian Chem.Soc., 47, 743 (1970).
44. C.Marongiu and E.C.Lingafelter, Acta Cryst., 27B, 1195 (1971).
45. A.H.Maki and B.R.McCarvey, J.Chem.Phys., 29, 35 (1958).
46. R.M.Kirschner, G.D.Andreetti, D.Barnhart, F.D. Tomas, D.Welsh, and E.C.Lingafelter, Inorg.Chim. Acta, 7, 17 (1973).
47. P.C.Jain and V.K.Syal, J.Chem.Soc., Dalton Trans., 1908 (1973).
48. P.C.Jain, J.M.Bindlish, and R.P.Kashyal, J.Chem. Soc., Dalton Trans., 2129 (1976).
49. Z.A.Starikova, M.A.Porai-Koshits, and P.M.Zorkii, Dokl.Akad.Nauk SSSR, 171, 155 (1966).
50. J.M.Bindlish, S.C.Bhatia, and P.C.Jain, Acta Cryst., 32B, 2848 (1976).
51. J.M.Stewart and E.C.Lingafelter, Acta Cryst., 12, 842 (1959).
52. N.C.Clark and A.L.Ogell, J.Chem.Soc., 520 (1956).
53. M.R.Fox and E.C.Lingafelter, Acta Cryst., 22, 943 (1967).
54. S.Yamada, E.Ohno, Y.Kuge, A.Takeuchi, K.Yamanouchi, and R.Iwasaki, Coordination Chem.Rev., 3, 247 (1968).
55. L.M.Shkol'nikova, A.N.Knyazeva, and V.A. Voblikova, Zhur.Strukt.Khim., 8, 94 (1967).
56. E.F.Frasson, C.Panattoni, and L.Sacconi, Gazzetta, 92, 1470 (1962).
57. R.Graziani and E.Forsellini, Inorg.Nuclear Chem. Letters, 8, 775 (1972).
58. J.Császár and J.Barta, Acta chim.Acad.Sci.Hung., 71, 269 (1972).
59. J.Balog and J.Császár, Acta chim.Acad.Sci.Hung., 86, 365 (1975).
60. M.R.Fox, P.L.Orioli, E.C.Lingafelter, and L.Sacconi, Acta Cryst., 17, 1159 (1964).
61. R.H.Holm, A.Chakravorty, and G.O.Dudek, J.Amer. Chem.Soc., 86, 379 (1964).
62. R.H.Holm and K.Swaminathan, Inorg.Chem., 2, 181 (1963).
63. R.L.Braun and E.C.Lingafelter, Acta Cryst., 21, 546 (1966).
64. L.Sacconi, P.Paoletti, and M.Ciampolini, J.Amer. Chem.Soc., 85, 411 (1963).
65. L.Sacconi, M.Ciampolini, and N.Nardi, J.Amer.Chem. Soc., 86, 819 (1964).
66. V.I.Minkin, O.A.Osipov, and D.Sh.Verkhovoda, Zhur.Neorg.Khim., 11, 2829 (1966) [Russ.J.Inorg. Chem., No.12 (1966)].
67. P.Salvadori, G.Rosini, K.Bertucci, and L.Lardini, Gazzetta, 105, 625 (1975).
68. T.Ashida, S.Iwata, T.Yamane, M.Kakuoto, and S.Yamada, Bull.Chem.Soc.Japan, 49, 3502 (1976).
69. L.Sacconi, P.L.Orioli, P.Paoletti, and M.Ciampolini, Proc.Chem.Soc., 256 (1962).
70. H.Nishikawa and S.Yamada, Bull.Chem.Soc.Japan, 37, 8 (1964).
71. L.Sacconi and P.L.Orioli, Ricerca sci.Rend., 32, 645 (1962).
72. H.Nishikawa and S.Yamada, Bull.Chem.Soc.Japan, 37, 1154 (1964).
73. E.Frasson and C.Panattoni, Z.Krist., 116, 154 (1961).
74. H.Nishikawa and S.Yamada, Bull.Chem.Soc.Japan, 38, 1506 (1965).
75. J.Balog and J.Császár, Acta Chim.Acad.Sci.Hung., 86, 365 (1975).
76. A.N.Knyazeva and L.M.Shkol'nikova, Zhur.Strukt. Khim., 14, 365 (1975).
77. R.G.Charles, J.Inorg.Nuclear Chem., 9, 145 (1959).
78. P.M.Zorkii, E.F.Korytnyi, and G.N.Tishchenko, Zhur.Strukt.Khim., 2, 609 (1961).
79. G.E.Batley and D.P.Graddon, Austral.J.Chem., 20, 877 (1967).
80. T.Ohno, S.Kato, and S.Yamada, Bull.Chem.Soc. Japan, 50, 6 (1977).
81. G.E.Batley and D.P.Graddon, Austral.J.Chem., 21, 1540 (1968).
82. K.Pachler and M.V.Stackelberg, Z.anorg.Chem., 305, 286 (1960).
83. L.Sacconi, M.Ciampolini, F.Maggio, and G.Delre, J.Amer.Chem.Soc., 82, 815 (1960).
84. E.Frasson, C.Panattoni, and L.Sacconi, Acta Cryst., 17, 85 (1964).
85. E.Frasson, C.Panattoni, and L.Sacconi, Acta Cryst., 17, 477 (1964).
86. P.C.Jain and E.C.Lingafelter, Acta Cryst., 23, 127 (1967).
87. R.L.Braun and E.C.Lingafelter, Acta Cryst., 22, 787 (1967).
88. V.W.Day, M.D.Glich, and J.L.Hoard, J.Amer.Chem. Soc., 90, 4803 (1968).
89. R.Temari and R.S.Srivastava, Acta Cryst., 27B, 1644 (1971).
90. T.Tanaka and O.Yamaushi, Chem. and Pharm.Bull. (Japan), 10, 435 (1962).
91. A.Chakravorty and T.S.Kannan, J.Inorg.Nuclear Chem., 29, 1691 (1967).
92. Wei Chin Hsuan, Inorg.Chem., 11, 2315 (1972).
93. R.H.Holm, A.Chakravorty, and L.J.Theriot, Inorg. Chem., 5, 625 (1966).
94. Wei Chin Hsuan, Inorg.Chem., 11, 1100 (1972).
95. R.Yeh and R.H.Barker, Inorg.Chem., 6, 1100 (1972) [sic].
96. G.W.Everett, Jr. and R.H.Holm, J.Amer.Chem.Soc., 87, 5266 (1965).
97. G.W.Everett, Jr. and R.H.Holm, Inorg.Chem., 7, 6776 (1968).
98. D.H.Gerlach and R.H.Holm, J.Amer.Chem.Soc., 91, 3457 (1969).
99. D.H.Gerlach and R.H.Holm, Inorg.Chem., 9, 588 (1970).
100. T.M.Ilsen, G.F.Martin, and T.Moeller, Inorg.Chem., 2, 587 (1963).
101. V.M.Potapov, G.V.Panova, N.K.Vikulova, and T.I. Lebedeva, Koordinats.Khim., 1, 1208 (1975).
102. E.Yoshikda and S.Yamada, Bull.Chem.Soc.Japan, 38, 2179 (1965).

103. P.Pfeiffer, E.Breith, E.Lubbe, and T.Tsumaki, Annalen, **503**, 84 (1933).
104. L.M.Shkol'nikova, E.A.Shugam, and L.T.Makarevich, Zhur.Strukt.Khim., **4**, 927 (1963).
105. M.Calligaris and D.Minichelli, G.Nardi, and L. Randaccio, J.Chem.Soc., (A), 2411 (1970).
106. G.M.Mockler, G.W.Chaffey, E.Sinn, and H.Wong, Inorg.Chem., 11, 1308 (1972).
107. I.Kiyoto, O.Isao, and N.Akitsugu, Bull.Chem.Soc. Japan, **43**, 2347 (1971).
108. G.E.Batley and D.P.Graddon, Austral.J.Chem., 20, 885 (1967).
109. M.Hariharan and F.L.Urbach, Inorg.Chem., 10, 2667 (1971).
110. G.E.Batley and D.P.Graddon, Austral.J.Chem., **21**, 1477 (1968).
111. R.H.Holm, J.Amer.Chem.Soc., **82**, 5632 (1960).
112. E.Sinn and C.M.Harris, Coordination Chem.Rev., **4**, 391 (1969).
113. J.Manassen, Inorg.Chem., **9**, 966 (1970).
114. H.Weigold and B.O.West, J.Chem.Soc. (A), 1310 (1967).
115. M.Hariharan and F.L.Urbach, Inorg.Chem., **8**, 556 (1969).
116. R.S.Gall, J.F.Rogers, W.P.Schaeter, and G.G. Christoph, J.Amer.Chem.Soc., **98**, 5135 (1976).
117. W.C.Hoyt and G.W.Everett, Jr., Inorg.Chem., 8, 2013 (1969).
118. G.M.Larin, V.A.Kolosov, N.K.Vikulova, and G.V. Panova, Zhur.Neorg.Khim., 19, 1873 (1974) [Russ. J.Inorg.Chem., No.7 (1974).
119. T.P.Cheeseman, D.Hall, and T.N.Waters, J.Chem. Soc. (A), 1396 (1966).
120. P.N.Breciani, M.Calligaris, P.Delise, and M.Randaccio, J.Chem.Soc., Dalton Trans., 2478 (1976).
121. B.Behera and A.Chakravorty, Indian J.Chem., **8**, 2012 (1969).
122. G.D.Fallon and B.M.Gatehouse, Acta Cryst., **32B**, 2591 (1976).
123. F.A.Cotton and G.Wilkinson, "Modern Inorganic Chemistry" (Translated into Russian), Mir, Moscow, 1969, Part 3.
124. S.G.McGeachin, Canad.J.Chem., **46**, 1903 (1968).
125. K.S.Patel and J.C.Bailar, Jr., J.Inorg.Nuclear Chem., **33**, 1399 (1971).
126. B.M.Higson and E.D.McKenzie, J.Chem.Soc., Dalton Trans., 269 (1972).
127. T.Nowlin and S.Subramanian, Chem.Letters, 57 (1973).
128. C.J.Ballhausen and A.D.Liehr, J.Amer.Chem.Soc., 81, 538 (1959).
129. H.C.Clark and R.J.O'Brien, Canad.J.Chem., **39**, 1030 (1961).
130. R.H.Holm and T.M.McKinney, J.Amer.Chem.Soc., **82**, 5506 (1960).
131. E.Uhlig, Coordination Chem.Rev., 10, 227 (1973).
132. V.P.Kurbatov, O.A.Osipov, and K.N.Konovalenko, Zhur.Neorg.Khim., **13**, 442 (1968) [Russ.J.Inorg. Chem., No.2 (1968)].
133. V.A.Kogan, O.A.Osipov, S.N.Shcherbak, and T.A. Ishchenko, Zhur.Obshch.Khim., **38**, 1607 (1968).
134. O.A.Osipov, A.D.Garnovskii, and V.I.Minkin, Zhur. Strukt.Khim., **8**, 913 (1967).
135. S.Yamada, A.Takiushi, K.Yamanauchi, and K.Iwasaki, Bull.Chem.Soc.Japan, **42**, 131 (1969).
136. T.P.Cheeseman, D.Hall, and T.N.Waters, J.Chem. Soc.(A), 694 (1966).
137. T.S.Kannan, B.Beneka, and A.Chakravorty, Indian J.Chem., 10, 215 (1972).
138. I.Takahiko and I.Takako, Bull.Chem.Soc.Japan, **43**, 1261 (1970).
139. A.Chakravorty and R.H.Holm, Inorg.Chem., 3, 1010 (1964).
140. C.R.Powers and G.W.Everett, Jr., J.Amer.Chem. Soc., **91**, 3468 (1969).
141. I.Bertini, L.Sacconi, and G.P.Speroni, Inorg.Chem., 11, 1323 (1972).
142. P.P.Olekhnovich, V.P.Kurbatov, O.A.Osipov, L.S. Minkina, and V.I.Minkin, Zhur.Obshch.Khim., 38, 2593 (1968).
143. S.S.Eaton and R.H.Holm, Inorg.Chem., 10, 1446 (1971).
144. B.Bosnich, J.Amer.Chem.Soc., **90**, 627 (1968).
145. R.E.Clarke and J.H.Weber, J.Inorg.Chem.Nuclear Chem., 30, 1837 (1968).
146. J.H.Weber, Inorg.Chem., **6**, 258 (1967).
147. M.Green and P.A.Tasker, Inorg.Chim.Acta, **5**, 65 (1971).
148. M.Green and P.A.Tasker, J.Chem.Soc.(A), 2531 (1970).
149. D.Losman, L.M.Engelhardt, and M.Green, Inorg. Nuclear Chem.Letters, **9**, 791 (1973).
150. G.M.Larin, V.A.Kolosov, G.V.Panova, and N.K. Vikulova, Izv.Akad.Nauk SSSR, Ser.Khim., 1881 (1974).
151. V.A.Kolosov, G.M.Larin, G.V.Panova, and N.K. Vikulova, Koordinats.Khim., 1, 1525 (1975).
152. V.M.Potapov, G.V.Panova, and N.K.Vikulova, Zhur. Obshch.Khim., **45**, 462 (1975).
153. V.M.Potapov, G.V.Panova, and N.K.Vikulova, International Conference on Coordination Chemistry, Moscow, 1973, p.175.
154. M.A.Jarski and E.C.Lingafelter, Acta Cryst., 17, 1109 (1964).
155. C.A.Ghilardi and E.C.Lingafelter, Acta Cryst., **25B**, 1807 (1969).
156. P.C.Chin and G.J.Palenik, Inorg.Chem., 11, 816 (1972).
157. L.M.Shkol'nikova, A.E.Obodovskaya, and E.A. Shugam, Zhur.Strukt.Khim., 11, 54 (1970).
158. D.Dale, J.Chem.Soc.(A), 278 (1967).
159. J.E.Parks and R.H.Holm, Inorg.Chem., 7, 1408 (1968).
160. P.L.Orioli, E.C.Lingafelter, and B.W.Brown, Acta Cryst., 17, 1113 (1964).
161. D.Hall, A.D.Rae, and T.N.Waters, J.Chem.Soc., 5897 (1963).
162. G.R.Clark, D.Hall, and T.N.Waters, J.Chem.Soc. (A), 223 (1968).
163. E.N.Baker, D.Hall, and T.N.Waters, J.Chem.Soc. (A), 396 (1970).
164. E.N.Baker, D.Hall, and T.N.Waters, J.Chem.Soc. (A), 400 (1970).
165. E.N.Baker, D.Hall, and T.N.Waters, J.Chem.Soc. (A), 406 (1970).
166. E.A.Shugam, L.M.Shkol'nikova, and A.N.Knyazeva, Zhur.Strukt.Khim., 9, 222 (1964) [sic].
167. I.Robertson and M.R.Truter, J.Chem.Soc.(A), 309 (1967).
168. A.J,McKinnon, T.N.Waters, and D.Hall, J.Chem.Soc., 3290 (1964).
169. D.Hall, A.J,McKinnon, and T.N.Waters, J.Chem. Soc., 425 (1965).
170. I.Kinya and O.Isao, Bull.Chem.Soc.Japan, **43**, 1040 (1970).

171. G.R.Clark, D.Hall, and T.N.Waters, J.Chem.Soc. (A), 823 (1969).
172. M.Gerloch and F.E.Malbs, J.Chem.Soc.(A), 1900 (1967).
173. D.Hall, T.N.Waters, and P.E.Wright, J.Chem.Soc., Dalton Trans., 1508 (1973).
174. G.D.Fallon and B.M.Gatehouse, Acta Cryst., 32B, 97 (1976).
175. P.M.Zorky, V.S.Psalidas, and M.A.Porai-Koshits, Proc.XV Internat.Conf.on Coordination Chemistry, Moscow, 1973 p.72.
176. G.V.Panova, N.K.Vikulova, V.M.Potapov, and T.I.Lebedeva, Koordinats.Khim., 1, 1066 (1975).
177. N.K.Vikulova, Candidate's Thesis, Moscow State University, 1974.
178. F.J.Llewellyn and T.N.Waters, J.Chem.Soc., 2639 (1960).
179. R.P.Scaringe and D.J.Hodgson, Inorg.Chem., 15, 1193 (1976).
180. F.J.Llewellyn and T.N.Waters, J.Chem.Soc., 2644 (1960).
181. R.S.Downing and F.L.Urbach, J.Amer.Chem.Soc., 90, 5344 (1968).
182. R.S.Downing and F.L.Urbach, J.Amer.Chem.Soc., 91, 5977 (1969).
183. M.Gollotti and A.Pasini, Inorg.Chim.Acta, 15, 129 (1975).
184. A.Pasini and M.Gullotti, Inorg.Nuclear Chem.Letters, 11, 705 (1975).
185. R.S.Downing and F.L.Urbach, J.Amer.Chem.Soc., 92, 5861 (1970).
186. M.Calligaris, G.Nardin, and L.Randaccio, J.Chem. Soc., Dalton Trans., 419 (1973).
187. I.Kiyoto, O.Isao, and N.Akitsugu, Bull.Chem.Soc. Japan, 43, 2347 (1971).
188. N.A.Bailey and S.E.Hull, Cryst.Struct.Comm., 5, 447 (1976).

Department of Organic Chemistry,
Chemical Faculty,
Lomonosov Moscow State University

Translated from *Uspekhi Khimii*, **49**, 1260-1288 (1980) U.D.C. 547.221+411

Advances in the Chemistry of Organofluorine Hypohalites and Related Compounds

F.M.Mukhametshin

Organofluorine compounds containing the groups O-Hal and O-O-Hal are surveyed. Methods of preparation, physical and chemical properties, structure, and possibilities of practical application are examined. A list of 247 references is included.

CONTENTS

I.	Introduction	668
II.	Methods of preparation	668
III.	Physical properties and structure	671
IV.	Chemical properties	672
V.	Possibilities of practical application	678

I. INTRODUCTION

A major achievement of organofluorine chemistry, based on the use of elementary fluorine, has been the discovery and study of new classes of compounds. Several of them contain functional groups that are essentially strong oxidants, which makes preparation of their hydrocarbon analogues almost impossible. Examples of such compounds are, in particular, many known organofluorine hypohalites and related *O*-halogenoperoxides.

These two groups of compounds owe their existence and relative stability to the alkyl fluorine atoms. This stabilising effect comprises (i) shielding of the carbon skeleton by the fluorine atoms and (ii) the inductive effect of fluoroalkyl groups, which strengthens the oxygen–halogen bond. Among the hypohalites the hypofluorites are more common than the corresponding hypochlorites. The less common peroxides are roughly equally represented by both halogens.

The first results on the synthesis and isolation of organofluorine hypohalites appeared in 1948, when trifluoromethyl hypofluorite CF_3OF was identified[1]; the hypochlorite CF_3OCl was first described in 1968;[2] and the *O*-halogenoperoxides have been characterised quite recently. Methods of preparation and individual properties of hypofluorites have been surveyed in several general[3–5] and specialised[6–8] reviews.

The present Review summarises the vast amount of published information on the preparation and properties of organofluorine hypofluorites and on the related hypochlorites and *O*-halogenoperoxides. It covers publications that had appeared by the end of 1977 inclusive. Perfluoroacyl hypofluorites[8] are not considered.

II. METHODS OF PREPARATION

Existing methods for the directed preparation of organofluorine hypohalites and *O*-halogenoperoxides can be arbitrarily divided into catalytic and non-catalytic. Each group includes various modifications, determined essentially by the type of initial organofluorine or other compound, the type of catalyst, and the experimental conditions. Carbonyl-containing compounds have been most widely used as starting materials for the preparations of organofluorine hypohalites. Reactants for production of the O–Hal group are elementary fluorine to obtain hypofluorites and chlorine monofluoride for hypochlorites. The same reactants are employed in the preparation of organofluorine *O*-halogenoperoxides.

1. Hypofluorites

The chief method for the preparation of organofluorine hypofluorites is the catalysed action of fluorine on perfluoroacyl fluorides[9–19]:

$$R_FC(=O)F + F_2 \xrightarrow{cat.} R_FCF_2OF .$$

Fluorides of sodium, potassium, rubidium, caesium, magnesium, calcium, strontium, barium, lanthanum, iron, copper, nickel, and silver as well as mixed compounds of the type $CsHF_2$ or $KAgF_4$ can be used as fluorination catalysts[9]. Caesium fluoride possesses extremely high catalytic activity: in its presence hypofluorites can be obtained not only from carbonyl difluoride or fluorides of mono- and per-fluorinated dicarboxylic acids[10–16] but also from the unstable peroxy-compounds $(FCOO)_2$,[15] CF_3OOCOF,[17] and $(SF_5OO)_2COF$.[18]

The preparation of hypofluorites in the presence of caesium fluoride is distinguished by simplicity and nearly quantitative yields of the end-products. Fluorine and the acyl fluoride are mixed in a vessel containing the catalyst, evaucated and cooled to −196 °C, which is then warmed to room temperature[11]. A disadvantage is the low ouput due to the need to use static conditions and small quantities of reactants.

Fluorides of alkaline-earth and transition metals are weaker catalysts than caesium fluoride, and require higher reaction temperatures (25–100 °C). Their catalytic activity has been examined in detail only in the conversion of carbonyl difluoride into trifluoromethyl hypofluorite. The reaction can be conducted in a flow system[1].

In general the formation of hypofluorites from acyl fluorides consists essentially in the addition of fluorine at the carbonyl multiple bond. The reaction mechanism has not been finally established: two possible alternatives, determined by the nature of the catalyst, are postulated. In the case of alkali-metal fluorides, especially caesium fluoride, it is assumed[20,21] that an alkoxide (I) is formed, which then reacts with fluorine:

$$R_FC(=O)F + CsF \rightarrow \underset{(I)}{R_FCF_2\bar{O}\overset{+}{C}s}$$

$$(I) + F_2 \rightarrow R_FCF_2OF + CsF .$$

The second stage is classified[22] as nucleophilic substitution S_N2 at the fluorine atom. However, it is more correct to regard it as a one-electron transfer process, as e.g. in the fluorination of the trinitromethyl anion by perchloryl fluoride[23].

In the case of fluorides of metals of variable valency (silver, copper, nickel) the role of the catalyst is essentially[21] to generate fluorine atoms, which initiate a radical process. A mechanism suggested[21] for the fluorination of carbonyl difluoride is

$$F_2 \xrightarrow{cat.} 2\dot{F}$$
$$\dot{F} + COF_2 \rightarrow CF_3\dot{O}$$
$$CF_3\dot{O} + \dot{F} \rightarrow CF_3OF$$
$$2CF_3\dot{O} \rightarrow CF_3OOCF_3 .$$

The chief arguments in favour of such a mechanism are the formation of trifluoromethyl peroxide and the inability of catalysts of this type to form alkoxides with perfluoroacyl fluorides. A heterogeneous mechanism has also been suggested[24], with formation of trifluoromethyl peroxide involving chemisorption processes:

$$AgF_2 + CoF_2 \rightarrow Ag(OCF_3)_2$$
$$Ag(OCF_3)_2 + F_2 \rightarrow [F_2 \cdot Ag(OCF_3)_2] \rightarrow AgF_2 + CF_3OOCF_3 .$$

None of the schemes is entirely satisfactory. The true mechanism of formation of trifluoromethyl hypofluorite and peroxide is probably catalytic, as indicated in particular by results for the activated adsorption of fluorine[25] and the dipole moment of carbonyl difluoride (0.95 D).[4]

Acyl fluorides can be converted catalytically into hypofluorites not only heterogeneously but also homogeneously. Thus at −20 °C carbonyl difluoride and fluorine do not interact, but in the presence of even small quantities of nitrosyl fluoride under the same conditions nearly quantitative yields of trifluoromethyl hypofluorite are formed[10]. The catalytic action of nitrosyl fluoride is attributed to the ease of its addition to the carbonyl bond:

$$COF_2 + NOF \rightleftarrows CF_3ONO$$
$$CF_3ONO + F_2 \rightarrow CF_3OF + NOF .$$

Because the addition of fluorine at the carbonyl bond is so strongly exothermic, catalysis by fluorides of metals of variable valency is in effect limited to the preparation of trifluoromethyl hypofluorite. Since this product has high thermal stability, it can be prepared not only from carbonyl difluoride but also from such compounds as carbon monoxide [24,26], carbon dioxide[26,27], carbonyl dichloride, and methanol† [11,26]. In all the above cases silver fluoride deposited on copper catalyses the formation of both intermediate and final products:

$$CO + F_2 \xrightarrow{cat.} COF_2$$
$$COF_2 + F_2 \xrightarrow{cat.} CF_3OF .$$

Caesium fluoride, which is incapable of sorbing fluorine and carbon monoxide, plays no part at the stage of formation of carbonyl difluoride[24]. Copper fluoride has a weak catalytic effect on both stages. The fluorination of carbon dioxide to trifluoromethyl hypofluorite in the presence of silver fluoride (or difluoride) is a complicated degradative process accompanied by the evolution of oxygen and other products. In the presence of the more active caesium fluoride, however, carbon dioxide is smoothly converted into difluoromethylene bishypofluorite[11,28–30]:

$$CO_2 + 2F_2 \xrightarrow{CsF} CF_2(OF)_2 .$$

† The fluorination of methanol probably involves intermediate formation of carbonyl difluoride.

The high yield of this product and the possibility of obtaining it from fluoroformyl hypofluorite[13]

$$FC(=O)OF + F_2 \xrightarrow{CsF} CF_2(OF)_2$$

suggest that the activation of carbon dioxide by the catalyst is analogous to that of an acyl fluoride or hexafluoroacetone[12]:

$$O{=}C{=}O + CsF \rightleftarrows [O{=}CF\bar{O}\overset{+}{C}s] \xrightarrow{F_2} FC(=O)OF + CsF$$
$$(CF_3)_2C{=}O + CsF \rightleftarrows (CF_3)_2CF\bar{O}\overset{+}{C}s \xrightarrow{F_2} (CF_3)_2CFOF + CsF .$$

Despite unsuccessful attempts to isolate the intermediate fluoroformyl hypofluorite, it is difficult to imagine a different reaction path for carbon dioxide and fluorine in the presence of caesium fluoride.

Non-catalytic methods for the preparation of hypofluorites can be divided into gas-phase, liquid-phase, and solid-phase according to the state of aggregation of the substances to be fluorinated. The first group has been used primarily to obtain trifluoromethyl hypofluorite by the fluorination of carbon monoxide, carbon dioxide, or carbonyl difluoride. The other two groups are suitable with certain limitations for obtaining higher perfluoroalkyl hypofluorites.

In the absence of a catalyst carbon monoxide and fluorine react smoothly at 300–400 °C.[31] A good yield of trifluoromethyl hypofluorite is achieved by the use of two reaction vessels connected in series, the first of which serves for the formation of carbonyl difluoride.

Carbon dioxide reacts with fluorine at 200–300 °C:[32]

$$CO_2 + F_2 \rightarrow CF_3OF + {}^1/_2O_2$$

The reaction is autocatalytic, presumably with regeneration of the fluorooxy-radical OF. Above 350 °C oxygen is accompanied by other products, which have not been identified. In the photochemically initiated reaction detailed investigation[33–35] has revealed the formation of the primary active radicals $O:C(O\dot{F})$ and $O:CF.\dot{O}$. The same radicals probably occur as intermediates in the thermal process.

Ultraviolet irradiation of a mixture of carbonyl difluoride and fluorine gives an approximately 80% yield of trifluoromethyl hypofluorite[36]:

$$F_2 + h\nu \rightarrow 2\dot{F}$$
$$\dot{F} + COF_2 \rightarrow CF_3\dot{O}$$
$$CF_3\dot{O} + F_2 \rightarrow CF_3O\dot{F} + F$$
$$2CF_3\dot{O} \rightarrow CF_3OOCF_3 .$$

The mechanism of this reaction has recently been reinterpreted[37]

$$F_2 + h\nu \rightarrow 2\dot{F}$$
$$\dot{F} + COF_2 \rightarrow \dot{C}F_2OF$$
$$2\dot{C}F_2OF \rightarrow (CF_2OF)_2^*$$

$$(CF_2OF)_2^* \xrightarrow[\text{conversion}]{\text{internal}} (CF_2OF)_2$$
$$(CF_2OF)_2^* \xrightarrow{\text{walls}} CF_3OF + COF_2$$
$$(CF_2OF)_2^* + COF_2 \rightarrow (CF_3O)_2 + COF_2$$
$$(CF_2OF)_2 + F_2 \rightarrow 2CF_3OF$$
$$F \xrightarrow{\text{walls}} {}^1/_2F_2$$

but this is not convincing. In contrast to the photoprocess the thermally initiated reaction is reversible, with equilibrium displaced towards formation of trifluoromethyl hypofluorite below 250 °C.[38]

Among the above methods the fluorination of carbon monoxide has the greatest preparative value. Its advantages consist in comparatively simple apparatus, high purity of the final product (especially in the presence of caesium fluoride),

and the ready availability of carbon monoxide. Among other gas-phase reactions, in which trifluoromethyl hypofluorite has been isolated as a by-product, we may note the ultraviolet-initiated fluorination of hexafluoroacetone[39] and the interaction of chlorotrifluoroethylene with nitrogen fluoride oxide[40], tetrafluoroethylene with dioxygen difluoride[41], and tetrafluoromethane with oxygen under the influence of γ-rays[42]. The formation of trifluoromethyl hypofluorite from methane or fluoroform and oxygen difluoride[43] is of some interest.

In the liquid-phase and solid-phase fluorination of organic compounds hypofluorites have been obtained by treating the starting material with fluorine in a static or flow-type reaction vessel at temperatures between 20° and −78 °C. The fluorine should be diluted with an inert gas; its concentration must be raised from 5–10% at the start of the experiment to 20–50% at the end. The interest taken by research workers in these methods is indicated by examples in which hypofluorites have been obtained from trichloro- and trifluoroethanol, hexafluoroacetone hydrate, trichloronitropropan-2-ol, perfluoro-t-butyl alcohol[44–48], trichloroacetic esters[49], higher polyfluorinated alcohols, salts of trifluoroacetic, oxalic, and higher perfluorinated acids[46,48,50–52], trifluoroacetyl nitrate[45,46], and other compounds[53,54]. Nevertheless, they are ineffective as methods of preparation.

The chief defects of these methods are lack of selectivity and low yields. For example, the sodium salt of hexafluoroacetone hydrate gives four different hypofluorites[45]:

$$(CF_3)_2C\begin{matrix}OH\\ONa\end{matrix} \xrightarrow{F_2,N_2} (CF_3)_2CFOF + (CF_3)_2C(OF)_2 + CF_3CF(OF)_2 + C_2F_5OF\ .$$

Three hypofluorites are formed from sodium trifluoroacetate[50]:

$$CF_3C\begin{matrix}O\\ONa\end{matrix} \xrightarrow{F_2,N_2} CF_2(OF)_2 + C_2F_5OF + CF_3CF(OF)_2\ .$$

Hexafluoroacetone hydrate, in contrast to the sodium salt, gives heptafluoroisopropyl hypofluorite and a large number of by-products[44]:

$$(CF_3)_2C(OH)_2 \xrightarrow{F_2,N_2} (CF_3)_2CFOF + CF_3COF + CF_4 + C_2F_6 + COF_2 + CO_2\ .$$

Trifluoroethanol and trifluoroacetyl nitrite are converted into pentafluoroethyl hypofluorite in at most 20% yield. Under mild conditions sodium oxalate gives difluoromethylene bishypofluorite[55], but with rise in temperature trifluoromethyl hypofluorite and peroxide are obtained[51]:

$$(COONa)_2 \begin{matrix}\xrightarrow{21°C} CF_2(OF)_2\\ \xrightarrow{84°C} CF_3OF + CF_3OOCF_3\end{matrix}\ .$$

Highly selective fluorination occurs only with perfluoro-t-butyl alcohol, which it is advisable to use in the form of an alkoxide[47]:

$$(CF_3)_3CONa \xrightarrow{F_2,N_2} (CF_3)_3COF\ .$$

Attempts have been made to use oxygen difluoride to introduce a fluorooxy-group into an organofluorine molecule. On ultraviolet irradiation, a mixture of dichlorotetrafluoroacetone and the difluoride gives mainly chlorodifluoromethyl hypofluorite[56]. When perfluoroalkenes are treated with the difluoride to obtain the oxides[57], trifluoromethyl and other hypofluorites are formed as by-products.

It has recently been shown that it is fundamentally possible to prepare trifluoromethyl hypofluorite by the electrochemical fluorination of carbon monoxide, carbonyl dichloride and difluoride[58–60], and more complicated compounds[61], but the yields are appreciably inferior to those of chemical fluorination.

2. Hypochlorites

Initial compounds investigated for the catalytic preparation of organofluorine hypofluorites have been carbonyl difluoride[2,62–69], perfluoroacyl fluorides[65,69–73], and perfluoroketones[69–73], with as catalysts potassium, rubidium, and caesium fluorides[2,67,69,70,72], hydrofluoric acid and Lewis acids [boron(III), arsenic(III), arsenic (V), and antimony(V) fluorides][65,66,71,73], nitrosyl fluoride[10,66,71], magnesium fluoride, and fluorinated aluminium oxide[62,68,74]. The first three types of catalysts possess a wide spectrum of action; magnesium fluoride and alumina have been tested only in the chlorofluorination of carbonyl difluoride.

The reaction of carbonyl difluoride with chlorine monofluoride yields trifluoromethyl hypochlorite:

$$COF_2 + ClF \xrightarrow{cat.} CF_3OCl\ .$$

Perfluorinated acyl fluorides and ketones give higher perfluoroalkyl hypochlorites:

$$R_FCOF \xrightarrow{cat.} R_FCF_2OCl$$
$$(R_F)_2CO \xrightarrow{cat.} (R_F)_2CFOCl\ .$$

Catalysis by alkali-metal fluorides is essentially the same as in the preparation of hypofluorites[73]. Owing to the polarity of chlorine monofluoride[75], however, the second stage—attack on the anionoid centre of the alkoxide—is considerably facilitated in comparison with fluorine:

$$R_F-\bar{O}\ ,\ Cs^+ \quad + \quad Cl^{\delta+}\ ,\ F^{\delta-} \rightarrow R_FOCl + CsF\ .$$

This is confirmed by the great selectivity, the mild conditions, and the nearly theoretical yields of hypochlorites.

The effect of polarisation of chlorine monofluoride in the ground state is clearly illustrated by the absence of reaction with carbon dioxide[70]:

$$CO_2 + 2ClF \xrightarrow{CsF} CF_2(OCl)_2\ .$$

A possible reason for the negative result is that the monofluoride (dipole moment 0.88 *D*) is removed from the reaction zone, by forming with the catalyst a complex—caesium difluorochlorate $Cs^+Cl^-F_2$—that is inert towards carbon dioxide[76].

On passing from alkali-metal fluorides to acids the action of the catalyst is directed at chlorine monofluoride. With catalysis by hydrogen fluoride as example it is assumed[73] that activation increases the positive charge on the chlorine atom by protonation:

$$\overset{\delta+\ \delta-}{Cl-F} + H-F \rightarrow \overset{+}{Cl}-\overset{\sim}{F\cdots H\cdots F}\ .$$

This is followed by electrophilic attack on the carbonyl oxygen and stabilisation of the carbocation:

$$\rangle C{=}O + \overset{+}{Cl}-\tilde{F}\cdots H\cdots F \longrightarrow \left[\rangle \overset{+}{C}-OCl\right]\cdot H\bar{F}_2 \longrightarrow \rangle CFOCl + HF\ .$$

In the case of catalysis by boron, arsenic, and especially antimony fluorides the reaction velocity is increased by their tendency to give onium complexes with donors of the fluoride ion, e.g. chloronium hexafluoroantimonate $Cl^+SbF_6^-$.[77]

Nitrosyl fluoride is a homogeneous catalyst in the formation of hypochlorites. As noted above it forms covalent adducts (nitrites) with carbonyl compounds. The ability of such nitrites to be converted into hypochlorite derivatives under the influence of chlorine monofluoride is shown by the

example of perfluoroisopropyl nitrite[10]:

$$(CF_3)_2CONO + ClF \rightarrow (CF_3)_2CFOCl + NOF .$$

It is significant that nitrosyl fluoride not only has a direct catalytic effect but also confers catalytic properties on the surfaces of the reaction vessels: trifluoromethyl hypochlorite is formed no less smoothly in stainless-steel and polychlorotrifluoroethylene reaction vessels that have been treated with nitrosyl fluoride and then evacuated than in the presence of nitrosyl fluoride as catalyst[10,71]. The nature of the activation is unknown, although it is undoubtedly connected with the high sorbability of nitrosyl fluoride.

"Fluorinated aluminium oxide" is a catalyst distinguished by a highly developed specific surface. It is prepared by treating γ-alumina with chlorine trifluoride[62,68,74]. In its presence trifluoromethyl hypochlorite can be obtained from carbonyl difluoride and chlorine trifluoride, although the product is contaminated with tetrafluoromethane and chloryl fluoride[74,78]:

$$COF_2 + ClF_3 \xrightarrow{cat.} [CF_3OClF_2] \xrightarrow{COF_2} CF_3OCl + CF_4 + FClO_2 .$$

Non-catalytic methods for obtaining hypochlorites use hydroxy-compounds—alcohols and ketone hydrates—as starting materials[72,79-82]. *O*-Chlorination is characterised by great selectivity, which enables hydrogen, alkyl, and aryl derivatives to be employed:

$$X(CF_3)_2C{-}OH \xrightarrow[-HF]{ClF} X(CF_3)_2C{-}OCl$$
$$X = H,\ CH_3,\ Ar,\ CF_3 .$$

A bishypochlorite can be obtained from hexafluoroacetone hydrate[72]:

$$(CF_3)_2C(OH)_2 \xrightarrow{2ClF} (CF_3)_2C(OCl)_2 .$$

However, an attempt to apply the reaction to perfluoropinacol was unsuccessful[79]:

$$(CF_3)_2C(OH){-}C(OH)(CF_3)_2 \xrightarrow{2ClF} (CF_3)_2C(OCl){-}C(OCl)(CF_3)_2 .$$

3. Organofluorine Halogenoperoxides

As with the hypohalites, catalytic methods are of the greatest interest for obtaining organofluorine halogenoperoxides. In the presence of caesium fluoride carbonyl and oxygen difluorides readily interact to give a good yield of trifluoromethyl fluoroperoxide[83,84]:

$$COF_2 + OF_2 \xrightarrow{CsF} CF_3OOF .$$

The mechanism is similar to that discussed above for the hypohalites[85].

The mechanism of the formation of trifluoromethyl fluoroperoxide from the hydroperoxide

$$CF_3OOH \xrightarrow{CsF,F_2} CF_3OOF$$

is not entirely clear[86]. Possibly caesium fluoride activates the hydroperoxide by forming the hydrogen bond $CF_3OOH...F^-Cs^+$, which facilitates subsequent attack by the halogen. This view is suggested by the ease with which the same hydroperoxide is converted into the ClO-derivative by chlorine monofluoride in the presence of sodium fluoride[87]:

$$CF_3OO{-}H{\cdots}F{-}Na \cdots Cl{-}F \xrightarrow{-110^\circ C} CF_3OOCl + NaF \cdot HF .$$

According to patent claims[88,89] this is a general method for the production of organofluorine chloroperoxides.

Other methods are the reaction of fluoroalkenes with dioxygen difluoride, demonstrated with hexafluoropropene as example[90,91], and the fluorination of salts of perfluoro-acids, in particular sodium trifluoroacetate[52]:

$$CF_3CF{=}CF_2 + O_2F_2 \xrightarrow{-183^\circ C} \underset{(75\%)}{CF_3CF(OOF)CF_3} + \underset{(25\%)}{CF_3CF_2CF_2OOF}$$
$$CF_3C(=O)ONa + F_2 \rightarrow CF_3OOF + C_2F_5OOF .$$

Because of possible ambiguity in the results very little preparative value attaches to these reaction.

III. PHYSICAL PROPERTIES AND STRUCTURE

Under ordinary conditions the great majority of hypofluorites obtained hitherto are gases having the characteristic odour of fluorine. In relation to physical properties, spectra, and structure the most fully studied of this group is trifluoromethyl hypofluorite. At −95 °C it condenses into a colourless liquid of density 1.9 g cm^{-3}. The heat of evaporation, the standard heat of formation from the elements, and the Trouton constant are respectively 3710 cal $mole^{-1}$, −181.5 kcal $mole^{-1}$, and 20.8.[4] The energy of the oxygen–fluorine bond has been estimated as 43.5 ± 0.5 kcal $mole^{-1}$,[92] and its refraction is 3.89.[93] Components of the dipole moment have been found from data on the rotational spectrum[94]. This compound does not solidify at −215 °C.

The boiling point rises as fluorine atoms in the trifluoromethyl group are replaced by other atoms or groups. For example, chlorodifluoromethyl[56] and dichlorofluoromethyl hypofluorites boil at −25 and 0 °C respectively.

Difluoromethylene bishypofluorite boils at −64 °C. When placed in liquid nitrogen, it is converted into a transparent vitreous material[28]#. The heat of evaporation is 4445 cal $mole^{-1}$, and the standard heat of formation −130.5 kcal $mole^{-1}$. The vapour pressure curve can be calculated by means of the equation[55]§

$$\lg p = 7.530 - 971.6/T .$$

The energy of the oxygen–fluorine bond has not been accurately determined, but is most probably less than in trifluoromethyl hypofluorite.

Among perfluoroalkyl hypochlorites only the first two—trifluoromethyl and pentafluoroethyl—are gaseous under ordinary conditions. The higher hypochlorites are colourless or slightly yellowish liquids. Trifluoromethyl hypochlorite boils at −45.8 [69] or −47 °C,[70] and solidifies at −164 °C.[70] The heat of vaporisation is 4684 [70] or 5090 [69] cal $mole^{-1}$, and the Trouton constant 20.7 [70] or 22.4.[69] The temperature dependence of the vapour pressure between −131 and −54 °C is given by the equation[70]

$$\lg p = 7.413 - 1025/T .$$

The corresponding physical constants for pentafluoroethyl and heptafluoroisopropyl hypochlorites will be found in Refs. 69 and 70.

Some idea of the physical properties of the halogenoperoxides is given by published data on trifluoromethyl fluoroperoxide[86] and chloroperoxide[87]. The former condenses at

---

Another worker[30] obtained a viscous liquid.

§ Here and subsequently *p* represents pressure in mmHg, and *T* K is the temperature.

−69.4 °C to a colourless transparent liquid of density 1.65 g cm^{-3}. The heat of vaporisation is 4360 cal mol^{-1}, and the vapour density equation between −117 and −70 °C is

$$\lg p = 6.8764 - 673.9/T - 28442/T^2 .$$

This peroxide does not solidify in liquid nitrogen. Trifluoromethyl chloroperoxide boils at −22 °C , and its melting point is −132 °C. Other constants for this compound can be found in Ref. 87.

The infrared spectrum of trifluoromethyl hypofluorite contains 12 fundamental absorption bands, among which that in the region of 945 cm^{-1} corresponds to oxygen–fluorine stretching vibrations[95–97]. The molecule has C_S symmetry and is a somewhat distorted tetrahedron. Bond lengths and angles are

C—F 1.319±0.003 Å; C—O 1.395±0.006 Å; O—F 1.421±0.006 Å;

∠FCF 109.4±1°; ∠COF 104.8±0.6°[98, 99].

For analysis of the infrared spectra in terms of absorption by carbon–fluorine bonds see Ref. 100. The infrared spectrum of difluoromethylene bishypofluorite contains 15 main bands, 2 of which in the region of 916 and 933 cm^{-1} have been assigned to absorption by the hypofluorite group (stretching vibrations)[101]. This molecule has C_{2v} symmetry.

Detailed analysis of the infrared spectra of hypofluorites has established that electron-accepting substituents (difluoroamino, nitro, trifluoromethyl)[8] shift the band due absorption by FO-groups to lower wavenumbers, in the limit to 882 cm^{-1}. It is interesting that in the Raman spectrum of trifluoromethyl hypofluorite the ν(O–F) band is more intense than the ν(C–O) band, whereas the opposite relation applies in the infrared spectrum[102]. This was attributed[102] to the more covalent character of the oxygen–fluorine than of the carbon–oxygen bond.

The many papers on the fluorine-19 magnetic resonance spectra of hypofluorites[10,11,28,29,44,45,55,103–105] have established the most important fact of a considerable down-field shift in the fluorine lines due to FO-groups (140–160 ppm relative to the standard fluorochloroform), which indicates a decrease in electron density on the fluorine atom. This should tend to increase the energy of the carbon–oxygen bond in hypofluorites. Indeed, mass-spectrometric measurements of the ionisation of trifluoromethyl hypofluorite[106] and calorimetric determinations on difluoromethylene bishypofluorite[107] show that the energy of this bond exceeds on the average by 10–15 kcal $mole^{-1}$ those in hydrocarbon derivatives of similar structure (alcohol, ethers). Further support is provided by PPDP/2 quantum-chemical calculations on the trifluoromethyl hypofluorite molecule[108].

Investigations have been published[69,70,86,87] on the infrared and nuclear magnetic resonance spectra of organofluorine hypochlorites and halogenoperoxides.

IV. CHEMICAL PROPERTIES

The reactivity of organofluorine hypohalites and halogenoperoxides is determined by the tendency to rupture of the oxygen–halogen bond, the weakest in the molecule. Because of the relatively low energy of rupture of this bond, radical processes are most typical of these two groups of compounds. However, in conformity with the diminished electron density on the halogen atom, the hypofluorites also undergo heterolytic reactions, in which they act as electrophiles.

The highly exothermic character of processes involving these two groups of compounds often leads to the formation of a relatively large number of by-products from direct decomposition of these compounds, interaction of the substrate with the decomposition products, rearrangements, etc. The following discussion of thermolysis and photolysis reveals several views on such reactions.

1. Thermolysis

Trifluoromethyl hypofluorite and difluoromethylene bishypofluorite are thermally the most stable among organofluorine hypofluorites. In an enclosed space the former begins to decompose at ~200 °C, and the rate becomes appreciable above 250 °C. In an already passivated nickel reaction vessel reversible decomposition takes place[109]:

$$CF_3OF \rightleftarrows COF_2 + F_2 .$$

Furthermore, small quantities of trifluoromethyl peroxide are formed. Above 400 °C decomposition becomes irreversible owing to interaction of fluorine with the material of the vessel. Degradation of trifluoromethyl hypofluorite in a cold-glow electrical discharge (quartz vessel) yields tetrafluoromethane, carbon dioxide, oxygen, and silicon tetrafluoride, whereas in a metal vessel the first two products are accompanied by carbonyl difluoride and fluorine[109]. Degradation is retarded by additions of carbonyl difluoride to the hypofluorite.

Difluoromethylene bishypofluorite does not decompose at 150 °C for several hours; at 250 °C after 3 h it is possible to recover 40% of the initial compound. Such slow thermal decomposition is described by the equation[55]

$$CF_2(OF)_2 \xrightarrow{\Delta} COF_2 + {}^1/_2O_2 + F_2 .$$

Under explosive conditions[107] a more complicated mixture is formed:

$$CF_2(OF)_2 \xrightarrow{\text{explosion}} COF_2 + CF_3OF + CF_3OOCF_3 + CF_3OOF + CF_4 .$$

Another stable member of this group is tetrafluoroethylidene bishypofluorite, which at 150 °C is only 5% decomposed after 6.5 h:[45]

$$CF_3CF(OF)_2 \begin{cases} \xrightarrow{\Delta} CF_4 + COF_2 + {}^1/_2O_2 \\ \xrightarrow{\Delta SiO_2} CO_2 + {}^1/_2O_2 + {}^3/_2SiF_4 . \end{cases}$$

Higher perfluoroalkyl hypofluorites are less stable. The decomposition products depend on the structure of the alkyl group: primary derivatives give alkanes and carbonyl difluoride, secondary yield alkanes and acyl fluorides, and tertiary form alkanes and ketones[44]—e.g.

$$CF_3CF_2OF \xrightarrow{\Delta} CF_4 + COF_2$$

$$(CF_3)_2CFOF \xrightarrow{\Delta} CF_4 + CF_3C(=O)F$$

$$(CF_3)_3COF \xrightarrow{\Delta} CF_4 + (CF_3)_2CO .$$

The tendency to form alkanes is due to stabilisation of intermediate alkoxy-radicals by homolytic fission of a carbon–carbon bond:

$$CF_3CF_2OF \xrightarrow{\Delta} CF_3CF_2\dot{O} + F$$

$$CF_3CF_2\dot{O} \rightarrow \dot{C}F_3 + COF_2$$

$$CF_3CF_2OF + \dot{C}F_3 \rightarrow CF_4 + CF_3CF_2\dot{O} \quad \text{etc.}$$

Thermal breakdown of higher perfluoroalkyl hypofluorites is evidently a chain process, in which the presence of traces of hydrocarbons, e.g. methane, may have a similar effect to heating[44]:

$$CF_3CF_2OF + CH_4 \rightarrow HF + \dot{C}H_3 + CF_3CF_2\dot{O}$$

$$CF_3CF_2\dot{O} \rightarrow \dot{C}F_3 + COF_2 \quad \text{etc.}$$

This indicates that hypofluorites are potentially explosive, and requires that appropriate precautions should be observed when working with them.

Perfluoroalkyl hypochlorites are considerably inferior to the corresponding hypofluorites in thermal stability. For example, trifluoromethyl hypochlorite decomposes completely when heated to 165 °C:[69]

$$CF_3OCl \xrightarrow{\Delta} CF_3\dot{O} + \dot{Cl}$$
$$CF_3OCl + \dot{Cl} \rightarrow Cl_2 + CF_3\dot{O}$$
$$2CF_3\dot{O} \rightarrow CF_3OOCF_3$$
$$CF_3\dot{O} \rightarrow COF_2 + F \cdot$$

Products of the thermal breakdown of pentafluoroethyl hypochlorite under still milder conditions are carbonyl difluoride, trifluoroacetyl fluoride, chlorotrifluoromethane, chlorine, and chlorine monofluoride. The thermal stability of the hypochlorites diminishes in the sequence

$$CF_3OCl > C_2F_5OCl > (CF_3)_3COCl \geqslant (CF_3)_2CFOCl.$$

Hydrogen- and alkyl-containing hypochlorites are stable only at room or slightly higher temperatures. Their thermal decomposition yields polyfluorinated derivatives: e.g.

$$CH_3C(CF_3)_2OCl \begin{cases} \rightarrow CF_3COCH_3 + CF_3Cl \\ \not\rightarrow CF_3COCF_3 + CH_3Cl \cdot \end{cases}$$

The relatively high stability of organofluorine halogenoperoxides is somewhat unexpected: trifluoromethyl fluoroperoxide and chloroperoxide can be kept at room temperature for a long time[86,87]. Heating the halogenoperoxide vapours to 100 °C is accompanied by decomposition:

$$CF_3OOF \xrightarrow{\Delta} CF_4 + O_2$$
$$CF_3OOCl \xrightarrow{\Delta, SiO_2} COF_2 + CO_2 + SiF_4 + FClO_2 \cdot$$

2. Photolysis

The character of the breakdown products resulting from the ultraviolet irradiation of organofluorine hypohalites and halogenoperoxides depends on the conditions. Gaseous trifluoromethyl hypofluorite gives a low yield of trifluoromethyl peroxide[36]. Photolysis in an argon matrix[110] (with $\lambda < 400$ nm at 8 K, followed by infrared analysis of the products) yields only carbonyl difluoride. Monitoring photolysis of the hypofluorite by electron spin resonance (e.s.r.) (at −196 °C, mixed with nitrogen trifluoride or carbon tetrafluoride) revealed the peroxy-radical $CF_3O\dot{O}$, whose formation was attributed to the presence of traces of oxygen[111]. Intermediate formation of the radical $CF_3OO\dot{O}$ has been explained[112] by photosensitised oxidation of carbon monoxide to the dioxide on ultraviolet exposure of a mixture of the hypofluorite with the monoxide and oxygen. The quantum yield of carbon dioxide is ~10^4 molecules.

Photodecomposition of trifluoromethyl hypochlorite at room temperature gives a high yield (91%) of trifluoromethyl peroxide, and has been proposed as a method of preparation of the latter[69]:

$$2CF_3OCl \xrightarrow{h\nu} CF_3OOCF_3 + Cl_2 \cdot$$

In an argon matrix ($\lambda < 280$ nm), however, breakdown of the hypochlorite is more complicated[110]:

$$CF_3OCl \xrightarrow{8K, h\nu} CF_3OOCF_3 + CF_3OF + COF_2 + COFCl \cdot$$

In relation to the photodecomposition of organofluorine halogenoperoxides it is known that they serve as sources of perfluoroalkylperoxy-radicals, the products of whose further breakdown depend on the nature of the initial compound[87,113]:

$$CF_3OOF \xrightarrow{h\nu} CF_3O\dot{O} + \dot{F} \rightarrow CF_4 + O_2$$
$$CF_3OOCl \xrightarrow{h\nu} CF_3O\dot{O} + ClO_2 + O_2 \cdot$$

3. Reactions with Inorganic Compounds

Perfluoroalkyl hypofluorites display both fluorinating and oxidising properties towards inorganic compounds. Their fluorinating power is somewhat weaker than that of elementary fluorine; nevertheless, they can replace the latter in many reactions.

Water hydrolyses hypofluorites considerably more slowly than perfluoroacyl fluorides[6]. They react with aqueous alkalis to form perfluorocarboxylates and oxygen[11,44,45]; a *gem*-bishypofluorite yields the carbonate[55]:

$$R_FCF_2OF + 4NaOH \rightarrow R_FCOONa + 3NaF + 2H_2O + {}^1/_2O_2$$
$$CF_2(OF)_2 + 6NaOH \rightarrow Na_2CO_3 + 4NaF + 3H_2O + O_2 \cdot$$

Very dilute aqueous alkalis resemble water in their hydrolytic action. Recommendations[92] for the purification of trifluoromethylhypofluorite from traces of carbonyl difluoride are based on this property.

Like elementary fluorine, hypofluorites readily react with dry alkali-metal halides on being heated, with evolution of the corresponding halogens[6]:

$$CF_3OF + 2NaCl \rightarrow COF_2 + 2NaF + Cl_2 \cdot$$

The redox reaction with aqueous potassium iodide

$$CF_3CF_2OF + 2KI + H_2O \rightarrow CF_3COOK + I_2 + KHF_2$$

has been proposed[6,44,45] for the detection and determination of fluorooxy-groups.

Hypofluorites withstand the action of strong inorganic acids. For example, perfluoro-t-butyl hypofluorite is only 5% decomposed after contact with 98% sulphuric acid for 2 h.[44]

Dry quartz and Pyrex glass do not react with trifluoromethyl hypofluorite at room temperature[6]. Copper, nickel, and stainless steel begin to react only when strongly heated[6]. Alkali metals and mercury interact with hypofluorites on simple contact[114]. In the presence of mercury decomposition is a radical process[44]:

$$(CF_3)_3COF + Hg \rightarrow (CF_3)_3C\dot{O} + {}^1/_2HgF_2$$
$$(CF_3)_3C\dot{O} \rightarrow (CF_3)_2CO + \dot{C}F_3$$
$$(CF_3)_3COF + \dot{C}F_3 \rightarrow (CF_3)_3C\dot{O} + CF_4 \quad \text{etc.}$$

Interaction with ferrocene occurs similarly. Because of the change in colour this reaction can be used to detect fluorooxy-groups[44]:

$$CF_3CF_2OF + 2Fe(C_5H_5)_2 \rightarrow CF_3COF + 2\dot{F}\dot{F}e(C_5H_5)_2 \cdot$$
(orange) (dark blue)

In the absence of impurities trifluoromethyl hypofluorite does not react with hydrogen at room temperature, but a reaction giving carbonyl difluoride and hydrogen fluoride can be initiated by copper powder[6]. The most significant example of the great fluorinating power of this hypofluorite is its reaction with xenon to form the difluoride[115]:

$$2CF_3OF + Xe \xrightarrow{250^\circ C} XeF_2 + CF_3OOCF_3 \cdot$$

The reactions of trifluoromethyl hypofluorite with sulphur and nitrogen derivatives are important. At 0 °C elementary sulphur forms mainly the tetrafluoride, disulphur difluoride, and carbonyl difluoride, presumably contaminated with the unstable trifluoromethyl fluorothiosulphite and bistrifluoromethyl thiosulphite[116]. Addition at the carbon–sulphur multiple bond is observed with thiocarbonyl dichloride[116], when one of the addition products could not be isolated in the free state:

$$Cl_2C{=}S \xrightarrow[-78^\circ C]{CF_3OF} \begin{cases} \rightarrow Cl_2CF{-}S{-}OCF_3 \\ \rightarrow [Cl_2C(OCF_3){-}SF] \xrightarrow{2CF_3OF} SF_4 + COF_2 + CF_3OCFCl_2 \cdot \end{cases}$$

The less reactive carbonyl sulphide reacts with trifluoromethyl hypofluorite to form bistrifluoromethyl sulphite and carbonate together with trifluoromethyl fluoroformate[116]. Electron spin resonance has established[117] that the radicals $(CF_3O)_2S^{\cdot}COOCF_3$ and $(CF_3O)_2S^{\cdot}COF$ are formed as active intermediate species.

Radical reactions include also those of trifluoromethyl hypofluorite with sulphur dioxide and tridoxide and with sulphur tetrafluoride. When heated to 175–185 °C sulphur dioxide is converted into a complicated mixture in which trifluoromethyl fluorosulphate and fluoropyrosulphate have been identified together with bistrifluoromethyl sulphate and pyrosulphate[118].

The reaction with sulphur trioxide is more unambiguous:

$$CF_3OF + SO_3 \rightarrow CF_3OOSO_2F \ .$$

Even in this case, however, trifluoromethyl and fluorosulphonyl peroxides have been isolated among the by-products. Detailed investigations indicate[92] that the reaction mechanism involves the primary stages

$$CF_3OF \rightleftarrows CF_3\dot{O} + \dot{F}$$
$$SO_3 + \dot{F} \rightarrow \dot{S}O_3F$$
$$2\dot{S}O_3F \rightleftarrows FSO_2OOSO_2F$$
$$CF_3\dot{O} + \dot{S}O_3F \rightarrow CF_3OOSO_2F$$
$$2CF_3\dot{O} \rightarrow CF_3OOCF_3 \ .$$

Reaction with sulphur tetrafluoride involves intermediate formation[119,120] of the radical $CF_3OS^{\cdot}F_4$, which under thermal conditions[121] abstracts a fluorine atom from the hypofluorite:

$$CF_3OSF_4 + CF_3OF \rightarrow CF_3OSF_5 + CF_3\dot{O} \ .$$

Ultraviolet exposure produces also bistrifluoromethyl tetrafluorodioxosulphate, in 10% yield[122]. It is significant that the reaction with sulphur tetrafluoride depends appreciably on the presence of particular impurities. For example, dissolved oxygen may be responsible for the formation of peroxy-compounds, and tetrafluorohydrazine for *NN*-difluoroamidosulphates[123]:

$$CF_3O\dot{S}F_4 + O_2 \rightarrow CF_3OSF_4O\dot{O} \xrightarrow{CF_3O\dot{S}F_4} CF_3OSF_4OOSF_4OCF_3$$
$$CF_3O\dot{S}F_4 + N_2F_4 \rightarrow CF_3OSF_4NF_2 + \dot{N}F_2 \ .$$

As a consequence of the ease of fission of the nitrogen–nitrogen bond tetrafluorohydrazine causes decomposition of trifluoromethyl hypofluorite even in the dark at room temperature[124]:

$$CF_3OF + NF_2 \rightleftarrows N_2F_4 \begin{cases} \rightarrow COF_2 + NF_3 \\ \rightarrow NOF + NF_3 + CF_4 \end{cases} .$$

For a similar reason the hypofluorite breaks down in the presence of nitrogen dioxide[125]:

$$CF_3OF + NO_2 \rightleftarrows FONO + CF_3\dot{O} \quad (N_2O_4)$$
$$CF_3\dot{O} + NO_2 \rightarrow FONO + COF_2; \quad FONO \rightarrow FNO_2 \ .$$

However, ultraviolet initiation yields *NN*-difluoro-*O*-trifluoromethylhydroxylamine[124,126–128]:

$$CF_3OF + N_2F_4 \xrightarrow{h\nu} CF_3ONF_2 + NF_3 \ .$$

Formation of similar derivatives from difluoroamine and difluoromethylene bishypofluorite[129] is a heterogeneous process involving an alkali-metal fluoride:

$$CF_2(OF)_2 + HNF_2 \xrightarrow{KF} CF_2(ONF_2)OF + CF_2(ONF_2)_2 \ .$$

Perfluoro-t-butyl hypofluorite reacts with tetrafluorohydrazine in perfluoropentane on ultraviolet irradiation to form a peroxide and nitrogen trifluoride by homolysis of the oxygen–fluorine bond[130]:

$$2(CF_3)_3COF + N_2F_4 \xrightarrow[-60°C]{h\nu} (CF_3)_3COOC(CF_3)_3 + NF_3 \ .$$

It has been stated[131] that the bond undergoes heterolytic fission in the absence of a solvent and radiation, to give a hydrazinium salt as a crystalline adduct:

$$(CF_3)_3COF + N_2F_4 \rightarrow (CF_3)_3C\overset{+}{O}\overset{+}{N}_2F_5 \ .$$

However, this has proved incorrect[247].

Perfluoroalkyl hypochlorites also exhibit strong polarisation of the oxygen–halogen bond and a tendency to undergo electrophilic processes. For example, they are very readily hydrolysed by water, with the rate of hydrolysis decreasing in the sequence[79]

$$(CF_3)_3COCl > CH_3C(CF_3)_2OCl > (CF_3)_2CHOCl > CF_3CH_2OCl \gg (CH_3)_3COCl \ .$$

Hypochlorites react smoothly with sulphur dioxide to form the corresponding alkyl chlorosulphates in theoretical yield[132,133]:

$$R_FOCl + SO_2 \xrightarrow{-20°C} R_FOSO_2Cl \ .$$

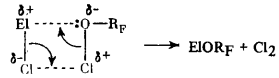
The reactions of hypochlorites with compounds containing negatively polarised halogen (boron trichloride, phosphorus chlorotetrafluoride, and hydrogen chloride) are probably of ionic type[134–136]:

$$R_FOCl \begin{cases} \xrightarrow{BCl_3} (R_FO)_3B + 2Cl_2 \\ \xrightarrow{PClF_4} R_FOPF_4 + Cl_2 \end{cases} .$$

Among these the reaction of trifluoromethyl hypochlorite with hydrogen chloride is especially interesting, yielding trifluoromethanol (m.p. −82 °C), which was stable up to −20 °C:[136]

$$CF_3OCl + HCl \xrightarrow[-120°C]{} \begin{cases} CF_3OH + Cl_2 \\ COF_2 + HF \end{cases} .$$

From general considerations it may be suggested that in all three cases positive polarisation of the halogen in the hypochlorite and a deficit of electrons in the other reactant result in a cyclic transition state:



El = H, > B, ≫ P

The reactions of hypochlorites with fluorine on heating and with tetrafluorohydrazine on ultraviolet irradiation are of radical type[69]:

$$CF_3OCl \begin{cases} \xrightarrow[65°C]{F_2} CF_3OF + Cl_2 \\ \xrightarrow[h\nu]{N_2F_4} CF_3ONF_2 + Cl_2 \end{cases} .$$

In contrast to certain organofluorine hypohalites, the halogenoperoxides react only by a radical mechanism. With trifluoromethyl fluoroperoxide products resulting from cleavage at oxygen–fluorine and oxygen–oxygen bonds could be isolated depending on the nature of the substrate. The former bond is broken when the fluoroperoxide is treated with nitrogen dioxide[137]:

$$CF_3OOF + N_2O_4 \rightarrow CF_3OONO_2 + FNO_2 \ .$$

The reactions with sulphur dioxide and tetrafluoride involve fission of the peroxy-bond[138]:

$$CF_3OOF + SO_2 \rightarrow CF_3OSO_2F + CF_3OSO_2OSO_2F$$
$$CF_3OOF + SF_4 \rightarrow CF_3OSF_4OCF_3 + CF_3OSF_5 \ .$$

Attempts to bring trifluoromethyl chloroperoxide into reaction with sulphur dioxide[87] and the hypochlorite into reaction with ozone[139] have been unsuccessful.

4. Reactions with Organic Compounds

The considerable literature on the reactions of organofluorine hypohalites and halogenoperoxides with organic derivatives covers addition at the multiple bonds C:O, C:N, and C:C, as well as the fluorination of various saturated compounds.

Among carbonyl derivatives the fullest information has been obtained for the action of the difluoride on trifluoromethyl hypofluorite, leading to formation of trifluoromethyl peroxide[140–146]:

$$CF_3OF + COF_2 \rightleftarrows CF_3OOCF_3 \ .$$

The reactants are heated in a static reaction vessel[142,143] or in the presence of a catalyst in a flow[24,143]. The optimum temperature of the uncatalysed preparation lies in the range 220–275 °C: up to 250 °C the equilibrium is displaced towards formation of the peroxide, and at higher temperatures slow decomposition of the latter begins. As could be expected, the yield is increased by raising the pressure in the system: thus with 100 atm at 275 °C the yield of the peroxide reaches 91%.[142]

Detailed kinetic investigations have been made[140,145–148] on these processes. The rate-determining stage is breakdown of the hypofluorite with cleavage of the oxygen–fluorine bond:

$$\left.\begin{array}{l} CF_3OF \rightarrow CF_3\dot{O} + \dot{F} \quad \text{slow} \\ \dot{F} + COF_2 \rightarrow CF_3\dot{O} \\ 2CF_3\dot{O} \rightarrow CF_3OOCF_3 \end{array}\right\} \text{rapid}$$

The possibility of the catalytic preparation of trifluoromethyl peroxide was discovered when the hypofluorite conterminated with carbonyl difluoride was stored in a steel vessel for a year[143]. Further investigations showed that the reaction is accelerated by the presence of fluorides of silver, copper, nickel, mercury, cobalt, iron[143,144], and caesium[24]. The fact that the peroxide is formed under mild conditions (at room temperature) casts doubt on the suggested[21] radical initiation of the process. In the presence of the most active catalyst (caesium fluoride) the reaction is probably analogous to the formation of trifluoromethyl hypofluorite from carbonyl difluoride and fluorine:

$$COF_2 + CsF \rightarrow CF_3\bar{O}\overset{+}{C}s$$
$$CF_3\bar{O}\overset{+}{C}s + CF_3OF \rightarrow CF_3OOCF_3 + CsF \ .$$

Activation of carbonyl difluoride by the remaining catalysts is probably not a chemisorption process. According to a patent[149] the peroxide can be obtained by the action of chlorine trifluoride on carbonyl difluoride in the presence of a fluoride of an alkali-earth metal, which is a modification of the method based on the action of fluorine on carbonyl difluoride[143].

Difluoromethylene bishypofluorite, unlike trifluoromethyl hypofluorite, does not give normal addition products at the carbonyl bond[150–153]. As a consequence of degradation the main products are bistrifluoromethyl trioxide and trifluoromethyl fluoroperformate:

$$CF_2(OF)_2 + COF_2 \xrightarrow{CsF} CF_3OOOCF_3 + CF_3OOC(O)F \ .$$

The latter compound on cautious hydrolysis gives the hydroperoxide[154]:

$$CF_3OOC(O)F \xrightarrow{H_2O} CF_3OOH \ .$$

The reaction of trifluoromethyl hypofluorite with difluorocarbamoyl fluoride is also anomalous, with formation of *NN*-difluoro-*O*-trifluoromethylhydroxylamine instead of the expected peroxide[155]:

$$NF_2COF + CF_3OF \rightarrow \begin{cases} NF_2OCF_3 \\ NF_2CF_2OOCF_3 \end{cases}$$

The fluorination of perfluoroglutaryl difluoride yields perfluorofuran, whose precursor is assumed to be an unstable fluorocarbonylperfluoroalkyl hypofluorite[16]:

$$FC(O)(CF_2)_3C(O)F + F_2 \xrightarrow{CsF} \left[FO(CF_2)_4C(O)F\right] \xrightarrow{-COF_2} \begin{array}{c} O \\ CF_2 \quad CF_2 \\ CF_2{-}CF_2 \end{array} \ .$$

The action of fluorine in cyclising copper and nickel hexafluoroacetylacetonates into cyclic peroxides is probably of the same type[53].

Under conditions of thermal and photochemical initiation trifluoromethyl hypofluorite reacts with carbon monoxide to form the fluoroformic and oxalic esters[156–159]. The mechanisms of photolysis and thermolysis differ in the first stage, which serves as source of trifluoromethoxy-radicals:

$$CF_3OF \xrightarrow{h\nu} CF_3\dot{O} + \dot{F}$$
$$CF_3OF + CO \xrightarrow{\Delta} CF_3\dot{O} + \dot{C}OF$$
$$CF_3\dot{O} + CO \rightarrow CF_3O\dot{C}O$$
$$CF_3O\dot{C}O + CF_3OF \rightarrow CF_3OC(O)F + CF_3\dot{O}$$
$$2CF_3O\dot{C}O \rightarrow CF_3OC(O)C(O)OCF_3 \ .$$

At room temperature in the dark no reaction takes place[159]. As a consequence of degradation, photolysis of a mixture of the hypofluorite with hexafluoroacetone forms small quantities of bistrifluoromethyl carbonate[160]:

$$(CF_3)_2CO + CF_3OF \xrightarrow{h\nu} (CF_3O)_2CO \ .$$

The reaction with carbon monoxide, like that discussed above with sulphur dioxide, provides additional evidence of the differing reactivities of fluorooxy- and chlorooxy-derivatives. Carbon monoxide reacts with the more active hypochlorites under mild conditions to give nearly quantitative yields of perfluoroalkyl chloroformates[61,69,79–81,159,161–163]:

$$R_FOCl + CO \rightarrow R_FOCOCl \ .$$

A kinetic scheme has been suggested[164] for the photochemical process, analogous to the formation of trifluoromethyl fluoroformate; with a pressure of 100 mmHg at 30 °C the quantum yield is 10^4 molecules of the hypochlorite. In the dark, reaction between carbon monoxide and trifluoromethyl hypochlorite probably begins with bimolecular initiation, which is secured by the relatively low energy of the oxygen–chlorine bond (~38 kcal mole^{-1}):[165]

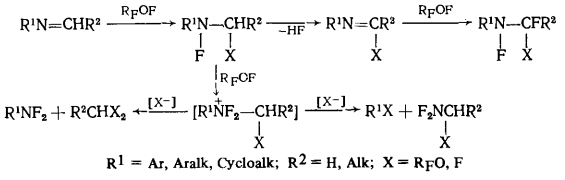
$$CF_3OCl + CO \rightarrow CF_3\dot{O} + \dot{C}OCl \ .$$

The capacity for addition at the carbonyl bond in organofluorine hypochlorites parallels their stability. For example, the very unstable *O*-chlorinated perfluoropinacol obtained *in situ* has only a weak chlorinating and oxidising action on benzaldehyde[166]:

$$(CF_3)_2C(ONa)-C(ONa)(CF_3)_2 \xrightarrow[CFCl_3]{Cl_2} \left[(CF_3)_2C(OCl)-C(OCl)(CF_3)_2\right] \xrightarrow[CCl_4]{h\nu,\ PhCHO}$$
$$\rightarrow PhCOOH + PhCOCl + (CF_3)_2CClCCl(CF_3)_2 \ .$$

The direction of addition of organofluorine hypohalites to compounds containing multiple carbon–nitrogen bonds is consistent with the electrophilic character of the former and

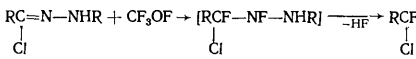
the donor power of the nitrogen atom. Because of the instability of the initial adducts the reaction is usually accompanied by degradation with formation of the corresponding *N*-fluoroamines or fluorination of the carbon–nitrogen bond. It has been shown for Schiff bases as example[167–170] that fluorination occurs mostly when the methine group is unsubstituted, but degradation occurs when alkyl or alkoxyl is attached to the carbon atom:



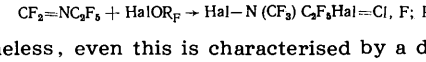
$R^1 = Ar, Aralk, Cycloalk;\ R^2 = H, Alk;\ X = R_FO, F$

Compounds in which the substituent $X = CF_3O$ are rarely met among the products. If the reaction is conducted in an inert solvent (e.g. fluorochloroform), derivatives with $X = F$ are obtained. If alcohols are added to the reaction mixture, ethers and acetals ($X = AlkO$) are formed.

Because of the good yields of difluoroamines it has been proposed to use the reaction between hypofluorites and Schiff bases as a method of preparation[169]. Hypofluorites prove quite useful also for obtaining azoalkanes[171]:

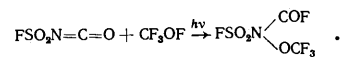


Perfluoroaza-alkenes react with organofluorine hypohalites under more severe conditions:

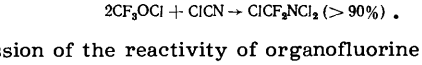


Nevertheless, even this is characterised by a difference in reactivity: hypochlorites do not require heating, whereas fluorooxy-derivatives have a fluorinating effect at high temperatures. This has been regarded[172] as indicating a transition from an ionic to a radical mechanism.

A radical mechanism obviously operates in the reaction between perfluoroguanidine and difluoromethylene bishypofluorite[173,174], from which a large number of products have been isolated. The only case in which a stable *N*-trifluoromethoxy-derivative has been obtained (in 30% yield) is the photochemical reaction between fluorosulphonyl isocyanate and trifluoromethyl hypofluorite[175]:



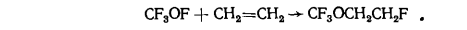
The reaction between trifluoromethyl hypochlorite and cyanogen chloride reveals the strong chlorofluorinating effect of the former on nitriles[72,176]:



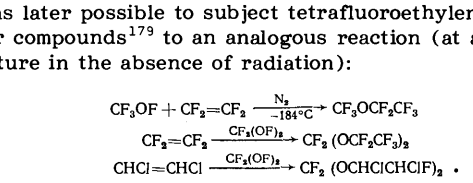
Discussion of the reactivity of organofluorine hypohalites and halogenoperoxides towards compounds containing an ethylenic bond have some bearing on the problem of anomalous electrophilic substitution, which has recently been widely discussed[177]. Since detailed examined in relation to the present compounds would be a major task outside the scope of the present Review, we shall consider only the most important points.

It must first be noted that the main criterion in assessing the nature of processes involving the ethylenic bond is the state of aggregation of the reactants. Reactions between gases usually take place by a free-radical mechanism. In the liquid phase organofluorine hypohalites and halogenoperoxides often exhibit electrophilic properties at the initiation stage, attacking the substrate at the site of maximum electron density.

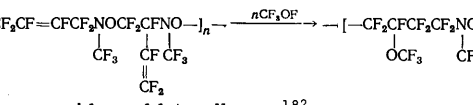
One of the earliest studies of the chemistry of hypofluorites had shown[178] that ethylene and tetrafluoroethylene react explosively with trifluoromethyl hypofluorite. Only great dilution with nitrogen and ultraviolet irradiation enabled the ethylene addition product to be isolated:



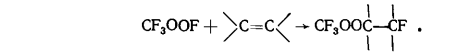
It was later possible to subject tetrafluoroethylene[41] and other compounds[179] to an analogous reaction (at a low temperature in the absence of radiation):



The stabilisation of polymeric materials by trifluoromethyl hypofluorite is a radical process[180,181]:

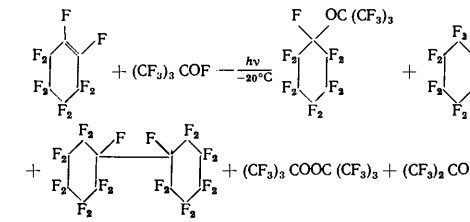


Fluoroperoxides add to alkenes[182]:



Reaction of the hypofluorite with symmetrical dichlorodifluoroethylene occurs similarly[183].

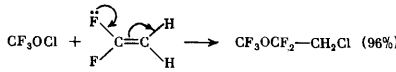
Under poorly controlled temperature conditions hypofluorites and unsaturated compounds form a large number of products, as in radical reactions of elementary fluorine. A similar result can be obtained in the case of intermediate radicals showing little tendency to attack a multiple bond. For example, the photochemical reaction of perfluoro-t-butyl hypofluorite with a perfluorocycloalkene gives a complicated mixture of peroxides, ethers, cycloalkanes, their dimers, hexafluoroacetone, and tetrafluoromethane[184]:



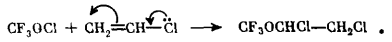
In the absence of ultraviolet radiation at 0 °C only decomposition of the hypofluorite is observed. On the other hand, with trifluoromethyl hypofluorite (ultraviolet exposure at −60 °C) the reaction is highly selective, as is indicated by the theoretical yield of perfluoromethoxycyclohexane.

The change in character of the reactions of organofluorine hypohalites and halogenoperoxides with alkenes from radical to electrophilic largely depends on the nature of the oxygen–halogen and ethylenic bonds. As in certain reactions with inorganic substances, such a change occurs primarily with hypochlorites. It is apparent in intermediate addition of the positively polarised halogen atom to the carbon atom possessing the greatest electron density.

Trifluoromethyl hypochlorite reacts with vinylidene difluoride to form in effect a single isomer[185]:



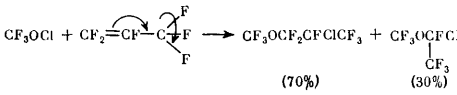
Similar orientation occurs with vinyl chloride[185]¶



Trifluoromethyl chloroperoxide reacts similarly[186]:

$$CF_2{=}CCl_2 + CF_3OOCl \rightarrow CF_3OOCF_2CCl_3\ (>50\%)$$
$$CH_2{=}CF_2 + CF_3OOCl \rightarrow CF_3OOCF_2CH_2Cl\ (>50\%)$$

with formation of 2,2,2-trichloro-1,1-difluoroethyl trifluoromethyl ether and 2-chloro-1,1-difluoroethyl trifluoromethyl ether (<10%) as by-products. Sometimes both isomers are formed, but with the "normal" addition product predominating[185,187,188]:



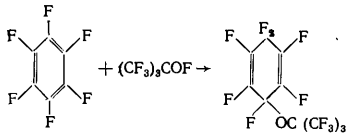
This is consistent with views on a radical-ion reaction mechanism, in which polar effects play a leading part.

The occurrence of electrophilic attack at the site of greatest electron density in the double bond is confirmed no less convincingly by many reactions involving perfluoroalkyl hypofluorites[47,189-223]. This property has not only theoretical applications but also wide synthetic use for introducing fluorine into biologically active compounds—uracil and cytosine derivatives[194-200], steroids[201-211], sugars[212-220], and aromatic compounds[189-193].

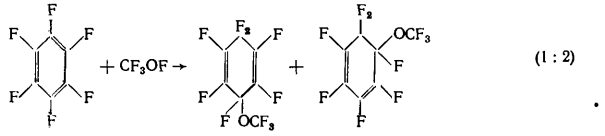
Because of the strong negative inductive effect of the perfluoro-t-butyl group electrophilic properties are most characteristically developed in the corresponding hypofluorite. The latter reacts with hexafluoropropene and with perfluoroalkoxyethylenes[47] to give predominantly the straight-chain isomers:

$$CF_3CF{=}CF_2 + (CF_3)_3COF \rightarrow CF_3CF_2CF_2OC(CF_3)_3$$
$$R_FOCF{=}CF_2 + (CF_3)_3COF \rightarrow R_FOCF_2CF_2OC(CF_3)_3$$

the yield of "anomalous" addition products not exceeding 5%. Hexafluorobenzene gives a substituted cyclohexa-1,4-diene[189]:



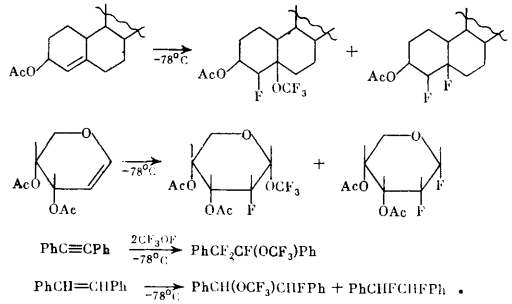
The 1,2-isomer is not formed, although in the case of trifluoromethyl hypofluorite both isomers have been isolated:



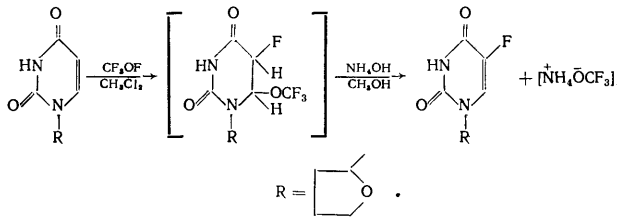
Addition of the latter hypofluorite to octafluorotoluene requires more severe conditions.

These results and the reaction with hexafluoropropene have suggested[189] that the action of hypofluorites on unsaturated compounds can be regarded as "electrophilic addition involving a fluoronium ion". It must be emphasised that this hypothesis applies only to the primary step—attack on the substrate by a polarised halogen atom—whereas the overall process obviously involves electron transfer. This is indicated in particular by the appearance of dimeric products in the reaction of hexafluorobenzene with perfluoro-t-butyl hypofluorite. It is also possible that the formation of isomeric cyclohexadienes from hexafluorobenzene and trifluoromethyl hypofluorite is a result of a cage process[177].

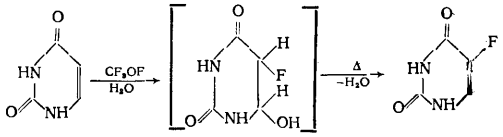
Trifluoromethyl hypofluorite adds at a double bond on reaction with steroids[190,202,204,210,211], anhydro-sugars[214,216,217,219-221], diphenylacetylene[190,204,206], stilbene[223], and uracil derivatives if an inert solvent (fluorochloroform, dichloromethane) is used. In several cases the corresponding difluorides are formed also, as a consequence of the fluorinating power of the hypofluorite:



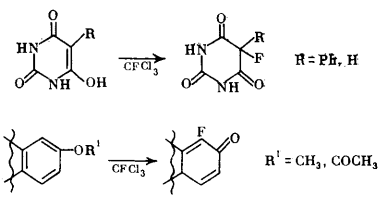
Trifluoromethoxy-derivatives are usually unstable, and pass into hydroxy-derivatives on subsequent treatment (heating) of the reaction mixtures. Treatment of such derivatives with basic reagents leads to elimination of the trifluoromethoxy-group. It is assumed[200] that an unstable alkoxide is formed, e.g. $^+NH_4O^-CF_3$ in the production of Fluorafur, an effective antitumour preparation:



Unstable intermediate products are formed also when unsubstituted uracil is treated with trifluoromethyl hypofluorite in trifluoroacetic acid containing water[195]:

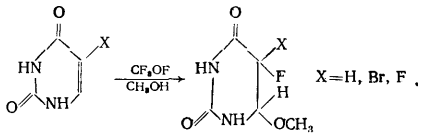


If hydroxyl, alkoxyl, or acetoxyl is present as substituent adjacent to the multiple bond, decomposition terminates in ketonisation[201-204,210,211]:

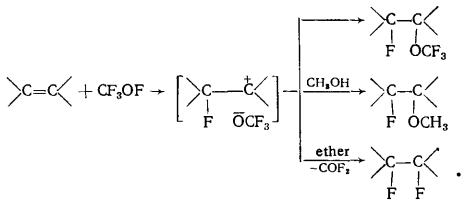


¶ Trifluoromethyl hypochlorite has been subjected to reaction also with ethylene and with tetrafluoroethylene.

If the fluorinating effect of trifluoromethyl hypofluorite is applied in the presence of methanol, the multiple bond undergoes fluoromethoxylation[199,201]:



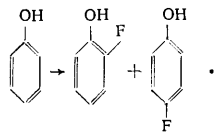
This extremely important experimental fact, together with other observations, led several authors to consider reactions between hypofluorites and activated unsaturated compounds to be ionic[199,201,203,210,216,217]. The first stage is regarded[199, 210,217] as involving formation of a carbocation, whose subsequent reactions depend on the experimental conditions and the nature of the substituents. In inert solvents the carbocation is stabilised by capture of a trifluoromethoxide anion. Electron-donor solvents (e.g. ether), which tend to stabilise the carbocation, displace the reaction towards formation of the difluoride:



Electron-donor substituents in the unsaturated compound have a similar effect. As the stronger base, methanol when present adds to the carbocation.

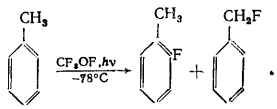
A detailed investigation of the stereochemistry of the processes, made on stilbene[223], showed *cis* addition independently of the nature of the products.

In the fluorination of aromatic compounds the electrophilic properties of hypofluorites are evident as *ortho* and (more rarely) *para* orientation when substituents such as hydroxy, alkoxy, and acylamino are present in the ring[190–193,224]:

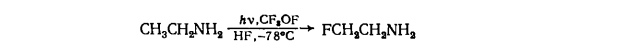


This case of "anomalous electrophilic substitution" has been reviewed[177] in terms of cage and free-radical processes.

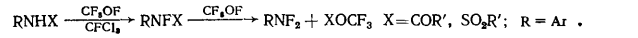
Under special conditions (ultraviolet irradiation) hypofluorites react with aromatic compounds probably by a radical mechanism. Thus toluene is fluorinated in the ring and in the side-chain[225]:



Photofluorination has enabled fluorine to be introduced into the ring and the side-chain of other aromatic hydrocarbons [226–229], and many aliphatic compounds to be fluorinated, including such polymeric materials as polycaprolactam and polyethylene[230,231]. The most suitable solvent for photofluorination is liquid hydrogen fluoride, in which the process occurs highly selectively, e.g. without affecting the amino-group[231]. This property has been utilised in the preparation of the antibacterial β-fluoro-α-alanine[232–235]:

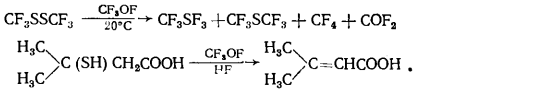


The high fluorinating power of hypofluorites is illustrated by their reactions with amines and amides to give *N*-fluorinated products[236–238]:

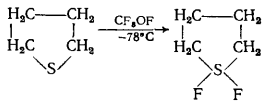


Amides in which the basicity of the nitrogen atom has been diminished constitute an exception. Thus the relatively inactive *N*-trifluoroacetyladamantylamine is fluorinated by trifluoromethyl hypofluorite at position 3 of the ring system[239].

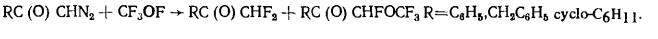
Organic compounds containing sulphur react variously with hypofluorites. Disulphides and thiols undergo degradation[240, 241]:



Aliphatic and cyclic sulphides form fluorothio-derivatives[242,243]:



Hypofluorites react very readily with compounds containing labile functional groups, e.g. with diazo-ketones[244]:



V. POSSIBILITIES OF PRACTICAL APPLICATION

A survey of published information on the chemistry of organofluorine hypohalites enables us to recommend certain reactions for practical use.

Thus various trifluoromethyl ethers possessing an anaesthetic action can be obtained by addition to halogenated alkenes. Dehalogenation or dehydrohalogenation of such ethers is of interest for the preparation of fluorinated alkyl vinyl ethers. Perfluoromethoxyethylene was first obtained in this way[183].

Hypofluorites, being less active fluorinating agents than elementary fluorine, can be used to obtain biologically active preparations—5-fluorouracil[195], fluorobarbituric acid[201], fluorinated cytosine bases[199], Fluorafur[200], etc.

Organofluorine hypohalites themselves are effective insecticides, fungicides, and brightening agents for paper and textiles[62–64]. Hypofluorites have been recommended for the surface sterilisation of materials that cannot readily be subjected to heat[245]. An important field of application of the hypohalites is the initiation of polymerisation[62–64,246].

However, the high toxicity of organofluorine hypohalites and their reactivity towards non-fluorinated organic compounds make their use potentially dangerous. The precautionary measures usual in work with elementary fluorine must be taken when these compounds are used.

REFERENCES

1. K.B.Kellog and G.H.Cady, J.Amer.Chem.Soc., **70**, 3986 (1948).
2. D.E.Gould, L.R.Anderson, D.E.Young, and W.B.Fox, Chem.Comm., 1564 (1968).
3. A.Sennig, Chem.Rev., **65**, 385 (1965).

4. R.D.W.Kemmit and D.W.A.Sharp, Adv.Fluorine Chem., **4**, 142 (1965).
5. R.E.Banks, "Fluorocarbons and their Derivatives", Oldbourne Press, London, 1964.
6. C.J.Hoffman, Chem.Rev., **64**, 91 (1964).
7. C.J.Hoffman, Chem.Rev., 64, 91 (1964). [sic].
8. M.Lustig and J.M.Shreeve, Adv.Fluorine Chem., **7**, 175 (1973).
9. R.C.Kennedy and G.H.Cady, J.Fluorine Chem., **3**, 41 (1973).
10. D.E.Young, L.R.Anderson, and W.B.Fox, Inorg. Nuclear Chem.Letters, 6, 341 (1970).
11. M.Lustig, A.R.Pitochelli, and J.K.Ruff, J.Amer.Chem. Soc., **89**, 2841 (1967).
12. J.K.Ruff, A.R.Pitochelli, and M.Lustig, J.Amer.Chem. Soc., **88**, 4531 (1966).
13. R.L.Cauble and G.H.Cady, J.Amer.Chem.Soc., **89**, 5161 (1967).
14. P.G.Thompson, J.Amer.Chem.Soc., **89**, 4316 (1967).
15. M.Lustig and J.K.Ruff, Chem.Comm., 870 (1967).
16. US P.3 679 709 (1970).
17. R.Talbott, J.Org.Chem., **33**, 2095 (1968).
18. M.J.Hopkinson and D.D.Desmarteau, J.Fluorine Chem., **7**, 501 (1976).
19. D.T.Meshri and J.M.Shreeve, J.Amer.Chem.Soc., **90**, 1711 (1968).
20. R.C.Kennedy et al., Symp.on Fluorine Chemistry, Durham, 1971, A-8.
21. G.H.Cady, Anales soc.quím.argentina, **59**, No.3–4, 125 (1971).
22. J.F.Leibman and B.B.Jarvis, J.Fluorine Chem., **5**, 41 (1975).
23. V.A.Tyurikov, L.V.Okhlobystina, B.I.Shapiro, V.M.Khutoretskii, A.A.Fainzil'berg, and Ya.K.Syrkin, Izv.Akad.Nauk SSSR, Ser.Khim., 2373 (1972).
24. M.Wechsberg and G.H.Cady, J.Amer.Chem.Soc., **91**, 4432 (1969).
25. N.Watanabe and M.Takashima, J.Chem.Soc.Japan, Ind. Chem.Sect., **74**, 321 (1971).
26. US P.2 689 254 (1954); Chem.Abs., **43**, 11 681 (1955).
27. US P.3 179 702 (1965).
28. R.L.Cauble and G.H.Cady, J.Amer.Chem.Soc., **89**, 1962 (1967).
29. F.A.Hohorst and J.M.Shreeve, J.Amer.Chem.Soc., 89, 1809 (1967).
30. F.A.Hohorst, Inorg.Synth., 11, 143 (1968).
31. G.H.Cady, Inorg.Synth., **8**, 165 (1966).
32. J.C.Chagny et al., Note CEA, No.856, 287 (1966–1967).
33. J.Czarnowski and H.J.Schumacher, Z.phys.Chem. (Frankfurt), **58**, 149 (1968).
34. A.H.Jubert, J.E.Siecre, and H.J.Schumacher, Z.phys. Chem.(Frankfurt), **67**, 138 (1969).
35. H.J.Schumacher, Photochem.Photobiol., **7**, 755 (1968).
36. P.J.Aymonino, Proc.Chem.Soc., 341 (1964).
37. M.I.Lopez, E.Castellano, and H.J.Schumacher, J.Photochem., 3, 97 (1974).
38. R.Veyre, Third European Symposium on Fluorine Chemistry, Aix-en-Provence, 1970, p.26.
39. P.J.Aymonino, Anales soc.quím.argentina, **55**, 47 (1967).
40. US P.3 422 159 (1966).
41. R.T.Holzmann and M.S.Cohen, Inorg.Chem., 1, 972 (1962).
42. J.Fajer, D.R.McKenzie, and F.W.Bloch, J.Phys.Chem., 70, 935 (1966).
43. L.B.Marantz, J.Org.Chem., **30**, 4380 (1965).
44. J.H.Prager and P.G.Thompson, J.Amer.Chem.Soc., 87, 230 (1965).
45. P.G.Thompson and J.H.Prager, J.Amer.Chem.Soc., **89**, 2263 (1967).
46. US P.3 415 865 (1968).
47. M.S.Toy and R.S.Stringham, J.Fluorine Chem., **5**, 25 (1975).
48. US P.3 420 866 (1969).
49. J.H.Prager, J.Org.Chem., 31, 392 (1966).
50. US P.3 442 927 (1969).
51. US P.3 344 194 (1967); Chem.Abs., 67, 116 565 (1967).
52. US P.3 692 815 (1972).
53. R.L.Talbott, J.Org.Chem., 30, 1429 (1965).
54. A.Ya.Yakubovich, M.A.Englin, and S.P.Makarov, Zhur.Obshch.Khim., 30, 2374 (1960).
55. P.G.Thompson, J.Amer.Chem.Soc., **89**, 1811 (1967).
56. V.A.Ginsburg and A.A.Tumanov, Zhur.Obshch.Khim., **38**, 1410 (1968).
57. US P.3 622 601 (1971).
58. US P.3 687 825 (1972).
59. Jap.P.35 888 (1972).
60. S.Nagase, T.Abe, H.Baba, and K.Kodaira, Bull. Chem.Soc.Japan, **43**, 2980 (1970).
61. T.Abe, S.Nagase, and K.Kodaira, Bull.Chem.Soc. Japan, **43**, 957 (1970).
62. BRD P.1 953 144 (1970); Chem.Abs., 73, 24 907 (1970).
63. BRD P.1 954 692 (1972); B.P.1 259 990 (1972).
64. BRD P.2 025 970 (1970); B.P.1 269 196 (1972); Chem. Abs., **74**, 63 905 (1971).
65. US P.3 842 156 (1974).
66. BRD P.1 958 346 (1970); Chem.Abs., 74, 53O36 (1971).
67. BRD P.1 928 539 (1970); Chem.Abs., 72, 54 743 (1970).
68. French P.1 589 946 (1970).
69. C.J.Schack and W.Maya, J.Amer.Chem.Soc., 91, 2902 (1969).
70. D.E.Gould, L.R.Anderson, D.E.Young, and W.B.Fox, J.Amer.Chem.Soc., 91, 1310 (1969).
71. B.P.1 273 408 (1972).
72. US P.3 769 312 (1973).
73. D.E.Young, L.R.Anderson, and W.B.Fox, Inorg. Chem., 9, 2602 (1970).
74. R.Veyre, Thesis for Docteur de l'Université de Lyon en Sciences physiques, Lyon, 1969.
75. N.S.Nikolaev, V.F.Sukhoverkhov, Yu.D.Shishkov, and I.F.Alenchikova, "Khimiya Galoidnykh Soedinenii Ftora" (Chemistry of Halogen Compounds of Fluorine), Nauka, Moscow, 1968.
76. A.A.Opalovskii, Uspekhi Khim., 36, 1673 (1967) [Russ. Chem.Rev., No.10 (1967)].
77. H.Meinert, Z.Chem., 7, No.2, 41 (1967).
78. R.Veyre, M.Quenault, and C.Eyraud, Compt.rend., **268C**, 1480 (1969).
79. D.E.Young and L.R.Anderson, J.Amer.Chem.Soc., **92**, 2313 (1970).
80. B.P.1 259 176 (1972).
81. US P.3 755 405 (1973).
82. US P.3 716 570 (1973).
83. J.J.Solomon, A.J.Kacmarek, W.K.Sumida, and J.K.Raney, Inorg.Chem., 11, 195 (1972).
84. L.R.Anderson and W.B.Fox, J.Amer.Chem.Soc., **89**, 4313 (1967).
85. I.N.Rozhkov, "Fifth International Symposium on Fluorine Chemistry", Zhur.Vses.Khim.Obshch.Mendeleeva, **15**, 92 (1970).
86. D.D.Desmarteau, Inorg.Chem., **11**, 193 (1972).
87. C.T.Ratcliffe, C.V.Hardin, L.R.Anderson, and W.B.Fox, J.Amer.Chem.Soc., **93**, 3886 (1971).
88. BRD P.2 103 370 (1971); French P.2 083 942 (1972); Chem.Abs., **76**, 3395 (1972).
89. US P.3 860 606 (1975).

90. J.J.Solomon, A.J.Kacmarek, et al., J.Amer.Chem.Soc., **90**, 6557 (1968).
91. US P.3 634 483 (1972).
92. J.Czarnowski et al., Z.phys.Chem.(Frankfurt), **65**, 225 (1969).
93. P.M.Christofer and L.L.Patterson, Austral.J.Chem., 21, 2373 (1968).
94. P.Buckley and J.P.Weber, Canad.J.Chem., **52**, 942 (1974).
95. P.M.Wilt and E.A.Jones, J.Inorg.Nuclear Chem., **30**, 2933 (1968).
96. P.M.Wilt and E.A.Jones, J.Inorg.Nuclear Chem., **29**, 2108 (1967).
97. P.M.Wilt and E.A.Jones, J.Inorg.Nuclear Chem., **29**, 2112 (1967).
98. F.P.Diodati and L.C.Bartell, J.Mol.Structure, **8**, 395 (1971).
99. V.S.Mastryukov, Zhur.Strukt.Khim., **17**, 86 (1976).
100. P.J.Aymonino, J.Inorg.Nuclear Chem., **27**, 2675 (1965).
101. R.W.Mitchell and J.A.Merrit, J.Mol.Spectroscopy, **24**, 128 (1967).
102. R.R.Smardzewski and W.B.Fox, J.Fluorine Chem., **6**, 417 (1975).
103. G.H.Cady and C.J.Merril, J.Amer.Chem.Soc., **84**, 2260 (1962).
104. L.Phillips and V.Wray, J.Chem.Soc.B, 2068 (1971).
105. L.Phillips and V.Wray, J.Chem.Soc., Perkin Trans.II, 220 (1972).
106. C.J.Thynne and K.A.G.Macheil, Internat.J.Mass. Spectrom.Ion Phys., **5**, 95 (1970).
107. G.D.Foss and D.A.Pitt, J.Phys.Chem., **72**, 3512 (1968).
108. C.Sieiro, P.Gonzalez-Diaz, and Y.G.Smeyers, J.Mol. Structure, **25**, 345 (1975).
109. R.S.Porter and G.H.Cady, J.Amer.Chem.Soc., **79**, 5628 (1957).
110. R.R.Smardzewski and W.B.Fox, J.Phys.Chem., **79**, 219 (1975).
111. N.Vanderkooi and W.B.Fox, J.Chem.Phys., **47**, 3634 (1967).
112. P.J.Aymonino and M.A.Blesa, Z.phys.Chem.(Frankfurt), **80**, 129 (1972).
113. R.R.Smardzewski, R.A.DeMarco, and W.B.Fox, J. Chem.Phys., **63**, 1083 (1975).
114. R.S.Porter and G.H.Cady, J.Amer.Chem.Soc., **79**, 5625 (1957).
115. G.L.Gard, F.B.Dudley, and G.H.Cady, Noble-Gas Compounds, 109 (1963).
116. R.E.Bayley and G.H.Cady, Inorg.Chem., **9**, 1930 (1970).
117. J.R.Morton and K.F.Preston, J.Phys.Chem., **77**, 2645 (1973).
118. W.P.VanMefer and G.H.Cady, J.Amer.Chem.Soc., **82**, 6005 (1960).
119. J.R.Morton and K.F.Preston, Chem.Phys.Letters, **18**, 98 (1973).
120. A.R.Gregory, S.E.Karavelas, et al., J.Amer.Chem. Soc., **97**, 2206 (1975).
121. G.Pass and H.L.Roberts, Inorg.Chem., **2**, 1016 (1963).
122. L.C.Duncan and G.H.Cady, Inorg.Chem., **3**, 850 (1964).
123. L.C.Duncan and G.H.Cady, Inorg.Chem., **3**, 1045 (1964).
124. W.H.Hall and S.M.Williamson, Inorg.Chem., **4**, 1342 (1965).
125. J.Czarnowski and H.J.Schumacher, Z.phys.Chem. (Frankfurt), **78**, 234 (1972).
126. J.M.Shreeve, L.C.Duncan, and G.H.Cady, Inorg. Chem., **4**, 1516 (1965).
127. R.Schmutzler, Angew.Chem., **80**, 466 (1968).
128. W.B.Fox, G.Franz, and L.R.Anderson, Inorg.Chem., 7, 382 (1968).
129. US P.3 633 588 (1972).
130. M.S.Toy and R.S.Stringham, J.Fluorine Chem., **7**, 315 (1976).
131. M.S.Toy and R.S.Stringham, J.Fluorine Chem., **7**, 229 (1976).
132. US P.3 681 423 (1972).
133. US P.3 654 335 (1972).
134. D.E.Young and W.B.Fox, Inorg.Nuclear Chem.Letters, 7, 1033 (1971).
135. D.E.Young, L.R.Anderson, and W.B.Fox, Inorg.Chem., **10**, 2810 (1971).
136. K.Seppelt, Angew.Chem., **89**, 325 (1977).
137. F.A.Hohorst and D.D.Desmarteau, Inorg.Chem., **13**, 715 (1974).
138. R.A.DeMarco and W.B.Fox, Inorg.Nuclear Chem. Letters, **10**, 965 (1974).
139. C.J.Schack and K.O.Christe, Inorg.Chem., **13**, 2378 (1974).
140. J.Czarnowski and H.J.Schumacher, Z.phys.Chem. (Frankfurt), **73**, 68 (1970).
141. H.J.Schumacher, Seventh International Symposium on Fluorine Chemistry, Santa Cruz, California, 1973, S.1, S.a., No.P-1.
142. H.L.Roberts, J.Chem.Soc., 4538 (1964).
143. US P.3 230 264 (1966); Chem.Abs., **64**, 12 550 (1966).
144. US P.3 100 083 (1963).
145. R.C.Kennedy and J.B.Levy, J.Phys.Chem., **76**, 3480 (1972).
146. J.B.Levy and R.C.Kennedy, J.Amer.Chem.Soc., **94**, 3302 (1972).
147. B.Descamps and W.Forst, J.Phys.Chem., **80**, 933 (1976).
148. B.Descamps and W.Forst, Canad.J.Chem., **53**, 1442 (1975).
149. US P.3 202 718 (1965).
150. L.R.Anderson and W.B.Fox, Inorg.Chem., **9**, 2182 (1970).
151. D.D.Desmarteau, Inorg.Chem., **9**, 2179 (1970).
152. US P.3 576 837 (1971); Chem.Abs., **75**, 35 130 (1971).
153. P.A.Bernstein et al., J.Amer.Chem.Soc., **93**, 3882 (1971).
154. P.A.Bernstein, F.A.Hohorst, and D.D.Desmarteau, Polymer Prepr., **12**, 378 (1971).
155. G.W.Fraser and J.M.Shreeve, Inorg.Chem., **6**, 1711 (1967).
156. P.J.Aymonino, Photochem.Photobiol., **7**, 761 (1968).
157. M.A.Blesa and P.J.Aymonino, Anales Asoc.quím. argentina, **56**, 101 (1968).
158. M.A.Blesa and P.J.Aymonino, Anales Asoc.quím. argentina, **56**, 113 (1968).
159. P.J.Aymonino, Chem.Comm., 241 (1965).
160. E.L.Varetti and P.J.Aymonino, Chem.Comm., 680 (1967).
161. US P.3 627 799 (1971).
162. D.E.Young and W.B.Fox, Tetrahedron Letters, 723 (1969).
163. US P.3 732 274 (1973).
164. L.Dicelio and H.J.Schumacher, Z.phys.Chem.(Frankfurt), **100**, 55 (1976).
165. R.H.Muller, D.L.Bernitt, and J.C.Hisatsuna, Spectrochim.Acta, **23A**, 233 (1967).
166. A.F.Janzen and R.Pollitt, Canad.J.Chem., **48**, 687 (1970).
167. M.J.Robins and S.R.Naik, J.Amer.Chem.Soc., **93**, 5277 (1971).

168. J.Leroy, F.Dudragne, J.C.Adenis, and C.Michaud, Tetrahedron Letters, 2771 (1973).
169. B.P.1 439 923 (1976).
170. D.H.R.Barton, R.H.Hesse, T.R.Klose, and M.M.Pechet, Chem.Comm., 97 (1975).
171. US P.3 737 533 (1973).
172. D.D.Moldavskii, V.G.Temchenko, and G.L.Antipenko, Zhur.Org.Khim., 7, 44 (1971).
173. US P.3 541 128 (1970).
174. US P.3 585 218 (1971).
175. R.E.Noftle and J.M.Shreeve, Inorg.Chem., 7, 687 (1968).
176. US P. 3 689 563 (1972).
177. I.L.Knunyants and V.R.Polishchuk, Uspekhi Khim., **44**, 685 (1975) [Russ.Chem.Rev., No.4 (1975)].
178. J.A.C.Allison and G.H.Cady, J.Amer.Chem.Soc., **81**, 1089 (1969).
179. F.A.Hohorst and J.M.Shreeve, Inorg.Chem., 7, 624 (1968).
180. P.Tarrant, Polymer Prepr., **12**, 391 (1971).
181. H.-G.Horn, Chem.-Ztg., **95**, 893 (1971).
182. D.D.Desmarteau, F.A.Hohorst, and N.Walker, Seventh International Symposium on Fluorine Chemistry, Santa Cruz, California, 1973, S.1, S.a., No.1–38.
183. W.S.Durrell, E.C.Stump, et al., J.Polymer Sci., **A3**, 4065 (1965).
184. M.S.Toy and R.S.Stringham, J.Fluorine Chem., 5, 481 (1975).
185. L.R.Anderson, D.E.Young, D.E.Gould, R.Juurik-Hogan, D.Nuechterlein, and W.B.Fox, J.Org.Chem., **35**, 3730 (1970).
186. N.Walker and D.D.Desmarteau, J.Amer.Chem.Soc., **97**, 13 (1975).
187. W.Maya, C.J.Schack, et al., Tetrahedron Letters, 3247 (1969).
188. D.D.Moldavskii, V.G.Temchenko, V.I.Slesareva, and G.L.Antipenko, Zhur.Org.Khim., 9, 673 (1973).
189. M.S.Toy and R.S.Stringham, J.Fluorine Chem., 5, 31 (1975).
190. D.H.R.Barton, J.Loughborough Univ.Technol.Chem. Soc., 7, 37 (1969).
191. T.B.Patrick and E.C.Hayward, J.Org.Chem., **39**, 2120 (1974).
192. H.Gershon, M.W.McNeil, et al., J.Medicin.Chem., **15**, 987 (1972).
193. J.Airey, D.H.R.Barton, A.K.Ganguly, R.H.Hesse, and and M.M.Pechet, Anales quím.real.Soc.españ.Pis.Quím., 70, 871 (1974).
194. T.B.Patrick, M.H.LeFaivre, and T.E.Koertge, J.Org. Chem., **41**, 3413 (1976).
195. D.H.R.Barton, R.H.Hesse, H.T.Toh, and M.M.Pechet, J.Org.Chem., **37**, 329 (1972).
196. US P.3 804 827 (1974).
197. BRD P.2 149 504 (1972); Chem.Abs., **77**, 126 674 (1972).
198. M.J.Robins, G.Ramani, and M.MacCoss, Canad.J. Chem., 53, 1302 (1975).
199. M.J.Robins, M.MacCoss, and S.R.Naik, J.Amer.Chem. Soc., **98**, 7381 (1976).
200. R.A.Earl and L.B.Townsend, J.Heterocyclic Chem., **9**, 1141 (1972).
201. D.H.R.Barton, W.A.Bubb, R.H.Hesse, and M.M.Pechet, J.Chem.Soc., Perkin Trans.I, 2095 (1974).
202. C.Chavis and C.M.Mousseron, Bull.Soc.chim.France, 25, 632 (1971).
203. D.H.R.Barton, Pure Appl.Chem., **21**, 285 (1970).
204. D.H.R.Barton, L.J.Danks, A.K.Ganguly, R.H.Hesse, and G.Tarzia, Chem.Comm., **227** (1969).
205. D.H.R.Barton, R.H.Hesse, L.Ogunkoya, N.D.Westcott, and M.M.Pechet, J.Chem.Soc., Perkin Trans.I, 2889 (1972).
206. D.H.R.Barton, L.J.Danks, A.K.Ganguly, R.H.Hesse, G.Tarzia, and M.M.Pechet, J.Chem.Soc., Perkin Trans. I, 101 (1976).
207. B.P.1 426 500 (1976).
208. US P.3 687 943 (1972).
209. D.H.R.Barton, R.H.Hesse, G.Tarzia, and M.M.Pechet, Chem.Comm., 1497 (1969).
210. D.H.R.Barton, R.H.Hesse, M.M.Pechet, G.Tarzia, H.T.Toh, and N.D.Westcott, Chem.Comm., 122 (1972).
211. D.H.R.Barton, A.K.Ganguly, R.H.Hesse, S.N.Loo, and M.M.Pechet, Chem.Comm., 806 (1968).
212. D.H.R.Barton, L.C.Godinho, R.H.Hesse, and M.M.Pechet, Chem.Comm., 804 (1968).
213. K.Bischofberger et al., J.Chem.Soc., Perkin Trans.I, 2457 (1975).
214. J.Adamson, A.B.Foster, and J.H.Westwood, Carbohydr.Res., 345 (1971).
215. J.Podesva and J.Pacak, Chem.Listy, **67**, 785 (1973).
216. A.B.Foster and J.H.Westwood, Pure Appl.Chem., **35**, 147 (1973).
217. C.J.Butchard and P.W.Kent, Tetrahedron, **27**, 3457 (1971).
218. J.Adamson and D.M.Marcus, Crabohydrate Res., 314 (1970).
219. E.L.Albano, R.L.Tolman, and R.K.Fobins, Carbohydrate Res., 63 (1971).
220. J.Adamson, A.B.Foster, L.D.Hall, et al., Carbohydrate Res., 351 (1970).
221. J.Adamson, A.B.Foster, L.D.Hall, and R.H.Hesse, Chem.Comm., 309 (1969).
222. D.H.R.Barton, R.H.Hesse, R.E.Markwell, M.M.Pechet, and S.Rozen, J.Amer.Chem.Soc., **98**, 3036 (1976).
223. D.H.R.Barton, R.H.Hesse, G.P.Jackman, L.Ogunkoya, and M.M.Pechet, J.Chem.Soc., Perkin Trans.I, 739 (1974).
224. US P.3 775 444 (1973).
225. J.Kollonitsch, L.Barash, and G.A.Doldouras, J.Amer. Chem.Soc., **92**, 7494 (1970).
226. French P.2 126 545 (1972).
227. BRD P.2 136 008 (1970); Chem.Abs., **76**, 154 488 (1972).
228. US P.3 859 276 (1975).
229. Austrian P.322 524 (1975).
230. US P.3 839 170 (1974).
231. French P.2 103 901 (1972).
232. J.Kollonitsch and L.Barash, J.Amer.Chem.Soc., **98**, 5591 (1976).
233. US P.3 956 367 (1976).
234. Swed.P.380 255 (1975).
235. DDR P.94 388 (1972); Ref.Zhur.Khim., 20 013 (1975).
236. US P.3 917 688 (1975).
237. B.P.1 437 074 (1974).
238. D.H.R.Barton, R.H.Hesse, M.M.Pechet, and H.T.Toh, J.Chem.Soc., Perkin Trans.I, 732 (1974).
239. D.H.R.Barton, R.H.Hesse, D.E.Markwell, M.M.Pechet, and H.T.Toh, J.Amer.Chem.Soc., **98**, 3034 (1976).
240. C.T.Ratcliffe and J.M.Shreeve, J.Amer.Chem.Soc., 90, 5403 (1968).
241. J.Kollonitsch, S.Marburg, and L.M.Perkins, J.Org. Chem., **41**, 3107 (1975).
242. D.B.Denney and D.Z.Denney, J.Amer.Chem.Soc., 95, 4064 (1973).
243. D.B.Denney and D.Z.Denney, J.Amer.Chem.Soc., **95**, 8191 (1973).
244. C.Wakselman and J.Leroy, Chem.Comm., 611 (1976).

245. US P.3 539 690 (1970).
246. US P.3 684 786 (1972); **Chem.Abs., 77, 140 762 (1972).**
247. K.O.Christe, C.J.Schack, and R.D.Wilson, J.Fluorine Chem., 11, 183 (1978).

Translated from *Uspekhi Khimii*, **49**, 1289 - 1311 (1980) U.D.C. 543.063

Concentration Methods for the Determination of Trace Elements

Yu.A.Zolotov

Methods of concentrating trace constituents are discussed, and the quantitative parameters used to describe them are defined. The main methods of concentration (extraction, sorption, coprecipitation, evaporation, etc.) are examined and compared. Rational combinations of methods of concentration and methods of determination of trace elements are recommended, and successful examples of such combinations are quoted. Special aspects of concentration methods applicable to the analysis of high-purity materials and of natural waters are discussed. 114 references.

CONTENTS

I. Introduction 683
II. Concentration methods 684
III. Combined concentration and determination methods 689
IV. Concentration methods in the analysis of specific substances 692

I. INTRODUCTION

Preliminary concentration is used when the relative detection limit of an analytical method is higher than the real concentration of the trace elements in the sample. Concentration allows the matrix (or most of it) to be removed, together with a number of interfering micro-components. The concentrate thus obtained contains a higher relative concentration of the micro-elements than the initial sample. Furthermore the larger sample size made possible by the adoption of concentration methods also ensures that larger absolute amounts of the micro-elements are available for analysis. As a result the detection limit can be lowered by a considerable amount, often 100- or 1000-fold. This is the main (but not the only) reason for the widespread adoption of concentration methods.

Preliminary concentration is almost unavoidable if the trace elements are inhomogeneously distributed in the sample. A representative sample in this case must be large, and direct analysis of such a large sample may be difficult, especially when the chosen method of determination requires a small sample (e.g. mass-spectrometric analysis, or emission spectrometry). The preparation of a small concentrate from a solution or a melt of a relatively large sample often provides a representative sample for analysis: for example, assay melting can be used to concentrate gold and other precious metals unevenly distributed in large samples of naturally occurring materials.

Concentration also facilitates calibration, especially when suitable standard samples are not available. It yields concentrates of a single type for the analysis of different types of material: for example, concentrates on carbon powder for spectroscopic analysis. The reference samples are produced as concentrates in the same form, and special standards for each type of material become unnecessary. Concentration with complete removal of the matrix is very desirable in the analysis of toxic, radio-active, or very expensive materials. Furthermore suitable internal standards can be conveniently introduced (if required) during the decomposition and concentration of the sample. Concentration sometimes extends the range of the trace elements which can be determined by a chosen method of analysis.

Because of all these advantages, concentration is an important step in the determination of trace elements. Its importance has not decreased as a result of the development of new, highly sensitive direct analysis methods. On the contrary, its perspectives are continually expanding, especially in combination with new methods of determination.

On the other hand concentration makes the analysis more laborious and complicated. It can lead to a loss of sample, or to contamination from outside. In some cases fewer micro-elements can be analysed than by direct analysis, and special operating procedures are needed (high-purity reagents, specially equipped laboratories, special materials or apparatus). However the advantages of concentration methods far outweigh their disadvantages.

Concentration methods cover a wide range of variants. It is important to distinguish absolute and relative concentration. Absolute concentration transfers the trace elements from a large mass of sample into a smaller mass, as for example when a solvent is evaporated or when the trace elements are extracted into a small volume of organic phase. Relative concentration increases the ratio of the trace element to the main macro-component (in this case the solvent is not treated as a macro-component). Relative concentration is a separation of components present at very different concentrations; its main aim often is to replace an interfering matrix by a suitable collector (usually of smaller mass). In some cases (e.g. in concentration by zone melting methods) the boundary between absolute and relative concentration is blurred, and concentration of both types is assumed to occur.

Both individual and group concentration of the elements can be carried out as required. Concentration involves either removing the matrix or separating the wanted trace components. Removal of the matrix is convenient for the simultaneous determination of several trace elements (for example, by spectroscopic analysis), but only if the matrix has a simple composition. Removal of the matrix is most frequently used in the analysis of high-purity metals. If the matrix consists of several elements combined as a compound (as in geological and biological samples) it is often simpler to separate the trace elements. Sometimes it is not necessary to remove the matrix completely (in this case we use the term "enrichment"). However in most cases it is best to concentrate the wanted element into a different matrix which satisfies the special requirements of the chosen method of determination, which makes calibration easy, etc. Some of these collectors can be used for determining micro-elements by several methods. For example, graphite powder can be analysed spectroscopically or by flameless atomic absorption.

The general problems underlying the pre-concentration of trace elements have been discussed in a number of review articles and monographs[1-8].

The three quantitative parameters used to describe concentration methods—the extent of extraction, the concentration coefficient, and the separation coefficient—are defined as follows: 1) the extent of extraction $R = Q_T/Q_T^0$, where Q_T and Q_T^0 are the quantities of the micro-element in the concentrate and in the sample respectively; 2) the concentration coefficient $K = (Q_T/Q_M)/(Q_T^0/Q_M^0) = Q_T Q_M^0/Q_M Q_T^0$, where Q_M^0 and Q_M are the amounts of matrix before and after the concentration respectively (obviously, for $R = 100\%$ we have $K = Q_M^0/Q_M$); 3) the separation coefficient $S = (Q_M/Q_T)/(Q_M^0/Q_T^0) = Q_M Q_T^0/Q_M^0 Q_T$ (so that $S = 1/K$).

II. CONCENTRATION METHODS

Many different methods are used for analytical concentration. The most rational classification of these methods is in terms of the nature of the separation process used. First of all we distinguish between chemical (or physicochemical) and physical methods of concentration. Among the chemical and physicochemical methods we include extraction and sorption methods, precipitation and coprecipitation, ashing and other methods of decomposing the sample, partial dissolution of the matrix, leaching, and electrochemical methods. The physical group of methods includes evaporation (e.g. distillation, sublimation), directional crystallisation, zone melting, and some other concentration techniques.

Methods can be classified also according to the number and type of phases involved. Among the most important methods of concentration are those based on the distribution of solutes between two immiscible phases, such that one phase becomes a concentrate of the trace element. This classification is expanded in Table 1. However there are also methods based on separation in a single phase (electrodialysis and diffusion methods).

Table 1. Methods of concentrating trace elements based on the distribution of compounds between two phases.

Phases*		Concentration methods
concentrate	matrix	
Liquid	liquid	extraction of trace elements, extraction of the matrix, distribution chromatography
Solid	liquid	sorption of trace elements, coprecipitation of minor constituents, electrolysis and cementation of trace elements
Liquid	solid	sorption of the matrix, precipitation of the matrix, electrolysis of the matrix, leaching of trace elements by solvents, directional freezing and zone melting
Gas	liquid	evaporation of trace elements
Liquid	gas	evaporation of the matrix and wet ashing
Gas	solid	evaporation of trace elements
Solid	gas	sublimation of the matrix, evaporation of the matrix after chemical conversion (dry ashing etc.)

*Phases present during and after concentration are quoted.

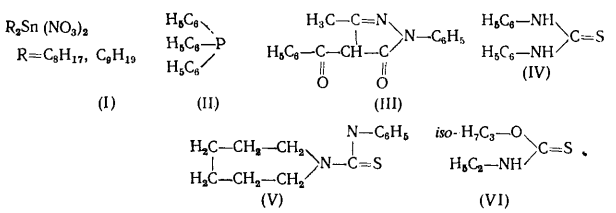
Of course, not all the methods are equally important. The IUPAC Commission for Microchemical Methods and Trace Analysis compared the methods of separation and concentration used in 188 laboratories throughout the world to determine impurities in chemical reagents[9]. The methods most generally used were found to be extraction (79 laboratories), ion exchange (21), precipitation of complexes (18), distillation and sublimation (8), and electrolysis (5). We shall discuss these methods in some detail, in approximately the same order.

1. Extraction Methods

Extraction methods are among the most convenient. They can be used either to transfer trace elements into the extract (individually, or in groups) or to remove the matrix. Important advantages of these methods are their universality, simplicity, and speed. Extraction usually offers very efficient concentration. Extraction methods are reviewed in Ref.8.

Various extraction systems are used for trace elements, though chelating agents are the commonest. Extraction of the trace element is possible only if the matrix does not react with the chosen reagent, as in the analysis of waters, acids, alkali, alkali metal salts, and metal compounds, which exist as anions during the extraction. Common reagents for group concentration include hydroxyquinoline, dithizone, and dithiocarbamates (especially diethyl- and pyrrolidinedithiocarbamate). In order to extract the largest possible number of elements extraction with a given reagent can be carried out at several pH values, or alternatively a mixture of different reagents can be used. For example, a method of determining 18 impurities in very pure alkali metal halides by extraction with a mixture of Cupferron, sodium diethyldithiocarbamate, and trioctylphosphine oxide has been reported[10]. All 18 elements are extracted simultaneously, and the extract is evaporated on graphite powder and analysed spectroscopically. Reagents which do not themselves become extracted by the organic phase under the condition of the metal extraction are chosen. Trioctylphosphine oxide goes into the extract, but it does not interfere with the spectroscopic determination of the elements.

Several new reagents for the concentration of trace elements by extraction have been proposed in recent years. The dinitrates of dinonyl- and dioctyltin (I) have a unique capacity for extracting multiply-charged anions. These reagents quantitatively extract phosphate and arsenate; sulphate, selenite, and selenate are removed less completely but still to an acceptable extent, and singly charged anions are only slightly extracted[11,12]. Organotin extractants are unlike any other previously known reagent: by using these materials methods of concentrating phosphorus, arsenic, and selenium have been developed, and in particular an extraction–photometric method of determining phosphorus and arsenic in vanadium[12].



Triphenylphosphine (II) has been recommended for the selective concentration of traces of gold and silver, followed by atomic-absorption analysis of the gold (in minerals and in cyanide solutions[13]) and of the silver (in ores and minerals[14]). A special feature of this reagent is its affinity for metal ions showing weak acid properties (according to Pearson's classification[15]).

1-Phenyl-3-methyl-4-benzoylpyrazol-5-one (III) can be used[16,17] for the group concentration of several elements. Spectroscopic methods of determining impurities in sodium hydroxide and other materials have been developed by applying this reagent. It can be used also for the selective extraction of certain elements before atomic-absorption[18], photometric, or luminescence analysis. The applications of this reagent are discussed in a recent monograph[16].

Diphenylthiourea (IV) and hexamethylenephenylthiourea (V) have been suggested for the concentration by extraction of chalcophilic metals, especially silver and metals of the platinum group. These reagents can be used to concentrate the precious metals and to separate them from non-ferrous metals. For example, a spectroscopic method of determining all the precious metals (except osmium) in solutions of natural or industrial materials containing large amounts of nickel, cobalt, iron, manganese, and zinc, and smaller amounts of copper, has been developed[19]. The method includes a preliminary concentration of the precious metals by extraction as diphenylthiourea complexes after treating the solution with tin(II) chloride: the limit of detection is 10^{-7}–10^{-5}%. Diphenylthiourea has been used to concentrate traces of silver in ores and in mineral concentrates[20], and also traces of copper, silver, and thallium in chemical reagents[21]. In both cases the elements were determined by atomic absorption spectroscopy.

The most important theoretical problems in the extraction of trace elements from a matrix in aqueous solution are the effect of other components of the matrix (salting-out, masking complex formation, etc.) and the concentration dependence of the distribution coefficient of the trace element. These problems offer some interesting topics for research.

Removal of the matrix is also very important in analytical practice. In this case the capacity of the organic phase must be large, and the extraction must be extremely selective (to ensure that the trace elements remain fully in the water phase). Chelates are not so attractive for this type of extraction, because their solubility in organic solvents is limited: the most suitable extraction forms are ionically associated, co-ordination solvated, and molecular compounds. An interesting and important general problem is the effect of the matrix being extracted on the behaviour of the trace element. In many cases undesirable co-extraction of the trace elements is observed. This problem has been studied for several years in the writer's laboratory[22,23]: rational and theoretically sound methods of suppressing co-extraction of trace elements have been developed.

Many different reagents have been used for extracting the matrix. Among the newer extractants we should mention *O*-isopropyl-*N*-ethylthiocarbamate (VI).[24] The extraction properties of this compound have been studied in detail, and several methods of separating and concentrating elements have been developed as a result. The reagent is a liquid, miscible with organic solvents, and therefore its capacity is large. Silver is extracted particularly well by reagent (VI). The only elements co-extracted with silver from a 1 *M* nitric acid solution are mercury, platinum, palladium, and (partly) gold. All the other elements remain in the water phase. A single-stage extraction by a 2 *M* solution of the reagent in chloroform removes 99.98% of the silver: i.e. the extraction is quantitative. This allows the determination of 23 impurities in high purity silver by a spectroscopic method[25]. With a concentration coefficient $K = 50$ the limits of detection are 2×10^{-6}–5×10^{-6}%. *O*-isopropyl-*N*-methylthiocarbamine is even more useful, because it is more easily available.

Ordinary extraction methods give a concentration coefficient not greater than 50–100. Improvements in this direction can be expected from current work on extraction chromatography[26], gel extraction (see, for example, Ref.27), and three phase extraction systems[28].

The latter method requires some explanation. In some extraction systems the organic phase separates into two layers, one of which (often very small in volume) contains practically the whole of the extracted element. This phase can be separated and used directly for spectroscopic or atomic absorption analysis. Several methods of this type have been proposed (see, for example, Refs.29 and 30).

2. Sorption Methods

Sorption methods of concentration rely on various types of sorption: physisorption, ion exchange, and chemisorption (with complex formation). The ion exchange methods are particularly important.

The use of conventional synthetic resins for ion exchange is complicated by the need to handle large volumes of solution, but nevertheless the method is used in many laboratories. Static, dynamic, and chromatographic variants of ion-exchange separation can be used to concentrate trace elements. Either the trace element or the matrix can be removed. If the trace elements are sorbed, they can be recovered for analysis by desorption or by ashing the sorbent (if a very high purity sorbent is available). Alternatively, concentrates on very pure sorbents can be analysed directly by spectroscopic or other methods. This approach is favoured in Refs.31–33 for the determination of impurities in boric anhydride[31] and other materials. The boric anhydride is dissolved in a mixture of glycerol and water, and the resulting glycerol complex of boric acid is not sorbed by the resin. The Cu, Ni, Cr, and other impurities are adsorbed on a cation-exchange resin in a micro-column, then the resin is transferred to a Teflon mortar, ground with sodium chloride, and treated with a drop of concentrated sulphuric acid. The decomposed resin is taken up in alcohol and analysed spectroscopically.

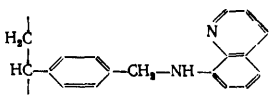
Rare-earth element impurities in metallic uranium have been determined by a two-stage ion-exchange concentration method[34]. The impurities were first sorbed (and thus separated from the main bulk of the uranium) from a sulphate solution on a column containing a cation exchanger. The rare earth elements were then eluted with a solution of hydrochloric acid. In the second concentration stage the uranium residues were sorbed as the chloro complex on an anion exchanger, while the rare earth elements were not sorbed. Impurities of gadolinium, europium, and samarium, can be determined in this way (using a luminescence method of end-analysis) at concentrations as low as 2×10^{-6}%.

Complex formation in ion-exchange concentration is used also to prevent unwanted elements from being sorbed, and to convert the wanted elements into an easily sorbed form. In addition to the normal inorganic ligands, many organic chelating reagents are found useful in this work. For example, traces of Cu, Zn, and Cd have been concentrated[35] on an ordinary anion exchanger by first converting them into 2(3'-sulphobenzoyl)-pyridine-2-pyridylhydrazone complexes. A concentration coefficient as high as 300 was obtained in this way.

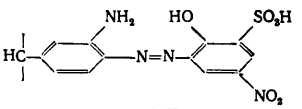
Under certain conditions trace-element complexes are readily sorbed by active carbon. This sorbent is known to behave as an anion exchanger in aqueous solutions: for example, it can selectively absorb anionic complexes of the precious metals. On the other hand oxidised carbon (i.e. carbon treated, for example, with nitric acid) acquires the properties of a cation exchanger and readily sorbs multiply-charged cations. The sorption properties of oxidised carbon towards Ag^+ have been studied in detail[36,37], and it was found that columns packed with oxidised carbon can be used to concentrate alkaline-earth metal impurities from solutions of alkali metal or ammonium salts. Active carbon can concentrate also metal chelates such as diethyldithiocarbamates. This property is used for concentrating traces of chalcophilic metals.

Synthetic chelating resins offer some very attractive possibilities. The existence of a very large number of organic analytical reagents, and the extensive information available on their interaction with various elements, can be used to synthesise resins incorporating special groups of different types,

for both selective and group reactions. Some examples of chelating resins are shown below: the sorbent (VII) takes up palladium and platinum, the sorbent (VIII), copper[38-40].



(VII)

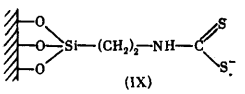


(VIII)

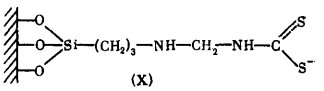
Resins of the Kelex-100,[41] XAD,[42] and other types have been studied and are now being used.

Many inorganic sorbents such as hydroxides, sulphides, and phosphates are being intensively studied. For example, copper and gold can be fully concentrated on copper sulphide from a 6 *M* solution of hydrochloric acid. However very pure inorganic sorbents are needed for the concentration of trace elements, and these materials are not readily available in a very pure form.

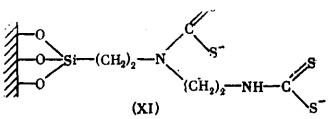
Sorbents containing grafted organic functional groups can be treated as a "hybrid" between inorganic sorbents and synthetic chelating resins. Leiden[42-45] has developed methods of concentrating ions on silica gel or on very small glass spheres with complex-forming groups of types (IX)–(XII) immobilised on their surface.



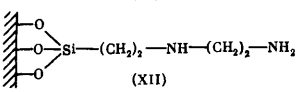
(IX)



(X)



(XI)



(XII)

The diethyldithiocarbamate group in reagents (IX)–(XI) assists the sorption of cations, the diamine group in (XII) the sorption of anions. Trace elements are sorbed fairly quantitatively even in the static variant. When traces have to be separated from a large volume of sample the column variant is used, and in this case the glass micro-spheres are better than silica gel. After sorption the glass of silica gel particles are mixed with an equal volume of powdered cellulose and pressed into a pellet which is analysed by X-ray fluorescence. Elements can be extracted from very dilute solutions: for example, selenium from 2 litre of water at a concentration of 2 ng ml^{-1}.

3. Coprecipitation and Precipitation Methods

The coprecipitation of the trace elements with a collector and the precipitation of the matrix are among the most important methods of pre-concentration of impurities. Trace elements are usually coprecipitated on amorphous precipitates of large surface area (hydroxides, sulphides, etc.). Coprecipitation on these carriers can be treated as a heterogeneous ion-exchange or chemical reaction leading to the formation of a solid solution or of chemical compounds between the trace component and the collector.

The choice of collector is dictated by various factors. It must be pure, and able to carry the wanted trace element on a small mass of the collector. A special requirement for spectroscopic end-determinations is that the emission spectrum must be as simple as possible: thus Al and Zn hydroxides are preferable to Fe and Mn hydroxides. A compound of a metal which can subsequently be removed by evaporation or other simple means makes a very convenient collector. For example, a mercury sulphide collector used for the coprecipitation of trace elements was removed as the bromide[46]. Some trace components are easily reduced to the elemental state and coprecipitated, for example, with elemental tellurium or mercury.

The collector does not necessarily have to be added to the solution: it can be part of the matrix. This type of concentration method was studied by Chuiko[47,48], Jackwerth[49], and others. The method is specially convenient with hydroxides. In the deposition of other precipitates the charge on the trace elements has to be "controlled", for example by converting them into complex anions. This is because when part of the matrix is precipitated as an insoluble crystalline compound the surface of the precipitate is usually positively charged. On the other hand nydroxides tend to sorb hydroxyl ions, and are not included in this rule.

Some very interesting organic coprecipitants were introduced into analytical practice in the 1950's, mainly by Kuznetsov and Myasoedova[50-52]. Organic collectors are easily eliminated, they are available in a variety of forms, and they minimise the uncontrolled coprecipitation of unwanted trace elements and of the matrix. In contrast to extraction methods, these organic reagents are needed in small amounts only. In the case of atomic-absorption or photometric end-determination the collector can be dissolved in a suitable organic solvent instead of being ashed: the solution thus obtained can be used directly for analysis. Hydroxyquinoline, Cupferron, and other reagents have been used as coprecipitants; they can be used in conjunction with indifferent coprecipitants of the naphthalene type. Many examples of concentration by using organic coprecipitants are quoted in Kuznetsov and Akimova's monograph[52]. Among the more recent work we should note that concentration of a large number of elements on germanium and aluminium salicylfluoronates[53], and the concentration of gold and palladium with dithizone before flameless atomic-absorption determination[54].

Deposition of the matrix leaving the trace elements in solution requires large amounts of reagents, usually involves a relatively large "blank" correction, and can be laborious. The large mass of precipitate can cause loss of the trace elements by coprecipitation. However in special cases many of these difficulties can be avoided, and many methods of concentration by precipitation of the matrix have been proposed. For example, in the analysis of high-purity lead the best method of concentrating impurities is to precipitate the lead as its nitrate from concentrated nitric acid solution[55]. Various methods of this type were developed by Karabash and coworkers[56], such as precipitation of bismuth iodide in the spectroscopic analysis of impurities in bismuth.

4. Evaporation Methods

Several variants of the evaporation method are used: simple thermal evaporation of the trace elements, evaporation after conversion of the trace elements into volatile compounds, and sublimation or distillation of the matrix either directly or after chemical reactions to convert it into volatile compounds.

Simple thermal evaporation is relatively free from contamination, but when reagents are used to produce volatile compounds the contamination problem increases, especially in the case of volatilisation of the matrix. Loss of the wanted elements is always possible, and can be serious when the matrix is evaporated. Usually only one element (or a small number of elements) is concentrated in the impurity evaporation variant. Evaporation of the matrix produces group concentration of the trace elements in the residue (either with or without a collector).

The evaporation of traces from a solid matrix requires the sample to be very finely divided, and this is a serious drawback of the method. Furthermore only small samples can be handled (50–100 mg). For many impurities vacuum distillation is effective, but it makes the method more complex. Evaporation of the trace elements in a stream of carrier gas has also been used. In the analysis of high-purity silicon dioxide the trace elements have been distilled in a stream of hydrogen chloride (an example of the removal of impurities at relatively low temperatures[57]). In that experiment the following impurities were distilled off and determined spectrometrically: Fe, Ni, Co, Al, Ti, Sn, Mn, In, Ga, and Be. The elements were condensed on a pure graphite tube which was cooled with water. Meyer and coworkers[58] developed a very sensitive method of determining selenium in high-purity copper by gas chromatography after evaporating the impurity in a stream of oxygen. The condensate (selenium dioxide) was converted into 5-nitropiaselenole [by reaction with 4-nitro-o-phenylene diamine, (Ed of Translation)], which was extracted with toluene and determined gas-chromatographically. The evaporation method is often used to evolve mercury vapour, especially before atomic-absorption analysis (see, for example, Refs.59 and 60).

Evaporation of the matrix is used when the matrix is much more volatile than the impurity elements being analysed. Under atmospheric pressure simple evaporation of the matrix can be difficult: the rate of evaporation increases with temperature, but temperatures in excess of 800 °C are not recommended because of the danger of losing the trace elements and of oxidising the matrix elements. However the evaporation of a large sample at low temperature is very time-consuming. The only matrices which are easily removed by evaporation are iodine, arsenic, antimony, and zinc. Both vacuum evaporation and evaporation in a stream of inert gas have been used, but the commonest variant is evaporation after chemical reactions to convert the matrix into a more volatile form. A simple and widely used method is dry ashing, i.e. combustion in air or in a stream of oxygen (in the case of organic materials and carbons). Ashing is often used as the final stage of a concentration procedure involving a different method. Ashing of the matrix is possible either in the presence or in the absence of a collector. The collector (e.g. graphite powder) helps to minimise the loss of trace constituents. Sulphur, arsenic, selenium, and osmium can also be removed by combustion. In addition to oxygen, the following can be used as chemical agents: hydrogen fluoride, hydrogen chloride, chlorine, and carbon monoxide. These produce volatile fluorides, chlorides, and carbonyls respectively. The carbonyls (e.g. nickel carbonyl) are formed under difficult conditions, and both carbon monoxide and the carbonyls are highly toxic.

Removal of the matrix from the liquid into the gas phase is widely used in practice. The commonest application of this method is the evaporation of a large liquid sample for analysis, with or without a collector: for example in the analysis of water, acids, liquid organic compounds, and a series of liquid inorganic compounds such as tin or silicon tetrachlorides. A similar method is the wet ashing of organic compounds, which requires large amounts of reagents and therefore suffers from contamination problems, but usually results in losses of trace elements lower than those produced by dry ashing.

5. Electrochemical Methods

Electrochemical methods are used occasionally (electrolysis on a solid electrode (metal or carbon), or on a mercury electrode, cementation, etc.). One of the most practical variants of this method is the electrolytic deposition of the trace elements on graphite disks or rods, which are used directly for spectroscopic or flameless atomic-absorption determination. Some workers[61–64] have deposited the trace elements either on carbon disks 4 mm in diameter and 1 mm thick, attached to a special holder, or on the end-face of a carbon rod (Fig.1). Deposition occurs at the cathode, and a platinum wire is used as the anode. The separated trace elements were then determined spectroscopically, using the carbon rod as the arc electrode. This method has been used in the analysis of compounds of the alkali metals, aluminium, organic acids, etc., in which Bi, In, Cd, Co, Cu, Ni, Pb, Zn, and Mn were determined. In another series of experiments[65–67] a similar method of concentration was used to determine trace elements by flameless atomic absorption spectroscopy. The trace elements were deposited on a platinum or tungsten wire, or on a graphite electrode.

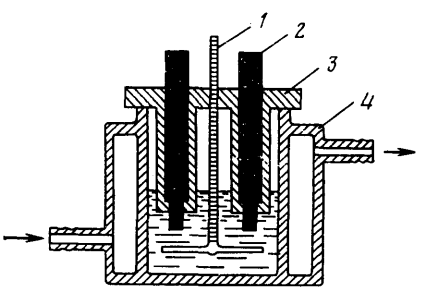


Figure 1. Electrolytic cell for depositing impurities on carbon rods: *1*) platinum anode, *2*) graphite cathodes, *3*) Teflon holder, *4*) quartz cell. Water circulation indicated by arrows.

The electro-osmosis method[68,69] is useful for concentrating ions from very dilute solutions, or from solutions of non-electrolytes. When membranes of aluminium oxide and polytetrafluoroethylene are used the concentration coefficient can be as high as 10^3–10^4, and the extent of extraction of the trace components is 85–99%. A special group of electrochemical concentration methods has been used as the basis of the inverse voltammetry method[70]. We shall refer to some of these methods below.

6. Crystallisation Methods

The reagentless concentration methods include the crystallisation methods (directional freezing and zone melting[71]).

The advantages of these methods are their universal application to all trace elements (i.e. they are group methods), the ease of automation, and the freedom from contamination (if the process is carried out in a closed apparatus at not too high temperature). Most of the sample can be recovered and re-used if necessary. However the methods have also some shortcomings: they are time-consuming, and the segregation coefficient tends to decrease at very low concentrations of the element being analysed, especially if this element is isomorphous with the main component.

The directional freezing method consists in melting the ingot completely and allowing it to crystallise from one end: as the crystallisation proceeds the impurities concentrate in the last part of the ingot to freeze. Directional freezing is much easier to carry out than zone melting. It can be applied to water–salt eutectics and crystal hydrates as well as to high-temperature melts. Various methods of concentrating impurities in metal halides have been developed at the All-Union Single Crystals Institute in Khar'kov (see, for example, Ref.72). Vertical directional freezing is used, and the melt is stirred by the strong convection currents.

7. Partial Dissolution of the Matrix

An unusual concentration method developed by Jackwerth[73] relies on dissolving part of the matrix under conditions such that the impurities do not go into solution but remain in the residue of the matrix. This is done by amalgamating the surface of metallic sample being dissolved. For example, in order to concentrate the impurities in high-purity zinc the sample (up to 100 g) is coated with 1–5% of the mercury. The zinc is then dissolved in hydrochloric acid until only a small residue is left, containing the Bi, Cd, Co, Pb, Ni, In, Tl, Sn, Ag, Au, and Pd in a concentrated form. Similar methods have been developed for the analysis of cadmium, lead (after assay melting), gallium, and aluminium (Table 2). In the case of aluminium[74] the extent of extraction of the impurities was >95%, and the concentration coefficient was ~10^3.

Table 2. Methods of concentrating trace elements in high-purity metals by partial dissolution of the matrix.

Matrix	Trace elements to be concentrated	Method of determination	Reference
Zinc	Ag, Au, Bi, Cd, Co, In, Ni, Pb, Pd, Sn, Tl	various	73
Aluminium	Bi, Cd, Ga, In, Pb, Tl, Zn	atomic absorption	74
Lead*	Precious metals	atomic absorption	75
Gallium	Ag, Au, Bi, Cu, Fe, Hg, Ni, Pb, Pd, Sn, Zn	atomic absorption	76
Mercury	Au, Pd	photometric	77
Cadmium	Ag, Au, Bi, Cu, Ni, Pb, Pd	atomic absorption	78

*After assay melting.

8. Assay Melting

Assay melting is a special form of pre-concentration. It combines, in a single operation, decomposition of the sample and concentration of the precious metals (for example, in molten lead). The result is a separation of the precious metals from their accompanying elements, which enables a large (and therefore representative) sample to be used in the analysis of ores and products of ore treatment. Concentration coefficients of 10^2–10^3 can be obtained. Assay melting is a convenient method of separation and concentration when combined with one of the modern, high-sensitivity methods of determination such as spectroscopic or activation analysis. Assay melting is valuable for the analysis of samples containing 10^{-7}–10^{-4}% of the precious metals. The method of concentrating the wanted elements into molten lead gives good results in the determination of gold, silver, platinum, and palladium. Metallic tin, and nickel sulphide, have been used as an alternative to lead. Conditions for concentrating iridium and rhodium have been found. The theory of assay melting continues to be poorly developed, though this is the oldest method of concentration (not counting evaporation).

9. Other Methods

Other methods have been used for the pre-concentration of trace elements. One of these is flotation, which can be used either to extract the matrix or to extract the trace components. The matrix can be floated after being precipitated, as an alternative to filtration. Examples of the separation of trace components by flotation include the extraction of silver[79], vanadium[80], and a group of nine elements[81] from seawater. Ultrafiltration, lyophilic drying, thermo-diffusion, and other methods have also been used.

As stated above, several concentration methods are often used in series, sometimes in unorthodox combinations. In the analysis of organic and biological materials the concentration of trace elements by any method is usually preceded by ashing. There are many examples of the combined use of extraction and sorption, precipitation and flotation, extraction and ashing, etc. Andrianov and Poladyan[82] concentrated traces of germanium by combining coprecipitation on iron(III) hydroxide with extraction of the iron by solutions of fatty acids in light petroleum. The germanium was co-extracted with the iron from the hydroxide precipitate.

A combined method of concentrating precious metals for their determination in natural and industrial materials has been developed[83]. After decomposition of the sample the traces of precious metals are coprecipitated from solution on copper sulphide in the presence of 2-mercapto-benzotriazole. In a second concentration stage the wanted elements are separated from the copper by sorption on a chelating sorbent. After concentration the precious metals are determined by spectral, atomic-absorption, or neutron activation methods.

10. Comparison of Methods

It is difficult to arrange the methods of concentrating trace components in order of merit. No comparison is significant without reference to the type of sample and to the method of analysis of the concentrate. However if allowance is made for these factors the order of merit can change radically. Yudelevich[84] compared matrix extraction, distillation, ion exchange, and directional freezing as methods of concentrating trace elements in the analysis of high-purity antimony with spectroscopic end-determination. From the sum of the indicators he concluded that matrix extraction is the best method of concentration.

The concentration coefficient is one of the main characteristics of concentration methods. The writer has tried to compare methods on the basis of this indicator (Fig.2). However it is important to note that this is only one of the relevant indicators: the other coefficients can be equally important on occasions.

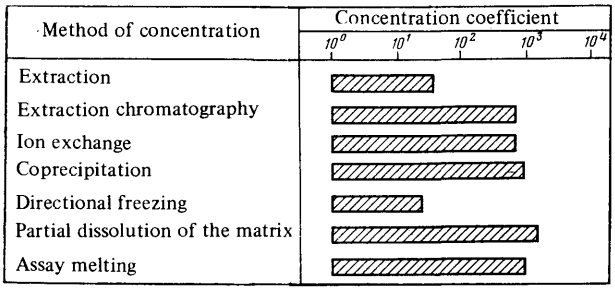


Figure 2. Concentration coefficients achieved by using various methods of pre-concentration.

III. COMBINED CONCENTRATION AND DETERMINATION METHODS

We shall now discuss rational ways of combining concentration methods and methods of end-determination, Evidently, non-specific (multi-element) determination methods should be used in conjunction with group concentration methods. The collector (i.e. the matrix of the concentrate) should be chosen so as to satisfy the requirements of the method of determination as far as possible: thus graphite powder is best for spectroscopic analysis, an organic extract for flame atomic-absorption spectroscopy, etc. It is useless to combine a high-precision method of determination with a method of concentration lacking adequate reproducibility, or *vice-versa*.

We can distinguish two groups of analytical procedures resulting from the combination of a concentration method and a determination method. In the first group the concentration and determination are not specially related: more or less independent methods of concentration and of determination are applied sequentially. The determination is not significantly affected by the properties of the concentrate. In these cases the method chosen for the concentration is immaterial from the standpoint of the determination: ion exchange, extraction (with or without re-extraction), or other methods are all equally suitable. The concentrate to be used in the determination can be, for example, an aqueous solution bearing little similarity to the original sample. Such a solution can be analysed by a variety of methods. Clearly, combinations of concentration and analysis methods of this type do not need to be specially discussed, though they have been used for a very long time and their applications are very widespread.

However on occasions the properties of the concentrate do have a substantial effect on the subsequent determination. In these cases we have to consider the special features of the combination, which can no longer be treated simply as the application of two methods in succession: a new qualitative aspect has appeared. For example, whereas with flame atomic-absorption analysis of aqueous solutions the method of extracting the trace elements is unimportant, substantial effects are observed in the atomic-absorption analysis of organic extracts. These effects arise from the difference in viscosity between organic solvents and water, and of course from the fact that the former are combustible. These differences can substantially affect the mechanism of processes in the flame. The effects are so marked that the methods are often placed in a class of their own. The situation is very similar in the combined extraction and photometric determination procedure when the organic phase is used directly for the determination. There have been recent attempts at combining extraction with direct polarographic analysis of the extract. Evidently the polarography of these organic solutions differs very substantially from the polarography of aqueous solutions.

The very close link between separation and determination methods is evident also from a different standpoint. Combinations of separation and determination methods in a single apparatus have been described (e.g. in gas chromatographs). Comparable unification is achieved in modern high-pressure liquid chromatographs. The need to separate the methods within a particular group is demonstrated most clearly by the gas chromatographic approach. Combined procedures of the second group can be termed hybrid methods.

We shall now discuss some specific examples of the combination of a pre-concentration method with some of the most important methods of determination.

Concentration is very important when *spectral analysis* is used: it has been applied for the past 25 years since the work of Semples, Pohl, and others[85,89]. Concentration is resorted to when direct analysis cannot reach the required limit of detection, and also for other reasons mentioned above. It is desirable to remove the matrix fully when its presence interferes with the determination of the trace elements because of overlapping spectral lines or if the excitation potential of the main element is unfavourable. All the samples should be converted into the same physicochemical form, so that a single series of reference standards can be used. The greater concentration of the trace elements in the concentrate (as compared with the original sample) avoids the need to use unreliable reference standards with extremely low concentrations of the wanted elements. Concentration also minimises the fluctuations of the spectroscopic results produced by uneven distribution of the trace elements in the sample[2]. All these reasons account for the very wide use currently made of these particular combinations. (In the USSR these combinations are termed chemico-spectral methods).

Group concentration of all the wanted trace elements is very desirable in these methods. In some cases complete removal of the matrix is unnecessary, and enrichment is sufficient. However the concentrate must always be in a form suitable for direct excitation of the spectrum of the trace elements: these elements must be concentrated on a small mass of the collector or on a small-area electrode.

Spectral analysis places a number of special requirements on the collector (i.e.on the matrix of the concentrate). It must be stable when stored, non-hygroscopic, and its constituent elements must have a simple emission spectrum. The collector material must be easily prepared in a reproducible form by a small number of simple operations. It should also be relatively involatile to ensure uniform access of the trace elements to the electric discharge during the spectral analysis. All these requirements are met by carbon (graphite) powder, often used in a mixture with sodium chloride. Very many specific methods of chemico-spectral analysis based on the use of this collector have been developed. Examples are given in Table 3.

One of the methods listed in Table 3 deserves special mention[90]. The aim was to determine small impurities (10^{-6}–10^{-4}%) of antimony, tin, lead, bismuth, zinc, cadmium, and copper in alloy steels. The above elements were extracted by methyl isobutyl ketone from a solution of 1 *M* ammonium iodide and 2.3 *M* sulphuric acid, and they were then re-extracted by 15% hydrogen peroxide into a 2.5 *M* solution of sulphuric acid. The re-extract was evaporated to dryness

with 10 mg of graphite powder, and the final concentrate was baked at 350–400 °C. The spectral determination was carried out by a fractional distillation method, using potassium iodide as a carrier. The limits of detection on a medium-dispersion spectrograph were 10^{-6}–10^{-4}%, the relative standard deviation 0.09–0.36. By using a high-dispersion spectrograph the limit of detection could be lowered to 10^{-7}–10^{-5}%.

Table 3. Examples of spectroscopic determinations with pre-concentration of the trace elements*.

Sample	Method of concentration	Elements to be concentrated	Limit of detection, %	Refs.
High-purity silver	matrix extraction	Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Ga, Fe, In, Mg, Mn, Ni, Pb, Sn, Te, Ti, V, Zn, Zr	10^{-7}–$2\cdot10^{-6}$	25
Alloy steels	trace element extraction	Bi, Cd, Cu, Pb, Sb, Sn, Zn	10^{-6}–10^{-4}	90
Aqueous solutions	trace element extraction	Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Ti, V	—	17
Sodium iodide	trace element extraction	Ag, Al, Bi, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sb, Sn, Ti, Zn	10^{-7}–10^{-5}	10
Solutions from dedompn. of ores and concentrates	trace element extraction	Ag, Au, Ir, Pb, Pt, Rh, Ru	10^{-6}–10^{-4}	19
Ditto	sorption on CuS and chelating resin	Ag, Au, Ir, Pd, Pt, Rh, Ru	10^{-7}–10^{-5}	83
Aluminium, gallium gallium arsenide, indium phosphide	coprecipitation on Bi_2S_3, $Bi(OH)_3$, In_2S_3	Ag, Au, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sn, Zn	10^{-7}–10^{-5}	91
Ores and minerals	trace element extraction	Au, Ag	$5\cdot10^{-8}$–$5\cdot10^{-5}$	92

*Powdered graphite used as collector in all cases.

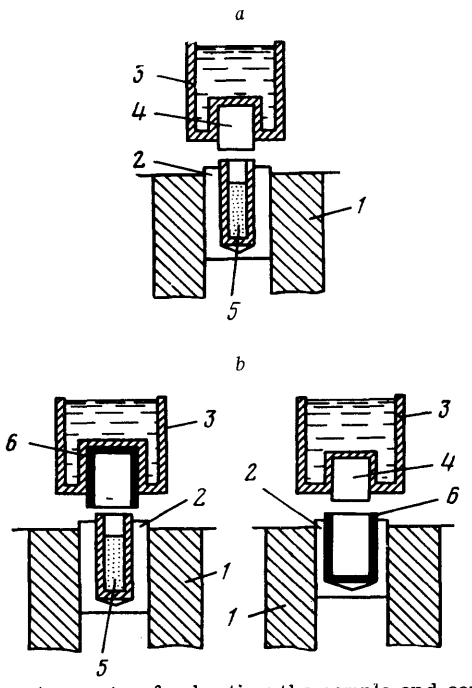


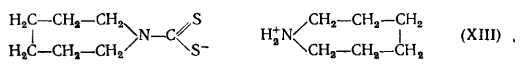
Figure 3. Apparatus for heating the sample and condensing the elements in the one-stage (*a*) and two-stage (*b*) method of evaporation: *1*) graphite flanges of water-cooled copper electrodes, *2*) graphite crucible, *3*) water-cooled holder for condensate receivers, *4*) condensate capsule, *5*) graphite beaker containing powdered sample, *6*) first condensate receiver.

A specific concentration procedure for spectral analysis is the evaporation method, a classical example of which is the fractional distillation method[93]. The evaporation method was proposed[94,95] for the analysis of pure materials used in the atomic energy industry. Two variants were described: evaporation in air and in a vacuum. An infusible powdered sample (usually oxides) is placed in a graphite cup (Fig.3) and heated by passing a heavy current through a graphite heater pressed between the graphite flanges of two water-cooled copper electrodes. The vapours of the evaporating trace elements are condensed on a cooled graphite or copper capsule which is then used as a spectrographic electrode. With samples of intermediate volatility (for example, silicon) a two-stage distillation of the trace elements can be carried out: the first stage uses a cooled graphite cup as the collector, and in the second stage the trace elements are distilled from this cup to the capsule electrode. This procedure offers a more complete separation of the matrix. Some workers have converted volatile matrices (for example, molybdenum or chromium oxide) into involatile carbides before this procedure.

The combination of pre-concentration and *atomic absorption spectrometry* is most often exploited in the extraction–flame atomic absorption variant, with direct atomisation of the extract into the flame. The main advantages of this method (as compared with the determination of elements in aqueous solution by atomic absorption) are a lower limit of detection and a faster and simpler analysis. The method avoids evaporation of the extracts, re-extraction, and other operations which result in higher blank corrections when widely occurring elements are being determined. In some procedures, using a highly combustible organic solvent, even the fuel gas can be dispensed with. Concentration is used also in conjunction with flameless atomic-absorption spectroscopy.

The high selectivity of the atomic-absorption determination allows the group concentration of the trace elements (for example, into an extract). Therefore group extraction is used as an alternative to individual extraction. The extraction of chelates is widely used for this purpose (i.e. complexes with hydroxyquinoline, β-diketones, xanthogenates, and especially dithiocarbamates). Chloroform and carbon tetrachloride, like benzene, are now rarely used as solvents because of their toxicity. Suitable solvents for flame atomic-absorption spectroscopy are methyl isobutyl ketone (MIBK) and butyl acetate. The ammonium pyrrolidinedithiocarbamate (PDTC)–methyl isobutyl ketone system is widely used for the group separation of trace elements, and many methods of analysis of waters, biological samples, and other materials have been based on this system. For example, Anders and Hailer[96] describe a method of direct extraction of cadmium and lead from wine which does not extract the sugars and acids of the wine.

Some workers[97,98] have successfully used hexamethylammonium hexamethylenedithiocarbamate (XIII) instead of PDTC:



(XIII)

This reagent is prepared from hexamethyleneimine, which is obtained as a side-product in the manufacture of Nylon and is therefore readily available. Several methods using this reagent have been developed, including the determination of Co, Cu, Fe, Mn, Ni, Pb, and Zn in sea-water[98].

Automatic apparatus for concentration by extraction has become available commercially: in particular, the model marketed by the firm "Technicon" has a throughput of 60 samples per hour[99]. Another variant of concentration by

extraction, developed for use in conjunction with a six-channel atomic fluorescence spectrophotometer, can handle 25 samples per hour[100]. Another useful method for determining traces of various elements and for analysing concentrates has been termed the "injection" method[101].

Typical atomic-absorption methods of determining trace elements in various materials are listed in Table 4. The special features of the combination of extraction and atomic absorption are discussed in detail in the recent monograph[58,105] and review literature[106].

Table 4. Examples of atomic-absorption determination with pre-concentration of trace elements by extraction.

Elements to be determined	Sample	Main extraction reagent	Detection limit, %	Refs.
Ag	minerals, ores, concentrates	diphenylthiourea	10^{-6}	20
Ag, Cu, Tl	metal halides	diphenylthiourea	10^{-7}—10^{-5}	21
Ag	ores and minerals	triphenylphosphine	10^{-6}	15
Au	minerals, cyanide solutions	triphenylphosphine	10^{-4} (2×10^{-3} $\mu g\ ml^{-1}$)	14
Cu, Fe, Mo, V, Zn	titanium tetrachloride	trioctylamine	$2 \cdot 10^{-5}$—$2 \cdot 10^{-5}$	102
Bi, Cu, Fe, Pb, Sb, Sn, Zn	alloy steels	trioctylamine	10^{-5}—10^{-4}	103
Fe	sodium and potassium halides	dithizone, sodium tetraphenylborate	—	104

In *X-ray fluorescence analysis* group concentration is used more often than individual concentration. In this case the concentrate should be a solid, which can be analysed directly. If the concentrate is liquid several additional operations are required: for example, after extraction the organic phase is often decomposed and the trace elements are sorbed on cellulose powder or on silica gel with grafted functional groups. Whenever possible the extraction is carried out with low-melting extractants at high temperature: the concentrate can then be simply pelleted and analysed. In some methods[43-45] of water analysis the trace elements are sorbed on silica gel microspheres with grafted chelating groups.

A widely used combination is concentration (usually by extraction) followed by *spectrophotometric determination* in the visible and u.v. regions of the spectrum. Individual concentration is often employed, or several elements are extracted sequentially. The matrix is very seldom removed in these methods. Usually the same reagent which gives a coloured complex is used also for concentrating the trace element. However two different reagents are used on occasions: a selective reagent is used first, to extract the trace element, and then a reagent not necessarily selective but having the most favourable photometric properties is added to the extract. This latter variant usually implies re-extraction, or decomposition of the extract. We should mention a method of concentrating copper, zinc, cadmium, mercury, manganese, and nickel as their 1-(2-pyridylazo)-2-naphthol (PAN) complexes: concentration occurs on an optically transparent membrane consisting of poly(vinyl chloride), tricresyl phosphate, and PAN.[107] The membrane is immersed into the solution for analysis, it is washed and dried, and its optical absorption is measured with a photometer.

Pre-concentration methods have been used also in combination with *spark source mass spectrometry*[108,109]. After being separated from the matrix (by extraction) the trace elements are deposited on a collector (usually high-purity alumina). In a determination[108] of eight trace elements in steel the impurities were extracted from an iodide solution into methyl isobutyl ketone, and they were then re-extracted by a dilute solution of sulphuric acid in the presence of hydrogen peroxide and evaporated on alumina. The concentrate was baked and analysed with a double-focussing mass spectrometer. A similar method was developed to determine impurities in sulphuric acid. A different, more specialised variant was proposed[109] for the determination of traces of the precious metals in both natural and technical materials. The precious metals are extracted from a solution in hydrochloride acid containing copper and other non-ferrous metals in the form of their hexamethylenephenylthiourea complexes. Copper(I) is co-extracted by this reagent. The extract is evaporated and baked to give a concentrate on copper oxide suitable for direct analysis in the mass spectrometer, since copper does not interfere with this determination.

Spark source mass spectrometry can be used to determine small quantities of at least 60–70 elements, and therefore it is most conveniently combined with concentration methods relying on removal of the matrix.

Concentration is used also in *activation analysis*. There are two basically different methods of concentrating trace elements in this method: concentration before irradiation and concentration after irradiation. Removal of the matrix before irradiation is essential when strong activation of the matrix would otherwise occur with production of long-lived radioisotopes. The concentration procedure can be used also to remove trace components liable to be strongly activated which are not being determined. However concentration before irradiation invalidates the main advantage of activation analysis: the absence of a blank correction. On the other hand this advantage is retained when concentration is carried out after irradiation. Both methods are used in analytical practice, though the second is by far the more common.

Two main types of pre-concentration method can be identified also in *electrochemical methods* of analysis. The first is inverse voltammetry. The trace elements are pre-concentrated electrochemically on a solid or a mercury electrode, and they are then determined by anodic dissolution. Cations produce a metallic deposit on the electrode: this deposit is conveniently handled by using a vitreous carbon electrode, which is chemically stable and mechanically strong. The concentration method used in the determination of anions consists in forming a film of an insoluble compound on a metallic (e.g. silver) electrode by the reaction between the electrode material and the anion being determined.

The alternative approach is polarography of extracts containing the trace elements. A background electrolyte and a homogenising solvent (for example, methanol) are added to the extract before polarographic analysis. This combination makes the analysis faster by avoiding the need for decomposition of the extract or for re-extraction. Furthermore it combines the selectivity of the polarographic method with that of concentration by extraction. For example, a method of determining indium doping impurities in the compound semiconductor $CdSiAs_2$ has been described[110]: the indium is extracted by chloroform at pH 1.2 as its chelate with 1-phenyl-3-methyl-4-benzoylpyrazol-5-one, and the cadmium and arsenic do not interfere with the extraction of indium. A solution of ammonium bromide in methanol is used as background electrolyte. Several developments of this type have been reported[111,112]. The first review of extraction-polarographic methods was published in 1939,[113] and it was followed by several other reviews.

An interesting "double" concentration is described by Karbainov[114]: concentration by extraction is followed by electrochemical concentration on an electrode. Both the approaches mentioned above are used in this variant.

IV. CONCENTRATION METHODS IN THE ANALYSIS OF SPECIFIC SUBSTANCES

It is interesting to examine the special features of concentration methods in the analysis of some important materials. In most cases concentration is applied in the analysis of high-purity materials, natural waters, and geological samples.

In the analysis of high-purity materials the purity of the air, of the glassware, of the apparatus, and of the reagents is of the utmost importance. Methods of concentration which do not require the use of reagents are often preferred (thermal evaporation of the matrix, crystallisation methods, etc). When choosing a concentration method it is important to know the previous history of the pure sample: if possible the concentration method should be different from the purification method used in the preparation of the sample.

The blank problem has a special significance in the analysis of pure materials. Usually the blank experiment includes all the reagents used in the concentration experiment, in the same amounts and under the same conditions, but without the sample for analysis. The amount of the wanted element determined in the blank experiment is a correction which is subtracted from the analysis result. Blank experiments of this type are often carried out, but they are not entirely correct: the degree of contamination by (or of loss of) the trace element in the presence of the main constituent of the sample may not be the same as in the blank experiment. Furthermore the residue of the matrix in the real concentrate may produce conditions for the determination of the trace element different from those which apply to the concentrate of the blank experiment, which is free from these residues. Several ways of overcoming these inconsistencies have been proposed, but space does not allow us to discuss them here. We will only stress the importance of using a method capable of handling different weights of the sample for analysis.

There are interesting reports[6,7] of the avoidance or minimisation of errors introduced by concentration methods. One of the recommended procedures involves very close integration (in both time and space) of the decomposition, concentration, and detection stages, preferably within a single enclosure. The adoption of micro- and ultra-micro methods is also recommended.

Natural waters are another important type of material whose analysis involves concentration methods. Without going into this problem in depth, we shall only stress the importance of the state of the trace elements in the water, which is often ignored. Often the trace elements are present as soluble complexes with naturally occurring or industrial organic substances, or alternatively they can be present as colloids.

Some methods allow direct concentration of the trace elements without previous treatment of the water: for example, Cu, Co, Zn, Mn, Cd, and In can be extracted as their complexes with hexamethyleneammonium hexamethylenedithiocarbamate without any preliminary operation. However in most cases a preliminary decomposition of the complexes is required, and the water is therefore treated with an oxidising agent (e.g. persulphate).

The complex formation problem is even more important in the analysis of surface fresh waters. The complexes formed by metal ions with humic and fulvic acid and with other organic compounds present in natural waters can strongly influence the extent of concentration of the trace elements achieved by extraction, sorption, and coprecipitation methods. Full concentration is usually possible only after decomposition of these organic materials.

In conclusion we note that this review has dealt with only a small part of the problem of the analytical concentration of trace elements. No mention was made, for example, of the validity and the reproducibility of the analysis, or of the effect of the concentration procedure on these characteristics, of the problem of controlling the degree of concentration, of the need to specify the concentration method used, etc. Among the important problems still to be solved are the development of automated methods of concentrating trace elements, the creation of unified procedures for the decomposition of the sample and the concentration and final analysis of the trace elements, and the development of new, simple, and rapid reagentless methods of concentration.

REFERENCES

1. O.G.Koch and G.A.Koch-Dedic, "Handbuch der Spurenanalyse", Bd.1,2, Springer-Verlag, Berlin, 1974.
2. Kh.I.Zil'bershtein, M.P.Semov, O.N.Nikitina, and Z.G.Fratkin, "Spektral'nyi Analiz Chistykh Veshchestv" (Spectral Analysis of Pure Substances), Izd.Khimiya, Leningrad, 1971, p.226.
3. J.Morrison (Editor), "Physical Methods of Trace Analysis" (Translated into Russian), Izd.Mir, Moscow, 1969.
4. T.G.Manova, Symposium "Khimicheskie Reaktivy i Preparaty" (Chemical Reagents and Preparations), Moscow, 1965, No.27, p.5.
5. R.Bock, "Methoden der analytischen Chemie, Eine Einführung", Bd.1, (Trennungsmethoden), Verlag Chemie, Weinheim, 1974.
6. G.Tölg, Talanta, **21**, 327 (1974).
7. G.Tölg, Pure Appl.Chem., **44**, 645 (1975).
8. Yu.A.Zolotov and N.M.Kuz'min, "Ekstraktsionnoe Kontsentrirovanie" (Concentration by Extraction), Izd.Khimiya, Moscow, 1971.
9. M.Pinta, Pure Appl.Chem., 37, 483 (1974).
10. L.I.Pavlenko, O.M.Petrukhin, Yu.A.Zolotov, A.V.Karyakin, G.N.Gavrilina, and I.E.Tumanova, Zhur.Anal.Khim., **29**, 933 (1974).
11. B.Ya.Spivakov, V.M.Shkinev, and Yu.A.Zolotov, Zhur.Anal.Khim., **30**, 2182 (1975).
12. V.M.Shkinev, B.Ya.Spivakov, V.A.Orlova, T.M.Malyutina, T.I.Kirillova, and Yu.A.Zolotov, Zhur.Anal.Khim., **33**, 922 (1978).
13. B.L.Serebryanyi, N.L.Fishkova, O.M.Petrukhin, and E.E.Rakovskii, Zhur.Anal.Khim., **28**, 2333 (1973).
14. N.L.Fishkova and O.M.Petrukhin, Zhur.Anal.Khim., **27**, 645 (1972).
15. O.M.Petrukhin, Yu.A.Zolotov, and L.A.Izosenkova, Zhur.Neorg.Khim., **16**, 3285 (1971)[Russ.J.Inorg. Chem., No.12 (1971)].
16. Yu.A.Zolotov and N.M.Kuz'min, "Ekstraktsiya Metallov Atsilpirazolonami" (Metal Extraction by Acylpyrazolones), Izd.Nauka, Moscow, 1977.
17. Yu.A.Zolotov, N.T.Sizonenko, E.S.Zolotovitskaya, and E.I.Yakovenko, Zhur.Anal.Khim., **24**, 20 (1969).
18. Y.Akama, T.Nakai, and F.Kawamura, Bunseki Kagaku, **25**, 496 (1976).
19. G.A.Vorob'eva, Yu.A.Zolotov, L.A.Izosenkova, A.V.Karyakin, L.I.Pavlenko, O.M.Petrukhin, I.V.Seryakova, L.V.Simonova, and V.N.Shevchenko, Zhur.Anal.Khim., **29**, 497 (1974).
20. G.A.Vall, M.V.Usol'tseva, I.G.Yudelevich, I.V.Seryakova, and Yu.A.Zolotov, Zhur.Anal.Khim., **31**, 27 (1976).

21. V.P.Shaburova, I.G.Yudelevich, I.V.Seryakova, and Yu.A.Zolotov, Zhur.Anal.Khim., 31, 255 (1976).
22. Yu.A.Zolotov and V.I.Golovanov, Zhur.Anal.Khim., 26, 1880 (1971).
23. Yu.A.Zolotov, V.V.Bagreev, and I.M.Kutytev, Analyt.Chim.Acta, 78, 397 (1975).
24. I.V.Seryakova, G.A.Vorobjeva, A.V.Glembotzky, and Yu.A.Zolotov, Analyt.Chim.Acta, 77, 183 (1975).
25. Yu.A.Zolotov, N.G.Vanifatova, T.A.Chanysheva, and I.G.Yudelevich, Zhur.Anal.Khim., 32, 317 (1977).
26. T.Braun (Editor), "Extraction Chromatography", Akademiai Kiado, Budapest, 1975.
27. Y.Sekizura, T.Kojima, T.Yano, and K.Ueno, Talanta, 20, 979 (1973).
28. V.P.Zhivopistsev, I.N.Ponosov, and E.A.Selezneva, Zhur.Anal.Khim., 18, 1432 (1963).
29. V.P.Zhivopistsev et al., Zhur.Prikl.Spektrosk., 11, 779 (1969).
30. V.I.Petrov, Yu.A.Makhnev, and V.P.Zhivopistsev, Zhur.Anal.Khim., 28, 911 (1973).
31. Z.I.Otmakhova, O.V.Chashina, and G.V.Kashkan, Zavod Lab., 42, 146 (1976).
32. Z.I.Otmakhova, O.V.Chashina, and G.A.Kataev, Zavod.Lab., 35, 685 (1969).
33. Z.I.Otmakhova, O.V.Chashina, N.I.Slezko, and G.A.Kataev, Symposium "Arsenid Galliya" (Gallium Arsenide), Izd.Tomsk.Politekh.Inst., Tomsk, 1969, p.476.
34. L.I.Anikina, V.V.Bagreev, T.S.Dobrolyubskaya, Yu.A.Zolotov, A.V.Karyakin, A.Z.Miklishanskii, N.G.Nikitina, P.N.Palei, and Yu.V.Yakovlev, Zhur. Anal.Khim., 24, 1014 (1969).
35. J.E.Going, G.Weselberg, and G.Andrejat, Analyt. Chim.Acta, 81, 349 (1976).
36. I.A.Tarkovskaya, Ukrain.Khim.Zhur., 33, 414 (1967).
37. I.A.Tarkovskaya, Symposium "Sintez i Svoistva Ionoobmennykh Materialov" (Synthesis and Properties of Ion-exchange Materials), Izd.Nauka, Moscow, 1968.
38. G.V.Myasoedova, G.I.Malofeeva, O.P.Shvoeva, E.V.Illarionova, S.B.Savvin, and Yu.A.Zolotov, Zhur.Anal.Khim., 32, 645 (1977).
39. G.V.Myasoedova, L.I.Bol'shakova, and S.B.Savvin, Zhur.Anal.Khim., 28, 2324 (1973).
40. G.V.Myasoedova, I.I.Antokol'skaya, L.I.Bol'shakova, O.P.Shvoeva, and S.B.Savvin, Zhur.Anal.Khim., 29, 2104 (1974).
41. T.M.Florence and G.E.Batley, Talanta, 23, 179 (1976).
42. J.S.Fritz and E.M.Moyers, Talanta, 23, 590 (1976).
43. D.E.Leiden and G.H.Luttrell, Analyt.Chem., 47, 1612 (1975).
44. D.E.Leiden, G.H.Luttrell, W.K.Nonidez, and D.B.Werho, Analyt.Chem., 48, 67 (1976).
45. D.E.Leiden, G.H.Luttrell, A.E.Sloan, and N.J.De Angelis, Analyt.Chim.Acta, 84, 97 (1976).
46. L.I.Pavlenko, G.I.Malofeeva, L.V.Simonova, and O.Yu.Andryushchenko, Zhur.Anal.Khim., 29, 1122 (1974).
47. N.V.Kovaleva and V.T.Chuiko, Zhur.Anal.Khim., 28, 1985 (1973).
48. V.T.Chuiko, A.A.Kravtsova, and N.V.Kovaleva, Zhur.Anal.Khim., 27, 85 (1972).
49. E.Jackwerth, E.Döring, and J.Lohmar, Z.Analyt. Chem., 253, 195 (1971).
50. V.I.Kuznetsov, Zhur.Anal.Khim., 9, 199 (1954).
51. G.V.Myasoedova, Zhur.Anal.Khim., 21, 598 (1966).
52. V.I.Kuznetsov and T.G.Akimova, "Kontsentrirovanie Aktinoidov Soosazhdeniem s Organicheskimi Soosaditelyami" (Concentration of the Actinides by Coprecipitation With Organic Coprecipitants), Atomizdat, Moscow, 1968.
53. V.A.Nazarenko and I.M.Grekova, Symposium "Odinnadtsatyi Mendeleevskii S"ezd po Obshchei i Prikladnoi Khimii. Referat Dokladov i Soobshchenii" (Papers and Contribution Presented to the Eleventh Mendeleev Congress on General and Applied Chemistry), No.5, Izd.Nauka, Moscow, 1975, p.71.
54. E.Jackwerth and P.G.Willmer, Talanta, 23, 197 (1976).
55. E.Jackwerth, Pure Appl.Chem., 51, No.5 (1979).
56. L.S.Krauz, A.G.Karabash, Sh.I.Peizulaev, V.M.Lipatova, and V.S.Moleva, Trudy Kom.Anal. Khim.Akad.Nauk SSSR, 12, 175 (1960).
57. Kh.I.Zil'bershtein and M.P.Semov, Izv.Sibirsk, Otd.Akad.Nauk SSSR, No.9, Ser.Khim.Nauk, 4, 72 (1967).
58. A.Meyer, E.Grallath, G.Kaiser, and G.Tölg, Z. analyt.Chem., 281, 201 (1976).
59. A.B.Carel, Analyt.Chim.Acta, 78, 479 (1975).
60. R.A.Vitkun, T.B.Kravchenko, Yu.V.Zelyukova, and N.S.Poluektov, Zavod.Lab., 41, 663 (1975).
61. V.Z.Krasil'shchik, G.A.Shteinberg, and A.F.Yakovleva, Zhur.Anal.Khim., 26, 1897 (1971).
62. V.Z.Krasil'shchik and G.A.Shteinberg, Zhur.Anal. Khim., 26, 1903 (1971).
63. V.Z.Krasil'shchik, T.G.Manova, et al., Zavod. Lab., 39, 935 (1973).
64. V.Z.Krasil'shchik and T.G.Manova, Zhur.Anal. Khim., 30, 971 (1975).
65. W.Lund and B.V.Larsen, Analyt.Chim.Acta, 70, 299; 72, 57 (1974).
66. W.Lund, B.V.Larsen, and N.Gundersen, Analyt. Chim.Acta, 81, 319 (1976).
67. Y.Thomassen, B.V.Larsen, F.J.Langmyhr, and W.Lund, Analyt.Chim.Acta, 83, 103 (1976).
68. L.N.Moskvich et al., Atomnaya Energiya, 36, 198 (1974); 39, 94 (1975).
69. L.N.Moskvich, N.N.Kalinin, L.A.Godon, S.B.Tomilov, and G.I.Kizym, Zhur.Anal.Chim., 31, 2396 (1976).
70. Kh.Z.Brainina, "Inversionnaya Vol'tamperometriya Tverdykh Faz" (Inverse Voltammetry of Solid Phases), Izd.Khimiya, Moscow, 1972.
71. H.E.Usdowski, "Fraktionierung der Spurenelemente bei der Kristallisation", Springer Verlag, Berlin, 1975.
72. A.B.Blank, V.G.Chepurnaya, L.P.Eksperiandova, and V.Ya.Vakulenko, Zhur.Anal.Khim., 29, 1705 (1974).
73. E.Jackwerth, E.Döring, J.Lohmar, and G.Schwark, Z.analyt.Chem., 260, 177 (1972).
74. R.Höhn, E.Jackwerth, and K.Koos, Spectrochim. Acta, 29B, 225 (1974).
75. R.Höhn and E.Jackwerth, Erzmetall, 29, 279 (1976).
76. E.Jackwerth and J.Messerschmidt, Z.analyt.Chem., 274, 205 (1975).
77. E.Jackwerth and A.Kulok, Z.analyt.Chem., 28, 257 (1971).
78. E.Jackwerth, R.Höhn, and K.Koos, Z.analyt.Chem., 264, 1 (1973).
79. M.Hiraide and A.Mizuike, Bull.Chem.Soc.Japan, 48, 3753 (1975).

80. M.Hagadone and H.Zeitlin, Analyt.Chim.Acta, 86, 289 (1976).
81. M.Hiraide, Yu.Yoshida, and A.Mizuike, Analyt. Chim.Acta, 81, 185 (1976).
82. A.M.Andrianov and V.E.Poladyan, Zavod.Lab., 40, 1064 (1974).
83. G.V.Myasoedova, G.I.Malofeeva, O.P.Shvoeva, E.V.Illarionova, S.B.Savvin, and Yu.A.Zolotov, Zhur.Anal.Khim., 32, 645 (1977).
84. I.G.Yudelevich, Thesis, Tomsk, 1972.
85. G.Semples, Spectrochim.Acta, 3, 346 (1948).
86. G.Gorbach and F.Pohl, Mikrochemie ver.Mikrochim. Acta, 36/37, 486; 38, 258 (1951).
87. F.Pohl, Z.analyt.Chem., 139, 241 (1953).
88. F.Pohl, Spectrochim.Acta, 6, 19 (1953).
89. A.G.Karabash, Sh.I.Peizulaev, R.L.Slyusareva, and V.M.Lipatova, Zhur.Anal.Khim., 14, 94 (1959).
90. N.P.Krivenkova, L.I.Pavlenko, B.Ya.Spivakov, I.A.Popova, T.S.Plotnikova, V.M.Shkinev, I.P.Kharlamov, and Yu.A.Zolotov, Zhur.Anal.Khim., 31, 514 (1976).
91. N.A.Rudnev, L.I.Pavlenko, G.I.Malofeeva, and L.V.Simonova, Zhur.Anal.Khim., 24, 1223 (1969); Symposium "Metody Analiza Veshchestv Vysokoi Chistoty" (Methods of Analysis of High-purity Materials), Izd.Nauka, Moscow, 1965, p.159.
92. G.A.Vall, L.P.Poddubnaya, I.G.Yudelevich, and Yu.A.Zolotov, Zhur.Anal.Khim., 34, 885 (1979).
93. B.F.Scribner and H.J.Mullin, J.Res.Nat.Bur.Stand. USA, 37, 379 (1946).
94. A.N.Zaidel', N.I.Kaliteevskii, L.V.Lipis, M.P.Chaika, and Yu.I.Belyaev, Zhur.Anal.Khim., 11, 21 (1956).
95. S.L.Mandel'shtam, N.I.Semenov, and Z.M.Turovtseva, Zhur.Anal.Khim., 11, 9 (1956).
96. U.Anders and G.Hailer, Z.Anal.Chem., 278, 203 (1976).
97. A.I.Busev, V.M.Byr'ko, A.P.Tereshchenko, N.N.Novikova, V.P.Naidina, and P.B.Terent'ev, Zhur.Anal.Khim., 25, 665 (1970).
98. D.L.Tsalev, I.P.Alimarin, and S.I.Neiman, Zhur. Anal.Khim., 27, 1223 (1972).
99. F.D.Pierce, M.J.Gortatowski, et al., Analyt.Chem., 47, 1132 (1975).
100. M.Jones, G.F.Kirkbright, L.Ranson, and T.S.West, Anal.Chim.Acta, 63, 210 (1973).
101. H.Berndt and E.Jackwerth, Spectrochim.Acta, 30B, 169 (1975).
102. V.A.Orlova, B.Ya.Spivakov, V.M.Shkinev, T.I.Kirillova, V.A.Ivanova, T.M.Malyutina, and Yu.A.Zolotov, Zhur.Anal.Khim., 33, 91 (1978).
103. B.Ya.Spivakov, V.I.Lebedev, V.M.Shkinev, N.P.Krivenkova, T.S.Plotnikova, I.P.Kharlamov, and Yu.A.Zolotov, Zhur.Anal.Khim., 31, 757 (1976).
104. Yu.A.Zolotov, O.A.Kiseleva, N.V.Shakhova, and V.I.Lebedev, Analyt.Chim.Acta, 79, 237 (1975).
105. M.S.Cresser, "Solvent Extraction in Flame Spectroscopic Analysis", Butterworth, Sevenoaks, 1978.
106. Yu.A.Zolotov, and N.M.Kuz'min, Zhur.Anal.Khim., 22, 773 (1967).
107. T.Tanaka, K.Hiiro, and A.Kawahara, Bunseki Kagaku, 24, 460 (1975).
108. Yu.A.Zolotov, N.V.Shakhova, O.I.Kryuchkova, S.I.Gronskaya, B.Ya.Spivakov, G.I.Ramendik, and V.N.Gushchin, Zhur.Anal.Khim., 33, 1253 (1978).
109. O.M.Petrukhin, Yu.A.Zolotov, V.N.Shevchenko, O.I.Kryuchkova, S.I.Gronskaya, V.N.Gushchin, G.I.Ramendik, V.V.Dunina, and E.G.Rukhadze, Zhur.Anal.Khim., 34, 334 (1979).
110. V.G.Revenko, V.V.Bagreev, Yu.A.Zolotov, and L.S.Kopanskaya, Zhur.Anal.Khim., 27, 187 (1972).
111. T.V.Nghi and F.Vydra, Anal.Chim.Acta, 80, 267 (1975); Coll.Czech.Chem.Comm, 40, 1485 (1975).
112. I.V.Pyatnitskii and R.P.Ruzhanskaya, Zhur.Anal. Khim., 24, 650 (1969).
113. N.M.Kuz'min, Yu.A.Zolotov, and Yu.A.Karbainov, Trudy Kom.Anal.Khim.Akad.Nauk SSSR, 17, 228 (1969).
114. Yu.A.Karbainov, Izv.Tomsk.Politekh.Inst., 164, 228 (1967).

Vernadskii Geochemistry and
Analytical Chemistry Institute,
Moscow

RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

August 1980

Translated from *Uspekhi Khimii*, **49**, 1457-1497 (1980)

U.D.C. 535.217; 541.128; 541.141; 620.91; 620.92

Possible Approaches to the Development of Photo-catalytic Solar Energy Converters

K.I.Zamaraev and V.N.Parmon

Possible approaches to the development of photo-catalytic solar energy converters, and their perspectives, are discussed with special reference to the conversion of solar energy into chemical energy by the photo-catalytic decomposition of water into hydrogen and oxygen. 408 references.

CONTENTS

I.	Introduction	695
II.	Methods of solar energy conversion	696
III.	Possible processes for the conversion of solar into chemical energy	698
IV.	Maximum theoretical efficiency of the conversion of solar into chemical energy	699
V.	The photo-catalytic decomposition of water	701

I. INTRODUCTION

According to recent estimates[1-4] the annual consumption of energy by mankind is currently 5×10^{16} kcal, rising rapidly and doubling every 15–20 years. On the other hand the known reserves of mineral fuels, which at present form the basis of our energy balance, are limited to an estimated energy equivalent of 10^{19} kcal. Thus the search for new sources of energy is a problem of fundamental importance. The most promising approaches appear to be the use of thermonuclear energy (based on deuterium) and the use of solar energy[1-18]. The large-scale exploitation of both these sources of energy presents serious difficulties, but it is important to note that whereas controlled thermonuclear fusion is still at the research stage solar energy is continuously reaching the Earth in amounts far exceeding the rapidly growing needs of mankind.

Thus the amount of solar energy which is incident on our planet is estimated[1,16,17] to be 1.2×10^{21} kcal per annum, but some of this energy is reflected by the atmosphere and by the Earth's surface and is irreversibly lost, while the remainder is absorbed by the atmosphere (2×10^{20} kcal), by the oceans and seas (4.2×10^{20} kcal), and by the land masses (1.8×10^{20} kcal). Part of this absorbed energy (6×10^{17} kcal per annum) is converted into chemical energy by the photosynthetic process in plants and micro-organisms. However, only a very small part of this energy is used by mankind: 8×10^{15} kcal per annum as fuel and other materials and 4×10^{15} kcal per annum as food. The amount of solar energy converted into electrical energy by hydroelectric and wind-operated power stations is also quite small: 4×10^{15} kcal per annum.

The most important attribute of solar energy is its ecological purity, i.e. the possibility of carrying out energy cycles without emitting harmful products into the surroundings and without additional heating of the Earth.

The wide-scale exploitation of solar energy must await practical solutions to the following three problems: 1) the relative diffuseness of solar energy (even outside the Earth's

atmosphere the flux of solar energy is only 1.395 kW m^{-2} = 12260 kW-h m^{-2} $year^{-1}$ = 3.33×10^{-5} kcal cm^{-2} s^{-1}),[19-24] 2) the annual, seasonal, and daily variations of the energy flow reaching the Earth's surface, and 3) the need to convert the energy of the light quanta into a more convenient form.

Let us consider the importance of the first two of the above factors. In the vicinity of the Earth a power of 1 GW (typical of a modern electric power station) is carried by the Sun's rays falling on a square 850 m in side: the area of such a square is comparable to that occupied by a thermal power station having that output. Of course, on the Earth's surface the insolation is much lower, since the Sun shines for only part of the day, and its rays are partly reflected by the atmosphere. But even in the middle latitudes of the USSR—in the region of Moscow or of Novosibirsk, say—the total amount of radiation falling on the surface of the Earth is staggeringly large: more than 1000 kW-h m^{-2} $year^{-1}$.[19,20] This is only 2.5 times lower than the radiation in the sunniest region of the Earth (near the Red Sea[20,22]). In Soviet Central Asia the total solar radiation is as high as 1600 kW-h m^{-2} $year^{-1}$. A simple calculation shows that an amount of energy equal to the annual output of a 1 GW electric power station is contained in the Sun's rays falling on a square 3 km in side in the middle latitudes of the USSR or 2.3 km in side in Central Asia. It is equally easy to show that the amount of energy produced by the combustion of 600 million tonnes of petroleum (the annual production of the USSR) is contained in the Sun's rays falling on a square 67.4 km in side in Central Asia: we note that just the Kara-Kum desert can accommodate over 60 of these squares.

An amount of energy of 1300 billion kW-h, equal to the annual output of electrical energy planned for 1980 in the USSR, could be collected in Central Asia from a square 64.7×64.7 km^2 in area assuming a conversion efficiency of 20%. Even in the region of Novosibirsk the annual output of electrical energy of the Novosibirsk hydro-electric station (1.7×10^9 kW-h)[25] could be matched with a square 2.9 km in side (again, assuming 20% conversion efficiency), which is very much less than the area of the Ob' sea which feeds the hydroelectric station (1070 km^2). For comparison we may note that in the USA the area of the existing network of hard-surfaced roads (having a total length of 6 million km in 1972[26]) is greater than the area of a square 150 km in side. Thus, in spite of the relatively low density of the solar energy flux and of its dependence on local conditions, even a complete change-over of our energy consumption to solar energy is not (in principle) an engineering impossibility. More detailed estimates have confirmed the economic justification for the development of energetics based on solar radiation[27-59]. However, the effective exploitation of solar energy awaits the development of economically acceptable methods of concentration, conversion, and storage of the Sun's energy.

II. METHODS OF SOLAR ENERGY CONVERSION

Existing methods of conversion of the Sun's energy can be arbitrarily classified into four types: 1) thermal, 2) photophysical, 3) photochemical (including photo-electrolysis), and 4) photobiological (based on natural photosynthesis).

The thermal conversion of solar energy is the simplest: it consists in heating heat-transfer media with ordinary or with concentrated Sun's rays. Many variants of the thermal method are currently in use, or are being developed: they are used for cooling or heating buildings, in solar kitchens and high-temperature furnaces, for powering mechanical engines and electrical generators, for feeding thermo-electric converters, in the desalination of water, etc. (see previous reviews[4,12,27-39]). In principle the efficiency of the conversion of the Sun's radiant energy into heat is quite high, and with a very simple concentrator it can reach 50–70% at noon[23,27,28,38,39,60]. Therefore even in the near future we can expect relatively large-scale use of thermal methods of solar energy conversion, matched to local needs. However, in the subsequent conversion of thermal into electrical or mechanical energy the efficiency (daily average) falls to 3–5% because of the low efficiency of heat engines and of the low effectiveness of the concentrators except at noon[23,27]. For these reasons thermal conversion of solar energy is still not being used for large-scale energy production.

Recent advances in the direct conversion of solar energy into electrical or chemical (fuel) energy have made these methods potentially more attractive for large-scale energy production.

The direct photophysical conversion of solar into electrical energy is most effectively realised in semiconductor p–n junction converters[4,22,28,51-55,61,62]. In these devices the absorption of a light quantum of energy $h\nu$ (greater than the energy gap) transfers an electron from the valence to the conduction band. The resulting hole–electron pair is separated by the electric field of the p–n function (see Fig. 1), causing electrical polarisation of the semiconductor wafer and thus producing an e.m.f. and a current i. Semiconductor converters based on crystalline silicon, with efficiencies up to 14%, have been developed and are being used successfully[51-55,61,62]. Even more effective semiconductor converters based on hetero-junctions (e.g. gallium arsenide) are also being developed: their efficiency can be as high as 20% or more[52-55]. This method of converting solar into electrical energy is attracting most of the research effort at the moment, and it appears to offer the best prospect of success†. A plan to set up a semiconductor electrical power station in space capable of re-transmitting the energy to the Earth in the form of UHF radiation is also being discussed[24].

The widespread use of semiconductor converters awaits practical solutions to two main problems: the high cost of the semiconductor converters themselves (currently[53-55] 10–15 thousand dollars per kW of power production capability), and the difficulty of combining semiconductor photo-electric converters with high-power electrical circuits. The former problem will be rapidly overcome by current advances in semiconductor production technology (it is estimated[53-55] that economically acceptable converters costing 200–250 dollars per kW, i.e. matching the cost of modern thermal converters, will be available in the mid-1980's). However, the second limiting factor, which applies to all Earth stations, is more serious. It stems from the annual, seasonal, and daily

† Work is proceeding also on photo-electrochemical converters of solar into electrical energy ("wet photocells"). According to their operating mechanism, these can be classified into two types: the photosensitive semiconductor electrode type[11,59,63-93] and the photosensitive electrolyte type[94-110]. Recent converters of the photosensitive electrode type have shown very promising efficiencies (up to 7.5% for CdSe with a polysulphide electrolyte[88]). However, much more work is needed before the true potential of the method can be assessed. The All-Union Research and Technical Information Institute (VINITI) issues a special bulletin entitled "Ekspress-informatsiya. Pryamoe Preobrazovanie Teplovoi i Khimicheskoi Energii v Elektrichestvo" (Express Information. The Direct Conversion of Thermal and Chemical Energy into Electricity), which summarises current foreign publications on the conversion of solar energy into electrical energy by photo-electric cells (including "wet cells").

variations of the energy output of the semiconductor converters. The consumption of electrical energy cannot be tailored to suit these variations. Energy accumulators (or buffers) have been based on the chemical energy of fuels or on the potential energy of water in reservoirs. The large-scale use of solar energy will also require some form of *accumulation* of this energy, preferably in the most effective form currently known (i.e. as a *chemical fuel*).

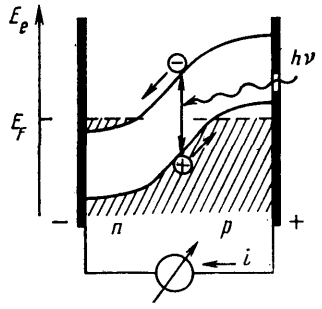


Figure 1. Basic operation of the semiconductor element. The potential energy of the current carriers (E_e) is plotted vertically. The thin full lines are the edges of the energy gap; the cross-hatched region denotes the energy levels filled with electrons; E_F is the Fermi level. The arrows show the direction of motion of the charges (electrons and holes) separated by the light in the region of the step in electrical potential.

Many experts consider hydrogen to be the most promising fuel[1,13-15,56-59,111-116]. Hydrogen is not only an exceptionally good fuel, whose combustion does not contaminate the environment, but it is also a valuable chemical product. The current world production of hydrogen is more than 30 million tonnes per annum, with an annual growth rate of 10%.[14,57] Given solar energy converters having an efficiency of 20% this amount of hydrogen could be produced in Central Asia from a square with 55.4 km sides.

One possible way of converting solar energy into chemical energy in the form of hydrogen is the electrolysis of water, using the electrical energy produced by semiconductor $p-n$ junction converters. Assuming an efficiency of 14% for the conversion of solar into electrical energy (which has already been achieved in modern silicon photocells), and an efficiency of 70% for the conversion of electrical into chemical energy (i.e. the efficiency of present-day industrial apparatus for the electrolysis of water), the overall efficiency for the conversion of solar energy into the chemical energy of hydrogen is 10%. This is an encouraging figure, especially since there are very real prospects of further improvements in the efficiency of semiconductor converters of radiant into electrical energy. Converters based on this two-stage scheme could in principle be operating now, but so far they have not been economically viable because of the existence of cheaper (natural) organic and nuclear fuels.

In addition to this two-stage method we can envisage the direct photochemical conversion of solar energy into fuel energy without intermediate production of electrical energy. Most of the photochemical conversion methods rely on the use of *photo-catalytic* processes. One of these methods is the photo-electrolysis of water on a semiconductor surface (e.g. an oxide), acting as a heterogeneous catalyst for the decomposition of water[117-119]. This method is attracting a great deal of attention at the moment[11,59,117-188] (see also Refs. 63–93).

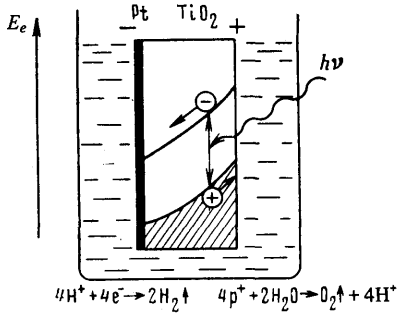


Figure 2. Operation of a semiconductor photo-catalyst for the decomposition of water; symbols as in Fig. 1.

In the most thoroughly investigated system, which uses titanium dioxide as the photo-catalytic semiconductor, the photo-electrolysis process can be described as follows[87,178]. The light generates a conduction electron and a hole in the semiconductor, and the two carriers are separated by the electric field at the semiconductor–electrolyte interface. The holes diffuse to the surface of the semiconductor catalyst, where they oxidise the water with evolution of molecular oxygen (see Fig. 2), and the conduction electrons reach the metal electrode (e.g. platinum) where they reduce the water with evolution of molecular hydrogen. Unfortunately the efficiency of the conversion of solar into chemical energy on TiO_2 is quite low (less than 1%) because this oxide has a wide band-gap (~ 3 eV) and hence the photo-catalytic process in this case requires u.v. quanta, which are present in small numbers in the Sun's spectrum.

Worthwhile progress in this area can be made only by changing to semiconductors which can decompose water under the influence of visible radiation, such as iron oxide[116,182,183] and tungsten oxide[182,183], though other semiconductors also could be used. However, in the absence of reliable quantitative measurements we cannot yet assess the efficiency of solar energy conversion with hydrogen accumulation on these photo-catalysts. Furthermore, most of these materials suffer strong photo-corrosion in aqueous solutions. There is evidence that the photo-corrosion of semiconductor photo-catalysts may be suppressed by chemical modification of the semiconductor surface (by introducing surface impurities, or by adsorption of special reagents). Surface modification can be used also to control the surface field which separates the photo-generated charge pairs.

Thus any progress in the exploitation of these converters will be determined to a large extent by advances in the surface chemistry of semiconductors.

Another method of direct conversion of solar energy into chemical energy relies on molecular photo-catalytic systems. These systems are found, for example, in natural photobiological converters such as plants and bacteria capable of photosynthesis[7,13,56,189-192]. In plants the energy of the Sun's radiation is converted mainly into chemical energy of

carbohydrates, synthesised by the reduction of carbon dioxide and the oxidation of water. The initial step of the photosynthesis is reminiscent of the formation of a conduction electron and a hole in semiconductors. The light quantum absorbed by a chlorophyll molecule (Chl) transfers one electron from the ground state to an excited level (Fig. 3), from which it can fall into the lower-lying levels of other molecules (the acceptors, A). On the other hand the hole which is formed at the same time in the ground level of the Chl molecule can accept an electron from the higher-lying levels of other molecules (the donors, D). As a result, the initial step of the photosynthesis process

$$A + D \xrightarrow[Chl]{h\nu} A^- + D^+ , \qquad (1)$$

produces a pair of particles (the reducing agent A^- and the oxidising agent D^+) analogous to the hole–electron pair of semiconductors.

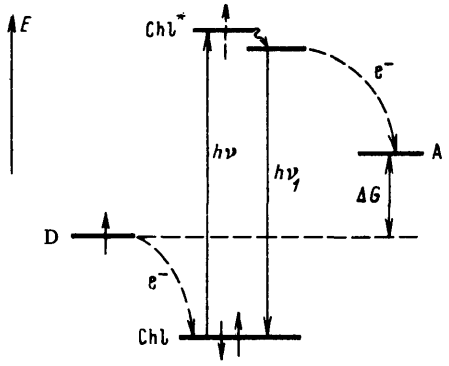


Figure 3. Charge separation by an electronically excited dye molecule (chlorophyll, Chl). Electron energy is plotted vertically, $h\nu$ is the absorbed light quantum, the wavy arrow denotes the conversion into a longer lived excited state, $h\nu_1$ is the luminescence quantum, and ΔG is the chemical energy stored as a result of the process.

During photosynthesis in plants the reducing agent A^- is used (through a complicated chain of catalytic reactions) to reduce CO_2 to sugars:

$$4A^- + 3H_2O + CO_2 \rightarrow 4A + {}^1/_6(C_6H_{12}O_6) + 4OH^- , \qquad (2)$$

and the oxidising agent D^+ completes the cycle of reactions by oxidising water to molecular oxygen:

$$4D^+ + 4OH^- \rightarrow 4D + 2H_2O + O_2\uparrow . \qquad (3)$$

Thus the overall photosynthesis process in plants can be described by the catalytic reaction scheme

$$H_2O + CO_2 \xrightarrow[Chl,\,A,\,D]{h\nu} 1/6\,(C_6H_{12}O_6) + O_2\uparrow \qquad (4)$$

in which an amount of free energy $\Delta G \cong 120$ kcal mole^{-1} O_2 is stored. In order to carry out one such cycle a plant needs no fewer than eight quanta of red light, each with an energy of ~40 kcal Einstein^{-1}.[7]

Theoretical calculations (see below) suggest that the maximum possible efficiency of the conversion of solar energy by the eight-quantum reaction (4) is 15% of the incident Sun's light. This value can be treated as the theoretical limit of the efficiency of photo-biological energy converters. In some water plants (e.g. *chlorellae*) the experimentally measured efficiency of solar energy conversion is as high as 6%.[12,193–195] Among cultivated (agricultural) plants the highest efficiencies are found in maize (3.2%), sorghum (3.2%), and sugar cane (2.4%).[194] Thus the best cultures of water plants offer an acceptably efficient conversion of solar into chemical energy. Economically sound processes for the microbiological fermentation of the products of plant photosynthesis to give convenient forms of fuel for large-scale energy production have already been suggested: hydrogen (see Fig. 4), methane, or ethanol[13,50,196–200]. Large Government programmes aimed at replacing hydrocarbon motor fuels by ethanol (obtained from sugar cane) are already in progress in Brazil and in the Philippines.[13]

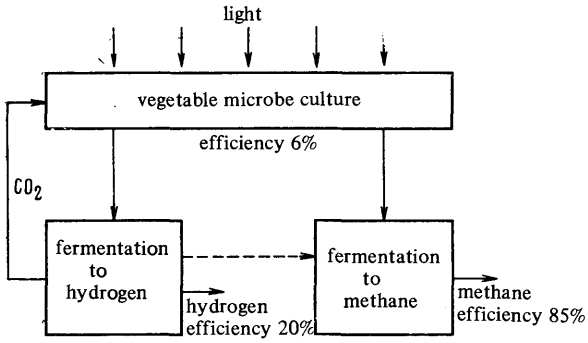


Figure 4. Microbiological conversion of solar energy and efficiencies achieved in the different steps.

Obviously, a major advance in the conversion of solar into chemical energy would be the development of synthetic molecular photo-catalytic systems with a narrow "chemical specialisation", which could be more efficient than plants[1]. If these systems could be handled in simple industrial plant, and manufactured from cheap starting materials, they could even be cheaper than existing semiconductor p–n junction devices. The problem of designing molecular photo-catalytic systems for the conversion of solar into chemical energy was fully formulated only recently[1], and is still in its initial stages of development. The various approaches to its solution are the main theme of the present review.

As will be shown below, molecular and semiconductor photo-catalytic converters have very similar mechanisms. Hence many of the data quoted in this paper can be applied also to calculations involving semiconductor photo-catalytic systems.

III. POSSIBLE PROCESSES FOR THE CONVERSION OF SOLAR INTO CHEMICAL ENERGY

The basic thermodynamic requirement which applies to chemical reactions for accumulating solar energy in the form of chemical energy is that the reaction should be endothermic in the dark. The condition is $\Delta H > 0$ (if the stored energy is to be used for the production of heat) or $\Delta G > 0$ (if the energy is being stored for the production of a more "noble" form of energy, e.g. the electrical energy of fuel cells). In order to allow their storage, transport, and use in practical situations the photo-reaction products must be stable, i.e. the reverse (exothermic) reactions must be slow.

Chemical energy can be stored either directly as the internal energy of molecules (for example, by converting a substance under the influence of light into an energy-enriched form such as a valency isomer), or as reaction products which can be used as fuels (combustibles and oxidisers), and which interact with evolution of energy in a useful form[13,56-59,122,179,201-208].

The exploitation of photochemical converters for large-scale energy production implies the storage and transport of hundreds of millions of tonnes of photo-catalytic reaction products in the form of useful fuels. Therefore the starting materials used in these reactions should be readily available, cheap, convenient to use, and easily transportable. The accumulation of energy in an intramolecular form obviously implies the use of fairly complex compounds[122,179,201,208-216], and this method will probably be limited to satisfying local needs even if very efficient forms of the method are developed. The same is true of converters relying on phase transitions[217,218] or on corrosive or dangerous materials such as SO_2, Cl_2, etc.[208]

Within the Earth's atmosphere the most convenient way to exploit chemical energy is to allow a fuel to react with the atmospheric oxygen. Hence the most attractive working processes for the conversion of solar energy are those leading to the reduction of readily available materials (as in natural photosynthesis).

Table 1. Possible reactions for the storage of solar energy as fuel.

No.	Reaction	n	ΔG^0_{298}, kcal mole^{-1}	ΔH^0_{298}, kcal mole^{-1}	ΔG^0_{298} (for 1 electron), eV	λ_{thr}, nm
1	$H_2O \rightarrow H_2 + {}^1/_2 O_2$	2	56.71	68.25	1.23	1008
2	$2H_2O + CO_2 \rightarrow CH_4 + 2O_2$	4	195.54	212.8	2.12	588
3	$2H_2O + CO_2 \rightarrow CH_3OH + {}^3/_2 O_2$	6	167.92	173.64	1.21	1025
4	$3H_2O + 2CO_2 \rightarrow C_2H_5OH + 3O_2$	12	318.34	336.82	1.15	1077
5	${}^3/_2 H_2O + {}^1/_2 N_2 \rightarrow NH_3 + {}^3/_4 O_2$	3	81.09	91.44	1.17	1059
6	$2H_2O + N_2 \rightarrow N_2H_4 + O_2$	4	181.33	148.74	1.97	629

Note. The thermodynamic data quoted are for liquid H_2O, CH_3OH, C_2H_5OH, and N_2H_4; n is the number of electrons transferred; λ_{thr} is the threshold wave length for the n-quantum mechanism (see Section IV).

In the light of the requirements outlined above the most convenient starting materials are water and atmospheric gases, and we must turn towards these materials (at least, initially) in our search for large-tonnage photo-catalytic energy production methods. Some processes potentially suitable for the storage of energy in a chemical form are listed in Table 1. In every case the product is a valuable chemical raw material. All these processes take place in living organisms (photosynthesis followed by fermentation of the photosynthesis products to H_2, CH_4, or alcohols, or fixation of atmospheric nitrogen). As was pointed out above, reaction No.1 of Table 1 has been achieved under artificial conditions on semiconductor photo-catalysts. Reactions No.2[219] and Nos.5 and 6[220] have also been observed on TiO_2 and $SrTiO_3$ photo-catalysts under the influence of u.v. light, though their quantum efficiency is still very low. The distinguishing feature which all these processes have in common is the oxidation of water with evolution of molecular oxygen. As we shall show below, this reaction step is the most difficult to implement.

The absorption of solar energy by the compounds listed in Table 1 is negligibly small, and photochemical conversion is necessary: this is provided by an additional intermediate agent (the photo-catalyst) which strongly absorbs the Sun's light and which is fully regenerated at the end of the working cycle. Many photo-catalytic reactions, both homogeneous and heterogeneous, have been described (see, for example, Refs.221 and 222 respectively). However, the effort currently devoted to the search for really effective catalytic processes for the conversion of solar energy is still inadequate.

The most promising chemical process for the conversion of solar energy at present is the photo-catalytic decomposition of water into hydrogen and oxygen. Water, of course, is a universally available, cheap, and very convenient starting material. The product of the reaction—hydrogen—is not only an excellent fuel but also an important raw material for the chemical industry, used on an enormous scale. Furthermore, existing information on chemical reaction mechanisms suggests that the photo-dissociation of water may be the most easily implemented of all the processes so far proposed for the accumulation of solar energy. Therefore we shall examine in detail the problems posed by the conversion of solar into chemical energy by this process.

IV. MAXIMUM THEORETICAL EFFICIENCY OF THE CONVERSION OF SOLAR INTO CHEMICAL ENERGY

The efficiency of the conversion of solar energy (η) is defined as the ratio of the amount of energy stored to the total amount of solar energy (E_0) falling on the converter. The latter quantity is equal to the product of the area of the system (S) and of the total flux of solar energy (i.e. of the flux of light quanta of all energies).

For thermal methods of solar energy conversion the efficiency is limited essentially by the use of the Carnot cycle for heating the working fluid in the first stage of the process, and by the conversion of heat into mechanical, electrical, or chemical energy in the later stages[23,60]. Other losses (such as incomplete absorption of radiation) are avoidable in principle to a large extent, and are being overcome as new technological improvements are introduced.

The photo-catalytic conversion of light energy also suffers losses of different types: incomplete absorption of the light by the system (or ineffective absorption by photochemically inactive parts of the system), partial recombination of the useful intermediates during the photochemical reaction, partial loss of energy (as heat) in overcoming activational barriers or in forming energy-consuming intermediates, etc. All these losses can be avoided to a large extent by improved photo-reactor design and by choosing a more effective cycle of chemical reactions.

However, the maximum theoretical efficiency of the photochemical conversion of solar into chemical energy is limited by a factor which is unavoidable in principle and is unrelated to the Carnot cycle: the same factor which sets a limit to the maximum theoretical efficiency of semiconductor p–n junction energy converters. This is the quantum character of the photochemical and photophysical changes[7,59,223].

The elementary endo-energetic photochemical processes all require the absorption of a quantum of light energy greater than some threshold value determined by the free energy ΔG of the process: $h\nu_{thr} = \Delta G$. The only exceptions are the multi-photon processes which take place in high-intensity light fluxes such as laser beams. The real threshold value $h\nu'_{thr}$ can be higher than $h\nu_{thr}$, since the activational barrier may have to be overcome in a system which does not absorb at the frequency ν_{thr}.

All the light quanta having an energy $< h\nu'_{thr}$ fail to induce the photochemical reaction and are wasted; on the other hand when quanta having an energy $> h\nu'_{thr}$ are absorbed only a fraction of their energy ($h\nu_{thr}$) is converted into chemical energy.

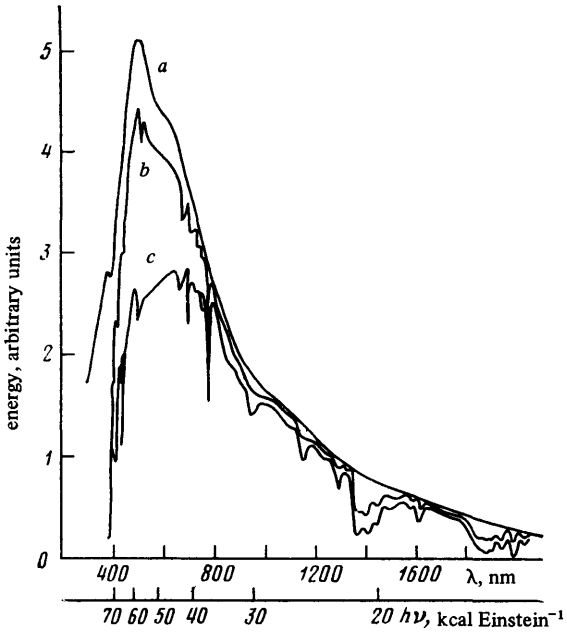


Figure 5. Spectral composition of solar radiation outside the atmosphere (*a*) and on the Earth's surface on a clear summer day at noon (*b*) and in the evening (c)[21].

Knowing the energy distribution function $\rho(\nu)$ of the quanta of solar energy (see Fig.5) we can easily calculate the maximum possible efficiency of a photochemical conversion for different assumed mechanisms. Thus in the simplest case of a one-quantum chemical reaction the stored useful energy E is equal to the product of the number N of acts of reaction (which under optimum conditions is given by the number of incident quanta with an energy $> h\nu'_{thr}$) and of ΔG or ΔH (depending on the final use of the stored energy) for a single act. For example, if the product is to be used in the production of electrical energy we can write $E = \Delta G \cdot N$, where $N = S\int_{\nu'_{thr}}^{\infty} \rho(\nu) d\nu$; furthermore $E_0 = S\int_0^{\infty} h\nu\rho(\nu) d\nu$, so that

$$\eta = \Delta G \int_{\nu'_{thr}}^{\infty} \rho(\nu)\, d\nu \Big/ \int_0^{\infty} h\nu\rho(\nu)\, d\nu.$$

The maximum efficiency theoretically achievable in the complete absence of losses#, i.e. for $h\nu'_{thr} = h\nu_{thr} = \Delta G$,[223] is

$$\eta = \Delta G \int_{\nu_{thr}}^{\infty} \rho(\nu) d\nu \Big/ \int_0^{\infty} h\nu\rho(\nu)\, d\nu = \nu_{thr} \int_{\nu_{thr}}^{\infty} \rho(\nu)\, d\nu \Big/ \int_0^{\infty} \nu\rho(\nu)\, d\nu. \quad (5)$$

According to the second law of thermodynamics we should decrease η by a factor of $\sim (T_0 - T)/T_0$, where $T_0 \cong 5800$ K is the Sun's temperature and T is the temperature of the absorber of quanta. However, this correction is unimportant in practice because $T_0 \gg T$.

Plots of the efficiency calculated by this formula against the threshold quantum energy for the $\rho(\nu)$ distributions which describe the solar spectrum outside the Earth's atmosphere and on the Earth's surface respectively are shown in Fig.6. These plots go through a maximum, where the efficiency reaches ~40% for photochemical processes with threshold energies corresponding to quanta in the red and near-i.r. regions. The existence of an optimum value of ν_{thr} indicates the interplay of two opposing tendencies as ν_{thr} increases: a decrease in the total number of quanta absorbed and an increase in the degree of utilisation of the energy of each of the quanta absorbed.

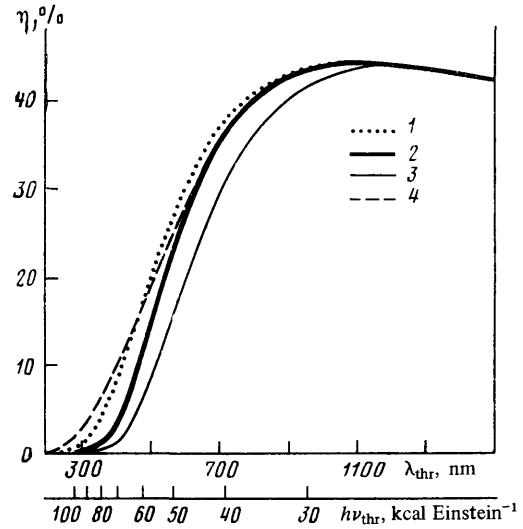


Figure 6. Maximum theoretical efficiency (η) of the one-quantum photochemical reaction against wave length of the threshold light quantum ($\lambda_{thr} = c/\nu_{thr}$) for solar radiation outside the Earth's atmosphere (*1*), on a clear summer day at noon (*2*) and in the evening (*3*), and for a perfect black body at 5800 K (*4*). Data on the solar spectrum taken from Refs.21 and 20.

In another possible situation (which exists, for example, during photosynthesis in plants) n quanta are needed for the chemical change, each quantum producing one particular active compound (the cation radicals of chlorophyll in the case of photosynthesis), and therefore we have

$$\eta = \Delta G \int_{\nu'_{thr}}^{\infty} \rho(\nu)\, d\nu / n \int_0^{\infty} h\nu\rho(\nu)\, d\nu, \quad (6)$$

where $h\nu'_{thr}$ is the threshold energy quantum for an individual photochemical reaction (for example, for the production of Chl^+), and ΔG is the energy stored as a result of the overall process [for example, as a result of reaction (4)].[7,224] In the optimum case $h\nu'_{thr} = h\nu_{thr} = \Delta G/n$, and formula (5) again applies. The following parameters apply to photosynthesis in plants (see Section II): $\Delta G \cong 120$ kcal mole^{-1} O_2, $n = 8$, $h\nu'_{thr} \cong 40$ kcal Einstein^{-1} (the red edge of the chlorophyll absorption band active in photosynthesis). Inserting into formula (6) these values together with the function $\rho(\nu)$

calculated from Fig.5*b* or 5*c* we arrive at $\eta \cong 15\%$ as the maximum efficiency of the photosynthesis process in plants. For the four-quantum ($n = 4$) dissociation of water discussed below ($\Delta G = 113.4$ kcal mole^{-1} O_2) the threshold quantum $h\nu_{thr} = \Delta G/4 = 28.4$ kcal Einstein^{-1} ($\lambda_{thr} = 1008$ nm) lies exactly at the maximum of the curve in Fig.6. This means that a maximum solar energy conversion efficiency of $\eta \cong 40\%$ could be achieved in the decomposition of water by a four-quantum mechanism.

The maximum conversion efficiency could be increased by using several endo-energetic reactions, with different ΔG, in the converter. In this case the photo-catalytic apparatus could be designed in such a way that quanta of low and of high energy are used in reactions with low and with high ΔG respectively. An analogous method of raising the efficiency has been proposed[225] for semiconductor photo-cells. However, there is a danger that chemical systems of this type will be so complex that their usefulness will suffer (as compared to that of the single endo-energetic process). Therefore an efficiency of $\eta \cong 30-40\%$ is perhaps the most realistic estimate which can be made at present.

Table 2. Standard electrode potentials of reactions involving water and its fragments in aqueous solutions.

No.	Reaction	E^0, V	ΔG^0_{298}, kcal mole^{-1}	Refs.
1	$e^-(aq) = e^-$	−2.7	62	227
2	$H^- = {}^1/_2H_2 + e^-$	−2.251	51.93	228
3	$H = H^+ + e^-$	−2.106	48.61	226
4	$H^- = H^+ + 2e^-$	−1.125	51.93	229
5	$2OH^- + H_2 = 2H_2O + 2e^-$	−0.828	19.1	226
6	$O_2^- = O_2 + e^-$	−0.32	7.4	226
7	$H\dot{O}_2 = O_2 + H^+ + e^-$	−0.13	3.0	228
8	$H_2 = 2H^+ + 2e^-$	0.000	0	226
9	$\dot{O}(g) + H_2O = O_2 + 2H^+ + 2e^-$	0.037	1.7	229
10	$HO_2^- = O_2 + H^+ + 2e^+$	0.338	15.6	229
11	$2OH^- = H_2O + {}^1/_2O_2 + 2e^-$	0.401	18.5	226
12	$H_2O_2 = O_2 + 2H^+ + 2e^-$	0.682	31.5	228
13	$\dot{O}H + H_2O = H_2O_2 + H^+ + e^-$	0.72	17	228
14	$2H_2O = O_2 + 4H^+ + 4e^-$	1.228	113.4	226
15	$O_2 + 2OH^- = O_3 + H_2O + 2e^-$	1.24	57.2	226
16	$H_2O_2 = H\dot{O}_2 + H^+ + e^-$	1.5	35	228
17	$3H_2O = O_3 + 6H^+ + 6e^-$	1.511	209.3	229
18	$OH^- + H_2O = HO_2^- + 2H^+ + 2e^-$	1.706	78.76	229
19	$2H_2O = H_2O_2 + 2H^+ + 2e^-$	1.776	81.72	229
20	$OH^- = \dot{O}H + e^-$	2.02	46.6	226
21	$O_2 + H_2O = O_3 + 2H^+ + 2e^-$	2.076	95.56	226
22	$H_2 = H + H^+ + e^-$	2.106	48.61	229
23	$H_2O = \dot{O}'(g)' + 2H^+ + 2e^-$	2.421	111.72	226
24	$H_2O = \dot{O}H + H^+ + e^-$	2.8	65	228

It is often suggested that the use of thermal processes in photochemical converters is irrational because of the low efficiency of the conversion of thermal into chemical energy. However, this shortcoming is compensated by the possibility of full conversion into heat of all the quanta contained in the Sun's light. As a result the overall losses may be lower than those encountered in quantum converters, in which we know that more than half of the energy can be lost. Evidently, photo-catalytic systems which exploit the advantages of the thermal and of the quantum conversion methods at the same time could be designed, thus overcoming their disadvantages to some extent. For example, a system could be designed in which the chemical equilibrium at various stages of the photo-catalytic process is shifted towards useful products by heating the system (or part of it) with photochemically inactive i.r. light. Several possible conversion systems with heating will be considered in the following Section.

V. THE PHOTO-CATALYTIC DECOMPOSITION OF WATER

1. Thermodynamics of the Water Decomposition Processes

The decomposition processes in the gaseous and the liquid phase are accompanied by the following changes in free energy and in enthalpy[226]:

$$H_2O(g) \rightarrow H_2(g) + {}^1/_2O_2(g);\ \Delta G^\circ_{298} = 54.6 \text{ kcal mole}^{-1},\ \Delta H^\circ_{298} = 57.8 \text{ kcal mole}^{-1};$$
$$H_2O(l) \rightarrow H_2(g) + {}^1/_2O_2(g);\ \Delta G^\circ_{298} = 56.7 \text{ kcal mole}^{-1},\ \Delta H^\circ_{298} = 68.3 \text{ kcal mole}^{-1}.$$

For the reaction involving the liquid phase ΔG decreases by ~ 3 kcal mole^{-1} when the temperature is increased from 25 to 100 °C.

The standard electrode potentials E^0 and the corresponding values of ΔG°_{298} for a number of one-electron and multi-electron reduction and oxidation processes involving water and its reaction products in aqueous solutions are listed in Table 2. We can see from the Table that from the electrochemical standpoint the decomposition of water into H_2 and O_2 is a four-electron process§ with a potential difference $\Delta E^0 = 1.23$ V and $\Delta G^0 = 113.4$ kcal mole^{-1} (obtained by combining reactions No.8 and No.14 of Table 2).

Most of the reactions in Table 2 involve the ions H^+ and OH^-. The electrode potentials of these reactions depend on the pH of the medium. The standard potentials listed in Table 2 correspond to pH = 0 for reactions involving H^+ and pH = 14 for reactions involving OH^-. At other pH values the E^0 values should be replaced by the formal oxidation–reduction potentials (ORP) E_m.[228]

Plots of E_m against pH for reactions No.14 and No.8 (evolution of oxygen and of hydrogen respectively) are shown in Fig.7.[229] Since the H^+ ions do not appear in the overall equation

$$H_2O \rightarrow H_2 + {}^1/_2O_2,$$

the difference between the E_m values for reactions No.14 and No.8 is independent of pH (1.23 V). Any oxidising agent with an E_m value lying above the "oxygen" line is thermodynamically able to evolve O_2 from water, and similarly any reducing agent with E_m below the "hydrogen" line can evolve H_2 from water[228–230].

As usual, removal of the reaction products assists the reaction: a rise in the "hydrogen" line and a fall in the "oxygen" line are clearly shown in Fig.7 in response to a decrease in the hydrogen and the oxygen pressure over the solution respectively.

§ The terms "one-electron" and "multi-electron" process are often used in a different context: they are applied to the number of electrons transferred through the electrical circuit in order to carry out the stated reaction by electrolysis. In papers on electron transfer reactions the same terms denote the number of electrons transferred in each elementary act. In this review we shall use the terms "one-electron" and "multi-electron processes (or reactions)" in the electrochemical sense, and the terms "one-electron" and "multi-electron mechanisms" with reference to the mechanism of the elementary act.

2. Requirements for Photo-catalysts for the Decomposition of Water by Visible Light

By comparing the above thermodynamic data with the photochemical properties of water and with the spectral characteristics of solar radiation we can formulate the most important requirements for photo-catalytic systems for the decomposition of water.

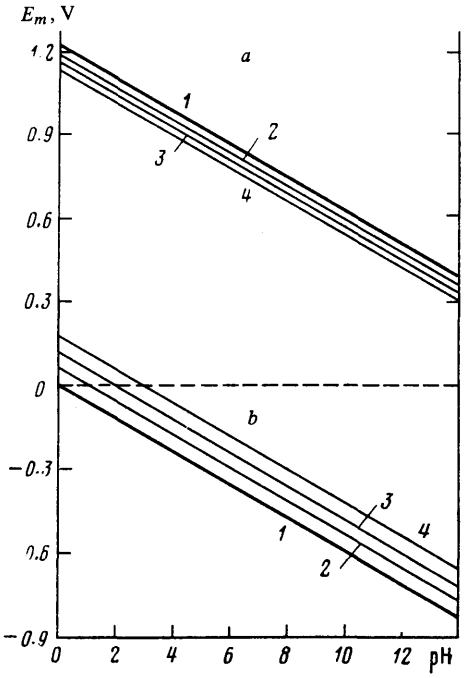


Figure 7. Formal ORP for the evolution of oxygen (*a*) and hydrogen (*b*) from water against the pH of the solution for different partial pressures of oxygen and hydrogen[229]: *1*) 1, *2*) 10^{-2}, *3*) 10^{-4}, *4*) 10^{-6} atm.

As Fig.5 shows, the solar spectrum at the Earth's surface contains practically no quanta corresponding to wave lengths < 300 nm, i.e. with an energy > 95 kcal Einstein^{-1}. At the same time the least endothermic of the possible monomolecular photo-dissociation processes

$$H_2O \rightarrow H_2 + O\ ,$$

requires an energy of 116 kcal mole^{-1} for a gas-phase reaction[222,231-233]. The lowest electronically excited state of water ($^3B_1$) is stated[234,235] to have an excitation energy $\geq$116 kcal mole^{-1}. This means that neither the direct nor the sensitised (by excited states) photolysis of water can be used for the conversion of solar into chemical energy. For the same reason it would be useless to try known heterogeneous photo-catalysts for the decomposition of water by hard u.v. radiation with λ < 250 nm (such as BeO and Al_2O_3[222,231,232]).

Thus the key element of any effective molecular system for the decomposition of water by solar radiation is the photo-catalyst: a dye K which can absorb the Sun's light without itself being decomposed by it and initiate a cycle of reactions in which water is reduced and oxidised. In natural photosynthesis the photo-catalyst is based on chlorophyll.

From the thermodynamic point of view any electronically excited K molecule (like chlorophyll, see Fig.3) can induce the photo-catalytic redox reaction

$$D + A \xrightarrow[K]{h\nu} D^+ + A^- \ . \qquad (7)$$

However, in practice these reactions take place only if the dye is excited into the "charge transfer bands"[202,236]. Hence the search for photo-catalysts should be confined to compounds which possess charge transfer bands in the visible region. This property is found in many organic dyes, though transition-metal compounds also seem promising in this respect. The latter compounds offer not only suitable absorption bands but also the ability to change their state of oxidation by several units, which should favour many-electron changes. Lastly, transition-metal compounds are able (in principle) to coordinate the Ḣ and ȮH free radicals formed by the one-electron reduction and oxidation of water. As will be shown below, this should lower the energy losses accompanying the photo-decomposition of water.

Since two molecules of H_2O have to be decomposed in order to produce one molecule of O_2 the total energy expenditure of a catalytic cycle cannot be less than 113.4 kcal mole^{-1}: in other words, the photo-catalytic decomposition of water cannot be a single-quantum process. A two-quantum process would need light of wave length < 504 nm (in the green region of the spectrum). As Fig.6 shows, the maximum efficiency at this wave length is less than the optimum by a factor of 2 or 3. The threshold wave length for a three-quantum process is 756 nm. Light of this wave length is found to offer the optimum conversion efficiency, but the decomposition of water involving fewer than four photons implies the simultaneous transfer of more than one electron under the influence of a single quantum. Until recently no such process had been reported, and therefore a serious discussion of three-quantum and two-quantum mechanisms for the decomposition of water would be inappropriate at present. However, there is no fundamental reason why one quantum should not induce the transfer of several electrons, and therefore we should continue to search for systems capable of reactions of this type[204].

The most rational process for the decomposition of water at present appears to be a four-quantum, sequential mechanism induced by red light, in which each light quantum is used to transfer one electron. As we have already pointed out, the threshold wave length for the decomposition of water in this case is $\lambda_{thr} = 1008$ nm, which corresponds to the optimum efficiency value. The fact that a non-optimum eight-quantum scheme is used in natural plant photosynthesis has been explained by the need to compensate for energy losses in long chains of redox reactions, or by evolutionary effects[192,237]. There is no reason to assume that an eight-quantum scheme is essential also in artificial photo-catalytic systems for the decomposition of water[1].

The energy ΔG stored by the photo-catalyst K for the absorption of one light quantum is equal to the difference in energy between the excited and the ground state of the photo-catalyst. However, the energy available for subsequent reactions is usually less than the energy of the light quantum because of the fast, spontaneous transition (conversion) of the K molecule from the primary excited state to some lower and longer-lived state, which then takes part in the chemical changes. The long life-times of these metastable excited states are due to the difference between their spin multiplicity and that of the ground state. These chemically active excited states are often luminescent, and therefore the energy stored by the photo-catalyst ($\Delta G = h\nu_1$) can

be determined by measuring the wave length ν_1 of the emitted light.

Knowing the formal redox potentials E_m for the ground state of the photo-catalyst, and the energies of its excited states, we can calculate the E_m values for the latter states. Obviously, in order to decompose water we must select a photo-catalyst whose excited states have E_m values consistent with the evolution of H_2 or O_2 from water. For example, in the case of isolated molecules of chlorophyll-*a* (Chl) we know[238] the formation potentials of the Chl^+ cation radical ($E^+ = +0.72$ V) and of the anion radical Chl^- ($E^- = -0.88$ V), and also the energies of the singlet (S) and of the triplet (T) excited state ($E_S = 1.86$ eV, $E_T = 1.26$ eV). The formal oxidation potential of the excited chlorophyll singlet state, i.e. the potential of the reaction

$$^{S}Chl + e^- \rightarrow Chl^{\div} ,$$

with respect to the normal hydrogen electrode, is $E_S^- = E^- + E_S = +0.98$ V, and the reduction potential of the same state, i.e. the potential of the reaction

$$^{S}Chl \rightarrow Chl^{+} + e^- ,$$

is $E_S^+ = E^+ - E_S = -1.14$ V. Similarly we find for the triplet state $E_T^- = +0.38$ V and $E_T^+ = -0.54$ V. These values agree exactly with direct electrochemical measurements of the potentials of the excited states of chlorophyll[238].

It follows from the relative values of E^+ and E^- that both the singlet and the triplet state of chlorophyll are potentially capable of reducing water with evolution of hydrogen, whereas only the singlet state (or the cation radical) can oxidise water with evolution of oxygen, at pH $\gtrsim$4 or 8 respectively (see Fig. 7).¶ The E_m value for the anion radical Chl^- obtained in the first reaction is sufficient in principle for the reduction of water, i.e. it is able to initiate the decomposition cycle.

We should note that many thermodynamically strong one-electron oxidising agents such as Ce^{4+}(aq), with $E^0(Ce^{4+}/Ce^{3+}) = 1.61$ V, cannot in practice cause oxidation of water because the reaction rate is very low. Their potential is probably not high enough to give a high enough rate to the first energetically unfavourable step. (This step is the one-electron oxidation of water to the $\dot{O}H$ free radical, which we shall discuss below in detail.) However, in the presence of catalysts (such as metallic platinum, or manganese or cobalt oxide) which allow the reaction to take place without formation of $\dot{O}H$ radicals in the free state the oxidation of water by Ce^{4+}(aq) is fairly fast[242].

3. Possible Mechanisms for the Decomposition of Water

The data listed in Table 2 allow us to compare the efficiencies of various theoretically possible mechanisms for the photo-catalytic decomposition of water. Thus we note that the reduction or oxidation of water by successive one-electron transfer reactions to give $\dot{H}$ or $\dot{O}H$ radicals in the free state require large (and unproductive) consumptions of energy, since in the subsequent reactions of these particles a significant fraction of their chemical energy is uselessly converted into heat. For example, the one-electron reaction

$$H_2O \rightarrow \dot{H} + \dot{O}H$$

(the difference between reactions No. 24 and No. 3) requires a heat input of 4.9 eV = 113 kcal mole^{-1}. At the same time the overall reaction

$$2H_2O \rightarrow 2H_2 + O_2$$

can store only 1.23 eV = 28.4 kcal mole^{-1} of energy for each transferred electron. In other words, ~75% of the chemical energy of the $\dot{H}$ and $\dot{O}H$ radicals is unavoidably converted into heat.

The effectiveness of the process may be increased in two ways: 1) by carrying out the reaction so that the $\dot{H}$ and $\dot{O}H$ particles are formed in a coordinated or adsorbed state as opposed to a free state, which lowers their energy of formation by an amount equal to the free energy of coordination (complex formation or adsorption), and 2) by avoiding the formation of $\dot{H}$ and $\dot{O}H$ particles through the use of multi-electron elementary acts. The possibility of two-electron transfer processes has been demonstrated[243,244], and even more complex, four-electron processes are believed[245,246] to be possible.

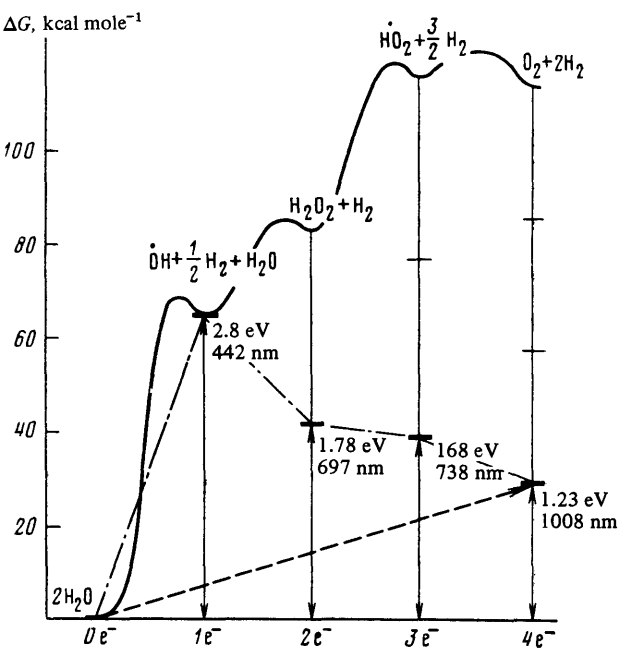


Figure 8. Energy profile of the decomposition of water to molecular hydrogen and the products of its one-, two-, three-, and four-electron oxidation. The numbers denote the energies and wave lengths of the threshold quanta for the transfer of one electron by the four-quantum mechanism of decomposition of water. The dot-and-dash line and the broken line show the changes in stored free energy (expressed for one transferred electron) attending the decomposition of water through the intermediate formation of $\dot{O}H$, H_2O_2, and $H\dot{O}_2$, and by its decomposition directly into H_2 and O_2 respectively.

As an illustration of the use of the data in Table 2 for estimating the effectiveness of various theoretically possible mechanisms of water decomposition we have shown in Fig. 8 an energy profile for conditions in which water is reduced

¶ According to the most recent views, the oxidation of water in natural photosynthesis occurs not on isolated molecules of chlorophyll-*a* but on associated groups of the dihydrated molecule $(Chl\text{-}a \cdot 2H_2O)_n$, with $n \geq 2$ and $E^+ = +0.92$ V[239-241].

directly to H_2 by a two-electron mechanism, and oxidised by sequential one-electron processes with formation of free $\dot{O}H$, H_2O_2, and $H\dot{O}_2$. It is evident from Fig. 8 that hydrogen peroxide (when formed through $\dot{O}H(ads)$ or by a two-electron mechanism) is a far more effective intermediate than the $\dot{O}H$ free radical. Over 70% of the stored chemical energy is retained when this intermediate decomposes with evolution of O_2. Active catalysts for the decomposition of hydrogen peroxide are well known[244]. The same approach can be used to estimate the effectiveness of other possible mechanisms.

We conclude from Table 2 and Fig. 8 that the most favourable energy profile is obtained if the water is decomposed directly into H_2 and O_2, without going through the intermediate formation of free $\dot{H}$, $\dot{O}H$, H_2O_2, HO_2, etc. The possibility of reducing water to H_2 (and of oxidising it to O_2) on the surface of heterogeneous catalysts while avoiding the formation of free $\dot{H}$ and $\dot{O}H$ particles follows directly from data on the electrolysis of water on metal electrodes. Thus at low current densities the overvoltage for the evolution of H_2 on a platinum cathode is of the order of 0.01 V, and the O_2 overvoltage of a cobalt anode is 0.2 V. These potentials are insufficient for the formation of $\dot{H}$ and $\dot{O}H$ in significant quantities.

It has recently been suggested[247,248] that the first step in the electrolytic reduction of water is the formation of adsorbed (as opposed to free) $\dot{H}$ particles:

$$H_3O^+ + e^- \rightleftarrows \dot{H}(ads) + H_2O ,$$

and that molecular hydrogen is formed directly from these particles by the reactions

$$2\dot{H}(ads) \rightleftarrows H_2\uparrow \text{ or } \dot{H}(ads) + H_3O^+ + e^- \rightleftarrows H_2\uparrow + H_2O .$$

The stronger the adsorption of atomic hydrogen on the electrode, the faster is the hydrogen evolution and the lower the overvoltage.

The first (and slowest) step in the oxidation of water on precious metal electrodes is thought to be[247]

$$OH^-(ads) \rightarrow \dot{O}H(ads) + e^- \text{ or } H_2O(ads) \rightarrow \dot{O}H(ads) + H^+ + e^- ,$$

This is followed by the fast step

$$2\dot{O}H(ads) \rightarrow \dot{O}(ads) + H_2O$$

or

$$\dot{O}H(ads) \rightarrow \dot{O}(ads) + H^+ + e^-$$

and finally

$$2\dot{O}(ads) \rightarrow O_2\uparrow .$$

On common metal electrodes the oxide film which covers the electrode can take part in the oxygen evolution process: for example,

$$MO + H_2O \rightarrow MO_2 + 2H^+ + 2e^-$$
$$2MO_2 \rightarrow 2MO + O_2\uparrow .$$

Thus the water electrolysis processes are essentially heterogeneous catalytic reactions taking place on the electrodes through the formation of adsorbed active particles. Effective heterogeneous catalytic systems for the conversion of electrical into chemical energy by the electrolysis of water are known, and therefore it should be possible in principle to develop similar systems for the conversion of solar energy.

4. Possible Organisation Schemes for the Photo-catalytic Process

Four different organisation schemes for the photo-catalytic decomposition of water can be suggested.

Scheme 1. The primary electron donor (or acceptor) for the excited state of the photo-catalyst is the water molecule itself, or its fragments OH^- and H^+, and the primary oxidation (or reduction) product goes into the solution, where it undergoes further reactions whilst the reduced (or oxidised) state of the photo-catalyst is potentially able to complete the water decomposition cycle in the dark, i.e. this species is a strong enough reducing (or oxidising) agent.

Scheme 2. Analogous to scheme 1 except that the oxidation (or reduction) product does not go into solution but remains coordinated (adsorbed) either on the photo-catalyst or on another compound until it takes part in further reactions.

Scheme 3. The primary photochemical reaction does not cause oxidation (or reduction) of water or its fragments, but it forms a strong oxidising agent and a strong reducing agent at the same time, which can decompose water in the dark.

All the three cases listed above imply a sequential four-quantum mechanism for the decomposition of water, and in every case the effectiveness of the process as a whole is determined by the effectiveness of the electrochemical charge separation process (to form a strong oxidising agent and a strong reducing agent), and of the evolution of hydrogen and of oxygen.

Scheme 4. In the initial step water is dissociated on the surface of a heterogeneous catalyst [for example, with formation of $\dot{H}(ads)$, $\dot{O}H(ads)$, or $\dot{O}(ads)$], or in the coordination sphere of a homogeneous catalyst. The light is used to cause recombination of the adsorbed (coordinated) intermediates with formation of H_2 and O_2 molecules and the photodesorption of these molecules.

Combinations of these schemes may be used in real water decomposition processes.

a) Photo-catalytic Decomposition of Water by Scheme 1

The main advantage of this scheme is its simplicity. Since one-electron oxidation or reduction of water is assumed even in the initial act of the photochemical reaction the use of a catalyst for the H_2 or O_2 evolution step becomes unnecessary, and the catalyst can consist (in principle) of a single component: the dye. The fast (and uncatalysed) recombination of the $\dot{O}H$ and $\dot{H}$ free radicals leads to evolution of O_2 or H_2, and the reduced or the oxidised form of the dye can be used to produce H_2 or O_2 if this is allowed by the redox potential. The need for stability of the dye in the presence of very reactive free radicals suggests that the most effective photo-catalysts will be found among inorganic compounds.

Data on the complexes and on the organic compounds which can evolve hydrogen (as H_2 or H) or oxygen as O_2 or $\dot{O}H$) from water under the influence of light are summarised in Tables 3 and 4. Unfortunately most of these materials are photochemically active only in the ultraviolet region of the spectrum. Photo-oxidation and photo-reduction processes in water have been reported also in the presence of inorganic anions (halide ions, S^{2-}, SO_4^{2-}, etc.)[202,249,278], but these too require energetic u.v. radiation. It is convenient to examine separately the formation of the oxidised (K^+) and of the reduced (K^-) form of the catalyst in the primary photochemical act (the oxidation and the reduction case).

Photo-oxidation in aqueous solutions with evolution of gaseous hydrogen is well known in aquo complexes of the transition metals in their lower states of oxidation (see Table 3).

The quantum yield of hydrogen in these reactions can be quite high: for example, a yield of 80% has been observed[255] for $Cu^+(aq)$. This suggests that both steps of the process have a high efficiency: the charge separation in the primary photochemical reaction and the evolution of H_2 in the subsequent dark reactions†. The effectiveness of charge separation is determined by the quantum yield of the formation of K^+ and $\dot{H}$ in the primary photochemical act:

$$K + H^+ \xrightarrow{h\nu} K^+ + \dot{H} ,$$

and by the relative rates of the different reactions which consume $\dot{H}$ particles:

$$\dot{H} + \dot{H} \rightarrow H_2\uparrow \quad (8)$$

$$K^+ + \dot{H} \rightarrow K + H^+ \quad (9)$$

$$4K^+ + 2H_2O \rightarrow 4K + O_2\uparrow + 4H^+ , \quad (10)$$

Table 3. Compounds which evolve hydrogen from aqueous solutions in the light.

Initial compound (K)	E_m (K/K+), V	Highest quantum yield of H_2, %* (λ of radiation, nm)	Red edge of charge transfer band**, nm	References
Co^{2+} (aq)	+1.82	>0***	220	202, 249, 250
Ce^{3+} (aq)	+1.61	0.14 (254)	350	202, 236, 249—254
Mn^{2+} (aq)	+1.51	>0***	225	99, 202, 249, 250
Fe^{2+} (aq)	+0.77	15 (254)	285	202, 236, 249, 250, 287
$Fe(CN)_6^{4-}$	+0.36	<66 (254)	300	249
Cu^+ (aq)	+0.15	80 (275)	>313	249, 250, 253—255
Ti^{3+} (aq)	+0.1	<1(290)	>290	253, 254
V^{2+} (aq)	−0.26	15 (313)	350	202, 249, 250, 253, 254
Ti^{2+} (aq)	−0.37	>0	330	249, 250
Cr^{2+} (aq)	−0.41	30 (254)	380	236, 249, 250, 253, 254
Eu^{2+} (aq)	−0.43	14 (365)	366	202, 249, 250, 253, 254, 256, 257
U^{3+} (aq)	−0.61	>0	400	202, 249, 250
Ni^{2+} (aq)	—	0***	220	202, 249, 250
$Mo_2(SO_4)_2^{4-}$	—	17 (254)	—	258, 259

* Depends on the nature of the counter-ion and on the pH of the medium.
** Depends on the nature of the counter-ion.
*** Only the photo-oxidation of K was reported.

The probability of formation of radicals from electronically excited states of molecules cannot yet be predicted theoretically. Therefore photo-catalysts offering a high quantum yield can be chosen only empirically at present.

As regards the relative rates of the subsequent reactions of the free radicals, that for scheme 1 should favour the formation of useful final products. For example, in the case of oxidation (which we are considering) the rate constant of reaction (8) ($\sim 10^{10}$ litre mole^{-1} s^{-1})[279] is usually not less than, and often significantly greater than, the rate constant of reaction (9),[227] and the H radicals formed under the influence of light will be evolved from the solution as gaseous hydrogen in high yield and without the need for a catalyst as long as accumulation of the oxidised form of the dye (K^+) is avoided.

† We should note that direct experimental proof of the formation of $\dot{H}$ (or $\dot{O}H$) free radicals is not available for all the systems listed in Tables 3 and 4. Hence (in some cases at least) the reaction may follow scheme 2 rather than scheme 1.

In the photo-catalytic decomposition of water under static conditions accumulation of K^+ is unavoidable, because of the slowness of reaction (10), even if an active catalyst is used to accelerate the multi-electron process. Therefore the practical realisation of scheme 1 implies the use of flow conditions, arranged so that the evolution of O_2 (or H_2) in the light and the complementary evolution of H_2 (or O_2) in the dark take place in different parts of the apparatus [for example, by pumping the solution enriched in the K^+ (or K^-) form through a reactor containing a catalyst for the evolution of O_2 (or H_2)].

Table 4. Compounds which evolve oxygen (or $\dot{O}H$) from aqueous solutions in the light.

Initial compound (K)	E_m (K−/K), V	Highest quantum yield of O_2 (or $\dot{O}H$), %* (λ of radiation, nm)	Red edge of charge transfer band**, nm	Refs.
Ce^{4+} (aq)	+1.61	36 (254)	400	202, 236, 252
Mn^{3+} (aq)	+1.51	>0 (400)	470	261
Fe (bipy)$_3^{3+}$	+1.1	0.8 (365)	700	236, 260
Fe (phen)$_3^{3+}$	+1.1	1 (365)	700	236, 260
Ag^+ (aq)	+0.799	3.2 (254)	260	262
Fe^{3+} (aq)	+0.77	19 (313)	365	202, 236, 248, 250, 263—265
$Mo(CN)_8^{3-}$	+0.73	>10 (365)	—	236, 260
$W(CN)_8^{3-}$	+0.457	>10 (366)	—	236
UO_2^{2+}	+0.05	>0	—	268, 269
Pb^{2+} (aq)	—	>0	320	262
V^{3+} (aq)	−0.255	>0***	—	270—273
Eu^{3+} (aq)	−0.43	>0 (190)	—	257, 274
Methyl Viologen (MV^{2+})	−0.44	1 (254)	—	275, 276
U^{4+} (aq)	−0.61	>0	300	202, 236
Quinones	+0.4÷+0.8	>10 (313)	—	266, 267
1,10-phenanthroline (phen)	—	0.01 (300)	—	277

* Depends on the nature of the counter-ion and on the pH of the medium.
** Depends on the nature of the counter-ion.
*** Only the photo-reduction of K was reported.

Of the systems listed in Table 3 the following aquo-complexes have a redox potential E_m high enough to complete the water decomposition cycle: Ce^{4+}(aq), Co^{3+}(aq), and Mn^{3+}(aq), the oxidised forms of Ce^{3+}(aq), Co^{2+}(aq), and Mn^{2+}(aq). For the Ce^3(aq)−Ce^{4+}(aq) system the photo-catalytic decomposition of water was observed and fully investigated[251,252] in the 1950's. It was shown that water is decomposed under the influence of u.v. light and in low yield, but we should note that the low quantum yield may have been due to the failure to use flow conditions in those experiments.

Methods of completing the cycle have been suggested even for systems in which the oxidised form K^+ is thermodynamically unable to evolve oxygen from water under normal conditions (for example, for the Cu^+(aq)−Cu^{2+}(aq) system[254]). Thus the E_m value of the K/K^+ couple can be increased by changing the temperature in the dark part of the apparatus. For aquo-complexes, say, the large (up to 20–40 e.u.) difference in entropy between the oxidised and the original form causes a shift in the equilibrium towards the evolution of oxygen upon heating.

In principle the oxidation photo-catalyst could also be a compound which yields a hydrated electron under illumination, since in acid solutions this species is immediately converted into the $\dot{H}$ radical[236,249,260,280]:

$$H_3O^+ + e^-(aq) \rightarrow \dot{H} + H_2O .$$

However, because of the large reduction potential ($E^0 = -2.7$ V), the energy losses in processes involving $e^-(aq)$ can be expected to be even greater than those of processes involving radicals. There is a report[281] of the production of hydrated electrons by green light (as opposed to u.v. light) in micellar heterophase systems. Of course, under these conditions the ORP of K^+ is not high enough to evolve O_2 from water, but it may be high enough in a photo-excited state of K^+. Thus the scheme could be realised in practice only for the decomposition of water by an eight-quantum mechanism.

Photo-reduction (the evolution of oxygen or ȮH radicals by light) has been observed in aqueous solutions of some transition-metal complexes in a higher state of oxidation as well as in some organic compounds (see Table 4). In this case the evolution of oxygen is the fast step as a result of the high chemical activity of the ȮH radicals[279]:

$$2\dot{O}H \rightarrow H_2O_2,\ 2H_2O_2 \rightarrow 2H_2O + O_2\uparrow .$$

As regards completing the cycle of the water decomposition process the most promising systems are UO_2^{2+}–UO_2^+, $U^{4+}(aq)$–$U^{3+}(aq)$, and MV^{2+}–$M\dot{V}^+$, according to the E_m values in Table 4, but the photo-catalytic decomposition of water has not so far been observed in these systems (though ȮH radicals have been detected in the UO_2^{2+} and MV^{2+} systems).

It is generally thought that the generation of free radicals in an aqueous solution must necessarily imply the use of u.v. radiation, with a disastrous effect on the efficiency of the solar energy conversion. In fact, the ȮH radical can be formed in an acid solution (pH = 0) at room temperature and for a zero value of E_m of the K/K^- couple by a quantum of $\lambda = 442$ nm (blue light), with an efficiency of $\eta \cong 5\%$, and furthermore the same radical can be formed in an alkaline solution (pH = 14) by a quantum of $\lambda = 612$ nm (orange light) with a very adequate conversion efficiency ($\eta \cong 20\%$, see Fig.6). Of course, in order to complete the cycle of water decomposition reactions in this solution at room temperature we have to use light with $\lambda \leq 442$ nm, since a reducing agent with $E_m < -0.828$ V is needed for the evolution of hydrogen in alkaline solutions.

The formation of Ḣ in acid solution (pH = 0) is also possible in light of reasonably long wave length ($\lambda = 558$ nm), but it is again impossible to complete the cycle at constant temperature without using u.v. light, because an oxidising agent with $E_m > +1.23$ V has to be generated in addition to the Ḣ radicals, and light with $\lambda = 371$ nm is required for this.

Nevertheless the decomposition of water by this mechanism under the influence of light of reasonably long wave length is possible in principle if the H_2 and O_2 evolution steps are separated. This can be attempted in two ways: by arranging for the H_2 and O_2 evolutions to occur at different pH, or at the same pH but different temperatures. The latter approach is the more attractive because it does not require unrecoverable additions of acids and alkalis. The rise in temperature of the solution needed to shift the equilibrium in the required direction could be obtained by exploiting the photochemically inactive long-wave quanta of the solar spectrum, thus raising the efficiency of the overall conversion. We also note that the lower energy losses expected from the relative simplicity of scheme 1 should compensate (at least partially) for the loss in efficiency associated with the irreversible conversion into heat of some of the energy of the Ḣ and ȮH radicals.

Thus the main problem to be overcome before scheme 1 can be used in practice is to find photochemically active dyes with charge transfer bands at sufficiently long wave lengths. All the compounds examined so far, listed in Tables 3 and 4, have this band in the u.v. region of the spectrum. It may be necessary to sensitise the evolution of H_2 and O_2 by adding to the solution an auxiliary dye which absorbs strongly in the visible region and can transfer this absorbed radiant energy to the chemically active excited levels of the photo-catalyst.

b) Photo-catalytic Decomposition of Water by Scheme 2

As we have already pointed out, the effectiveness of the utilisation of the solar spectrum could be substantially increased by arranging for the Ḣ and ȮH radicals produced in the primary photochemical act to be in the coordinated or adsorbed state (as opposed to the free state). The absence of free radicals would also make it easier to use organic photo-catalysts (as compared with scheme 1).

Complexes of the active intermediates of the decomposition of water with transition-metal compounds in excited states have recently been detected experimentally. These include hydroxylated chromium(III) complexes in an electronically excited state[282] and protonated complexes of the aquo uranyl ion (UO_2H^{2+}),[283,284] bipyridyl ruthenium(II) complexes[285,286], and binuclear molybdenum complexes[259].

Kinetic data on the photochemical evolution of hydrogen from acid aqueous solutions of the aquo complexes $Eu^{2+}(aq)$[253–255] are consistent with the hypothesis that the active role in this process is played by complexes of the metal with free radicals:

$$\begin{gathered} Eu^{2+}(aq) + H_2O \xrightarrow{h\nu} [EuOH \cdot H]^{2+} \\ [EuOH \cdot OH]^{2+} + H^+ + Eu^{2+}(aq) \rightarrow EuOH^{2+} + Eu^{3+}(aq) + H_2\uparrow . \end{gathered} \qquad (11)$$

A similar scheme applies to the photochemical evolution of hydrogen from acid solutions of the $Fe^{2+}(aq)$ aquo complex[287]. Detailed studies of acidity changes in organic dyes during electronic excitation are also in progress[277,288–290].

Existing experimental data are insufficient for a meaningful discussion of the application of scheme 2 to homogeneous reactions. We shall only point out that hydrogen evolution from a protonated excited state

$$K^* + H^+ \rightarrow KH^+$$

requires the collision of these protonated forms either in pairs

$$2KH^+ \rightarrow 2K^+ + H_2\uparrow$$

or with a strong reducing agent [e.g. as in reaction (11)], or alternatively it requires further protonation in a secondary excitation:

$$KH^+ + H^+ \xrightarrow{h\nu} KH_2^{3+} \rightarrow K^{3+} + H_2\uparrow .$$

In the first case the effectiveness of the process may be raised by adding a dehydrogenation catalyst, and in the second by choosing a compound in which the protonated excited forms are long-lived.

The most promising media for the realisation of scheme 2 may be heterogeneous systems, especially supported catalysts and zeolites containing adsorbed, attached, or interstitial dye molecules (organic or inorganic). The affinity of Ḣ and ȮH radicals for adsorption on these heterogeneous surfaces should favour the charge separation in the primary photochemical act and the subsequent recombination of the adsorbed radicals with evolution of H_2 and O_2 (as in catalytic electrodes during electrolysis).

The formation of ȮH radicals in the adsorbed state during irradiation with visible or near-u.v. light has been observed in suspensions of ZnO, TiO_2, and V_2O_5 in water[118,291], and in Aerosil containing adsorbed Methyl Viologen bi-cations[276]. Hydrogen evolution by illumination of freshly precipitated iron(II) hydroxide has also been reported[292], but the mechanism of this process was not studied in detail.

Some recent papers describe the decomposition of water under the influence of solar radiation in the presence of silver-substituted type Y and A zeolites[208,293,294]. The following reaction is assumed to take place with a high quantum yield:

$$2Ag^+ + 2ZO^- + H_2O \xrightarrow{h\nu} 2Ag^0 + 2ZOH + {}^1/_2O_2\uparrow .$$

The water decomposition cycle is completed in the dark by heating the system to 600 °C. Clusters are thought to be formed in the zeolite under these conditions, and these clusters are assumed to have an enhanced reducing power:

$$2Ag_n^0 + 2n\ ZOH \xrightarrow{T} 2n\ Ag^+ + 2nZO^- + n\,H_2\uparrow .$$

The main advantage of this type of scheme is the ease with which the final products (H_2 and O_2) can be separated. Furthermore these catalysts can be operated over a much wider range of temperature than homogeneous catalysts.

By replacing the silver by a metal with a greater reducing power in its lower state of oxidation it may be possible to avoid the need for a high temperature during the dark step. Auxiliary dyes may also be added to the zeolite to improve the sensitivity to long-wavelength light.

Another possibility is the photo-catalytic decomposition of water on metal-containing zeolites without the participation of electronically excited states. As in aqueous solutions, the entropy of interstitial transition-metal ions in zeolites is very sensitive to the degree of oxidation of the ions. Therefore a change in temperature will strongly affect the redox properties of the ions, and this should allow the decomposition of water by cyclic changes in the temperature of the catalyst (for example, using concentrated solar radiation). There is evidence[295] that such a cyclic process would be thermodynamically possible in zeolites containing Cr^{3+}, In^{3+}, or Cu^{2+} ions.

Table 5. Systems which evolve hydrogen by scheme 3.

No.	Dye (K)	Acceptor (A)	Donor (D)	Catalyst	Refs.
1	Proflavin; Acridine Orange	MV^{2+}	ethylenediamine-tetra-acetic acid (EDTA)	hydrogenase	296
2	Methylene Blue, acridine	cytochrome → acridine → MV^{2+}*	Fe^{2+}(aq), allyl-thiourea, isopropanol, ethanol, toluene, ascorbic acid, EDTA	not stated	297
3	Acridine Yellow, tripaflavin	salicylato complexes of V(III) and Eu(III)	cysteine, triethanol-amine, EDTA, H_2S	PtO_2, colloidal Pt	298
4	Acridine Yellow	MV^{2+}	EDTA	Pt	298
5	Benzophenone	V^{3+}(aq), Cr^{3+}(aq), Eu^{3+}(aq)	ethanol, isopropanol	PtO_2	299
6	Immobilised chloroplast	MV^{2+}	glycerol, H_2O	hydrogenase, metallic Pt	224
7	Immobilised chloroplast	immobilised ferredoxin	H_2O	hydrogenase	300
8	$Ru(bipy)_3^{2+}$	MV^{2+}	EDTA	hydrogenase	296
9	$Ru(bipy)_3^{2+}$	$Rh(bipy)_2Cl_2^+$	triethanolamine	collodial Pt	301

* A chain of acceptor was used.
** The scheme proposed for completing the cycle involves O_2 evolution by heating the system with Fe^{3+} to 50–350 °C.

In principle scheme 2 can offer the maximum efficiency for the conversion of solar energy. Therefore further work on these problems is of the utmost importance.

c) Photo-catalytic Decomposition of Water by Scheme 3

In spite of the simplicity of schemes 1 and 2, most of the research now in progress is devoted to scheme 3, in which the primary photochemical act does not decompose the water but produces strong one-electron oxidising (D^+) and reducing agents (A^-) simultaneously, able to evolve oxygen and hydrogen from water in the absence of light. The interest in this scheme is not fortuitous: it stems from its similarity to natural photosynthesis.

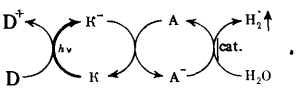
The main difficulty in the practical implementation of scheme 3 is that the complex multi-electron processes leading to the evolution of oxygen and hydrogen from water by the D^+ and A^- species have to compete with the recombination of D^+ and A^-. Therefore the reduction to practice of scheme 3 is possible only if an adequate method of charge separation is available.

Many photo-catalytic systems able to evolve hydrogen from water with a good quantum yield are known (see Table 5). However, in every case the electron donor is not water but a special reducing agent which is consumed irreversibly. Photo-catalytic systems for the evolution of oxygen from water have also been described: chlorophyll and coproporphyrin of iron(III) adsorbed at an octane–water interface[302] or on a vesicle membrane[303]. But in this case the electron acceptor is not water but $Fe(CN)_6^{3-}$, which is again consumed irreversibly. Thus it has not yet been possible to complete the water decomposition cycle without using structures of biological origin#.

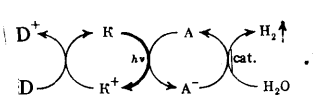
All the systems listed in Table 5 attempt to model the photosynthetic system of bacteria and the "photo-system I" of plant photosynthesis, which synthesises reduced forms of carbon from CO_2 by using good electron donors[189–192].

We note that in system No. 3 of Table 5 (as in the photosynthesis of sulphur bacteria) the electron donor is hydrogen sulphide (an analogue of water, but with more marked reducing properties), which can be oxidised fully by the transfer of only two (as opposed to four) electrons.

The choice of an appropriate photo-catalyst is of the utmost importance for the decomposition of water by scheme 3. Thus, in systems Nos. 1–5 of Table 5 (using benzophenone and organic dyes of the xanthene, acridine, and fluorescein type as the photo-catalyst, i.e. compounds with a fairly high oxidation potential in their initial state) the reaction takes place by the "reduction mechanism"§



However, even the excited form of the photo-catalyst could not bring about the oxidation of water. In systems Nos. 6–9 of Table 5 [for which the photo-catalysts are chloroplasts immobilised in micelles, or the *tris*-bipyridyl complex of ruthenium(II)] the reaction took place by the "oxidation mechanism":



A complete water decomposition cycle has been reported[304] for monolayers of the surface-active bipyridyl complex of ruthenium(II), but many attempts at repeating the experiment have proved unsuccessful[305–310].

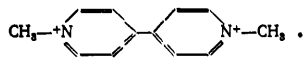
§ The double arrow denotes the instant when radiant energy is stored.

The range of compounds potentially suitable as photo-catalysts for the decomposition of water by scheme 3 is still very narrow. It includes chlorophyll and its nearest analogues, and also bipyridyl (and similar) complexes of ruthenium(II)[311-341], osmium(II)[311,312,320,342,343], and probably also iron(II)[344-347] and chromium(III)[330,348]. Thus the field is wide open for further research.

There are qualitative reports of the production of the very strong oxidising agents Co^{3+}(aq), Mn^{3+}(aq), Ce^{4+}(aq), and Ag^{2+}(aq) by the excited state of uranyl[349-351], and of the reduction of Zn^{2+}(aq) to Zn^0 by the excited state of Mn^{2+}(aq), which becomes oxidised to MnO_2.[352] If a charge separation process with an acceptable quantum yield were available these systems could be of interest as components of the photo-catalytic system.

Special mention is due of the *tris*-bipyridyl complexes of ruthenium, which are not decomposed under the action of light, are not hydrolysed, and offer a unique set of redox properties in their ground and their triplet excited state: as a result, they can take part in both the "oxidation" and the "reduction" mechanism of decomposition of water in solutions of practically any acidity. For the *tris*-bipyridyl complex of ruthenium(II) the following energy levels have been reported[333]: $E^- = -1.3$, $E^+ = +1.3$, $E_T^+ = +0.8$, and $E_T^- = -0.8$ V. The evolution of oxygen from water in the dark by the oxidised states of these[353] and of the corresponding iron complexes[354-358] is well characterised.

Fairly rigid limits are imposed on the intermediate donor D and acceptor A. For example, the E_m value of the acceptor must lie below the "hydrogen" line of Fig.7, but it must also be higher than the E_m value of the K^-/K couple (for the "reduction mechanism") or of the K/K^+ couple (for the "oxidation mechanism"). In the systems listed in Table 5 the intermediate acceptors which satisfy this condition are V(III) and Eu(III) complexes [for example, V^{3+}(aq) and Eu^{3+}(aq)], and also the bipyridyl complex of rhodium(III) and the organic bi-cation[359] Methyl Viologen (MV^{2+})



Reduced forms of all these acceptors in the presence of a catalyst can evolve hydrogen from water at the appropriate pH. Intermediate donors D for the oxidation of water are still unknown.

Let us consider possible ways of increasing the efficiency of charge separation in the primary photochemical reaction. The effective charge separation in natural chloroplasts (systems Nos.6 and 7 of Table 5) is evidently the result of their rigid structure. The molecules of chlorophyll and of the primary electron acceptor (still not definitely identified) are separated by a significant distance (>13 Å) in the chloroplast membranes[360]. Fast charge separation in this system (the process $Chl^* + A \rightarrow Chl^+ + A^-$) can only occur by a tunnel mechanism[360,361]. The reverse process (the tunnelling transfer of an electron from A^- to Chl^+) is much slower[360]. This may be due to the rapid conversion into heat of part of the energy stored in the Chl^+ and A^- particles (since changes in the energy of the system can disturb the conditions favourable to tunnelling transitions[361-363]), or alternatively it may be due to rapid conformational changes in the membrane produced by the forward reaction, which can increase the distance between the reactants[360,362,363].

By analogy with natural photosynthesis we can expect that a spatial separation of the photo-catalyst from the primary acceptor by ~10–20 Å (on a solid carrier surface, in a lipid membrane, or in a micellar solution) will improve the efficiency of charge separation in artificial systems also. Stabilisation of the charge separation by the "tunnel" principle can be attempted also in a homogeneous solution, for example by using rigid molecules within which charge transfer can occur (from one fragment to another) under the influence of light[364-381]. After charge separation of this type the molecule can behave bifunctionally, i.e. both as an oxidising agent and as a reducing agent.

It has been found experimentally that charge separation is assisted by fast chemical changes (for example, protonation or deprotonation) of the D^+, A^-, K^+, or K^- species. Thus fast protonation of the reduced form of the dye in reactions Nos.1–5 of Table 5 is the most probable explanation of the substantial decrease in the recombination rates of D^+ and K^-; furthermore, protonation leading to the formation of hydride complexes of rhodium may occur also in system No.9 of Table 5.

Effective chemical stabilisation of the separated charges by deprotonation of the phenothiazine cation radical has been observed[382] as a result of the interaction with the *tris*-bipyridyl complex of ruthenium(II) in an excited state.

Since chemical stabilisation requires a stabilisation rate greater than the recombination rate the only likely candidates are the fast stabilisation processes involving unimolecular decomposition, conformational transitions, or interactions with substances present in very high concentration (e.g. the solvent).

Stabilisation mechanisms other than the tunnel mechanism and the chemical mechanism discussed above may be considered. One of these consists in precipitating as a solid phase (or extracting from the aqueous solution) the product of the primary photochemical act (e.g. A^-). Thus the elemental sulphur produced by the oxidation of hydrogen sulphide in system No.3 of Table 5 is precipitated into a solid phase. Precipitation as a hydroxide may also be effective: for example, by varying the state of oxidation of metal aquo ion used in the cycle. Stabilisation of the separated charges by extraction was demonstrated in the 1960's for a system consisting of thionine (an organic dye) and the iron(II) aquo ion[383]: the same stabilisation mechanism was later applied to the thionine–thallium(I) aquo ion system[384].

However, phase transformations and extraction are relatively slow processes. Hence we may assume that an initial stabilisation is provided by chemical effects in every case (reconstruction of the solvation shells, dimerisation, etc.), followed at a later stage by the phase transformation.

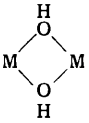
Yet another stabilisation method depends on using an electric field for charge separation, as in the semiconductor energy converters. In liquids, very high electric field gradients are easily obtained at the surface of colloidal particles (for example, the micelles of ionogenic surface-active particles, knots of polymer chains containing ions, etc.)[385,386]; high electric field gradients can exist also in zeolite holes[387]. Thus if singly charged cations are used as the initial forms of the photo-catalyst and of the electron acceptor, and if these cations are adsorbed on the surface of anionic micelles in the form of a Stern layer[385], the doubly charged cation of the photo-catalyst formed by the transfer of an electron under the influence of light will be adsorbed even more strongly in the Stern layer whereas the uncharged form of the acceptor will pass into the bulk of the solution. In this way charge stabilisation may be obtained as a result of the increase in the rate of reaction of the excited photo-catalyst with the acceptor produced by the increased local concentrations resulting from adsorption on the micelle (micellar catalysis)[388,389], combined with the decrease in the rate of recombination of the reaction products. This stabilisation mechanism was studied for a reaction in aqueous solutions containing an anionic surface-active compound or an ion-containing polymer[334,335]:

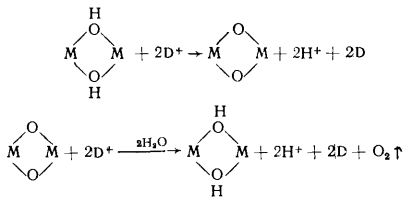
$$Ru(bipy)_3^{2+} + Cu^{2+}(aq) \xrightarrow{h\nu} Ru(bipy)_3^{3+} + Cu^{+}(aq) \cdot$$

No fundamental difficulties can be foreseen in the evolution of hydrogen from a solution containing a strong one-electron reducing agent. Effective catalysts for this process are known: for example, finely divided or colloidal platinum, or the enzymes nitrogenase and hydrogenase (see Table 5). Of course, the main problem is to choose the most effective and stable catalyst for the specific experimental conditions.

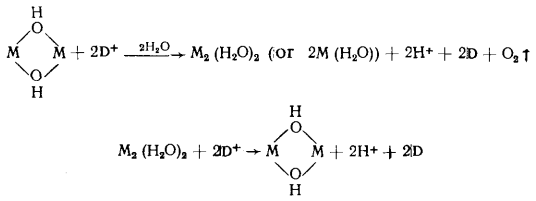
More serious difficulties are found in the oxygen evolution step. In the absence of a catalyst this step proceeds very slowly if at all, even if very strong oxidising agents such as $Ce^{4+}(aq)$ or PbO_2 are present. On metallic catalysts (such as platinum) the reaction takes place only if the oxidation potential is raised well above the thermodynamic minimum value[242]: this is true even in the presence of an oxidising agent as strong as $Ru(bipy)_3^{3+}$. Heterogeneous catalysts of the PtO_2, IrO_2, and RuO_2 type are also not very effective towards the oxidation of water by Ce^{4+} and $Ru(bipy)_3^{3+}$ ions: in this case quantitative evolution of oxygen in acid solutions is observed only after several hours[390,391].

There are reports that the O_2 evolution catalyst in plant photosynthesis systems includes polynuclear manganese and copper complexes[1,13,392], but neither their composition nor their structure has yet been determined. Homogeneous O_2 evolution catalysts were unknown until quite recently. Thus the development of catalysts for the evolution of oxygen from water under mild conditions is the most difficult of the problems which must be solved before photo-catalytic converters relying on scheme 3 can be used in practice.

The writers have recently developed effective homogeneous catalysts for the evolution of oxygen from water by one-electron oxidising agents (D^+) of the $Ru(bipy)_3^{3+}$ type[393]. The mechanism of the action of these catalysts is still being investigated, but there is evidence of a catalytically active intermediate with the binuclear μ-dihydroxo  structure (where M is a metal atom), so that the evolution of oxygen and the regeneration of the intermediate occur by successive one-electron oxidations. For example, the catalytic action of partially hydrolysed bipyridyl complexes of iron(III)[296] could be described by one of the following schemes:



or



so that the overall equation is

$$4D^+ + 2H_2O \xrightarrow{cat} 4H^+ + 4D + O_2\uparrow$$

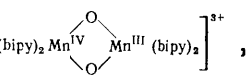
[where M = Fe(III), and $D^+ = Ru(bipy)_3^{3+}$, $Fe(bipy)_3^{3+}$, or $Fe(phen)_3^{3+}$].

We have also observed[393] catalytic effects in some compounds of Co(II) (see also Ref. 394), Cu(II), Ni(II), Mn(II), Ir(III), and Ru(III). Especially interesting catalytic effects were found[393] in the water-soluble cobalt(II) phthalocyanines: we should note that the cobalt(II) and iron(III) phthalocyanines are now considered to be the most effective catalysts for the cathodic (electrolytic) reduction of oxygen in aqueous solutions (i.e. for the reverse of the oxygen evolution reaction)[395].

The evolution of oxygen from water should be favoured by alkaline conditions (see Fig. 7), and therefore the search for photo-catalytic systems operating in alkaline solutions is of interest. Data on the photochemical oxidation of water by iron[292,263,265] or cerium[252] hydroxides are relevant in this context. We note that the ability of hydroxo complexes to form polynuclear structures may be an important factor in the development of multi-electron processes for the decomposition of water.

The mechanism of oxygen evolution from water by oxidising agents (such as MnO_4^- [358,396,397]) stronger than $Ru(bipy)_3^{3+}$ is currently being studied, and so is the mechanism of the electro-catalytic oxidation of water[394,398].

The work on the intermediate steps of the decomposition of water has generated a great deal of interest in the photochemical reduction of binuclear complexes of the type of[56,204,399,400]



as well as in the light-induced generation of hydrogen from solutions of hydride complexes such as[204,401–403]

$$\text{iso-Co(phen)}(PR_3)_2H_2^+ \xrightarrow{h\nu} \text{Co(phen)}(PR_3)_2^+ + H_2\uparrow$$

$$2HIr(PF_3)_4 \xrightarrow{h\nu} (PF_3)_4Ir{-}Ir(PF_3)_4 + H_2\uparrow$$

$$[Rh_2(AA)_4H]Cl^{2+} + H^+(aq) + Cl^- \xrightarrow{h\nu} [Rh_2(AA)_4Cl_2]^{2+} + H_2\uparrow$$

$$[Mo(\eta^5\text{-}C_5H_5)_2H_2] \xrightarrow{h\nu} [Mo(\eta^5\text{-}C_5H_5)_2] + H_2\uparrow$$

(where phen = 1,10-o-phenanthroline, and AA = 1,3-diisocyanopropane), and also in the reaction[258,259]

$$Mo_2(SO_4)_2^{4-} + H^+(aq) \xrightarrow{h\nu} Mo_2(SO_4)_2^{3-} + {}^1/_2H_2\uparrow.$$

The binuclear complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ has also been found[404] to evolve hydrogen from potential donors under the influence of light.

The semiconductor photo-catalysts discussed in Section II (e.g. TiO_2) can also be classified with the converters operating by scheme 3.

The main distinguishing feature of semiconductor converters (as opposed to molecular converters) is the primary charge separation by electronic transitions between the collective levels (bands) of the solid under the influence of light, as opposed to transition between levels in individual molecules. With this exception, however, the mode of action of semiconductor converters is not very different from that of molecular converters. Thus the electron and the hole formed by the charge separation in semiconductors contribute to the decomposition of water in exactly the same way as the A^- and D^+ particles formed in molecular systems.

The spatial separation of the electron and hole is assisted by the internal electric field in the surface layer of the semiconductor (i.e. in the region where the light is absorbed). As was stated above, separation of the A^- and D^+ particles by an electric field is one method of stabilisation in molecular converters. The electrons and holes which have failed to recombine diffuse to the electrode surface where (as in molecular systems) they can take part in catalytic reactions leading to the reduction of water with hydrogen evolution

(in the case of the electron) or to the oxidation of water with oxygen evolution (in the case of the hole).

The main shortcomings of the present semiconductor photo-catalysts (see Section II) are their low photosensitivity in the visible region, and also inadequate charge separation in the surface field and low catalytic activity towards the later steps (oxygen and hydrogen evolution). In order to suppress the recombination of electrons and holes, and to impose on them an oxidation–reduction potential sufficient to decompose water at an acceptable rate, additional potentials must be applied from an external voltage source to the semiconductors in existing systems.

These shortcomings may be overcome by the use of semiconductors with a narrower (1–1.5 eV) energy gap and by doping their surface layer (see Section II). The addition of electron donor or acceptor species to the surface layer may generate stronger electric fields and thus allow effective charge separation without resorting to an external source of potential. Sensitisation by adsorbed or "grafted" dye molecules could produce sensitivity to visible light even in wide-gap semiconductors. Lastly, it may be possible to raise the catalytic activity of the semiconductor surface towards hydrogen and oxygen evolution by doping it with suitable impurities.

Thus there is no fundamental difference between the mechanisms of semiconductor and of molecular photo-catalytic converters, and current approaches to the development of molecular photo-catalysts may be expected to apply equally to the development of semiconductor photo-catalysts.

d) Photo-catalytic Decomposition of Water by Scheme 4

Very few data are available on the photo-catalytic decomposition of water by scheme 4. Nevertheless this scheme seems extremely promising. It was recently shown[219] that the following reaction can take place on illuminated single crystals of the semiconductors TiO_2 and $SrTiO_3$:

$$2H_2O\ (gas) + CO_2 \xrightarrow{h\nu} CH_4 + 2O_2 .$$

The first step of this reaction is believed to be the dark dissociative adsorption of water, followed by light-induced desorption of the products. There are also reports[405,406] of the photo-decomposition of gaseous water by visible light on the surface of another semiconductor (monocrystalline germanium).

The dissociative chemisorption of water on metal surfaces (e.g. Raney nickel[407], and possibly iron[408]) is well known. It is assisted by the high heats of adsorption of hydrogen and oxygen atoms on some metals. These results suggest at least the possibility of practical exploitation of scheme 4 on metallic catalysts in the future.

At the present stage of development in science and technology a substantial penetration of solar energy into the energy balance of mankind seems to be a soluble problem, deserving very serious study. At the moment the semiconductor (p–n junction) and thermal methods of solar energy conversion are nearest to large-scale practical application. Existing information on the mechanisms of catalytic and photochemical reactions confirm the reality (in principle) of photo-catalytic energy conversion (using both molecular and semiconductor systems), initially at least as applied to the photo-catalytic decomposition of water. Semiconductor photo-catalysts able to decompose water into hydrogen and oxygen are already known. Though their efficiency is still low, the way is clear to the achievement of higher efficiencies by varying the chemical composition of the surface layer and by using narrow-gap semiconductors. Another realistic (though difficult) goal is the development of molecular photo-catalytic systems for the conversion of solar energy: simpler analogues of the photosynthetic systems found in living organisms.

From the practical view-point—the development of energy converters offering the maximum possible efficiency—the most promising systems are those which do not depend on the formation of free radicals and atoms in the intermediate steps. Nevertheless we should not dismiss the systems in which radicals are formed in the free state. They are simpler, and therefore they may (at least initially) offer more favourable efficiencies than the more complex systems. Hence, elements developed on simple systems may in future find applications in more advanced types of converter.

Combined energy converters, in which visible light is used to induce photochemical changes and infrared light to heat the reactants in order to displace chemical equilibria in the desired direction, are a particularly imaginative development. The maximum theoretical efficiency of these converters must be greater than that of systems relying purely on quantum effects, since the Sun's light is more fully utilised in them.

The decomposition of water on molecular as well as on semiconductor photo-catalysts occurs in three steps: light-induced charge separation (to give a strong oxidising agent and a strong reducing agent), evolution of oxygen from the water by the strong oxidising agent, and evolution of hydrogen from the water by the strong reducing agent.

The main stumbling block on the way to the realisation of the first step is the fast recombination of the strong oxidising agent and the strong reducing agent, which uselessly converts the stored energy into heat. However, it may be assumed that means will be found to suppress this recombination by one of the methods of stabilising charge separation discussed above (based on tunnelling, chemical, phase separation, or electrostatic effects). Of the remaining two steps the evolution of oxygen is the more difficult to carry out in practice. Whereas effective catalysts for the evolution of hydrogen from water by strong reducing agents are already known, equally effective catalysts for oxygen evolution have not yet been reported. The search for these catalysts has become a problem of the greatest importance.

Work on the photo-catalytic conversion of solar energy began only recently, and is still in the research stage. This review has attempted to examine the essential aspects of the problem against the background of the general state of solar energy conversion, and to point out possible solutions. There is every reason to believe that the photo-catalytic method will lead to the development of systems for the conversion of solar energy into chemical fuel (hydrogen) energy with an acceptable efficiency. However, the problem is not an easy one, and its solution needs further extensive studies in the fields of catalysis, photochemistry, and photophysics.

Only the future can show which of the many theoretically possible methods of solar energy conversion will prove to be the most economical.

REFERENCES

1. N.N.Semenov, "Nauka i Obshchestvo" (Science and Society), Izd.Nauka, Moscow, 1973, p.109; Vestnik Akad.Nauk SSSR, No.4, 11 (1977).
2. M.A.Styrikovich, Vestnik Akad.Nauk SSSR, No.2, 13 (1975).
3. G.Lyusti, UNESCO Courier, No.1, 4 (1974).
4. B.J.Brinkworth, "Solar Energy for Mankind" (Translated into Russian), Izd.Mir, Moscow, 1976.

5. P.Ya.Antropov, "Toplivno-energeticheskii Potentsial Zemli" (The Fuel and Energy Potential of the Earth), Izd.VINITI, Moscow, 1976.
6. L.P.Kapitsa, "Eksperiment, Teoriya, Praktika" (Experiment, Theory, and Practice), Izd.Nauka, Moscow, 1977, p.82.
7. L.N.Bell, Vestnik Akad.Nauk SSSR, No.2, 33 (1973).
8. Z.F.Chukhanov, Vestnik Akad.Nauk SSSR, No.9, 104 (1976).
9. E.A.Walters and E.M.Wewerka, J.Chem.Educ., 52, 282 (1975).
10. A.Ramachandran and J.Gururaja, UNESCO Courier, No.7, 16 (1978).
11. P.R.Ryason, Energy Sources, 4, 1 (1978).
12. J.R.Bolton, Science, 202, 705 (1978).
13. M.Calvin, Internat.J.Energy Research, 1, 299 (1977).
14. V.A.Legasov, Priroda, No.3, 3 (1977).
15. V.A.Legasov (Editor), "Atomno-vodorodnaya Energetika i Tekhnologiya" (Atomic Hydrogen Energetics and Technology), No.1, Atomizdat, Moscow, 1978.
16. A.A.Nichiporovich, Symposium "Itogi Nauki i Tekhniki. Fiziologiya Rastenii" (Advances in Science and Technology. Plant Physiology), Vol.3, Izd.VINITI, Moscow, 1977.
17. A.A.Nichiporovich, Symposium "Preobrazovanie Solnechnoi Energii" (Solar Energy Conversion), Izd.Nauka, Moscow, 1980.
18. N.S.Babaev, V.F.Demin, I.I.Kuz'min, and V.I.Stepanchikov, Priroda, No.10, 3 (1978).
19. "Radiatsionnyi Rezhim Territorii SSSR" (Radiation Regimes of the Territories of the USSR), Gidrometizdat, Leningrad, 1961.
20. K.Ya.Kondrat'ev, "Aktinometriya" (Actinometry), Gidrometizdat, 1965.
21. I.A.Shul'gin, "Solnechnaya Radiatsiya i Rastenie" (Solar Radiation and Plants), Gidrometizdat, Leningrad, 1967.
22. A.M.Vasil'ev and A.P.Landtsman, "Poluprovodnikovye Fotopreobrazovateli" (Semiconductor Photo-converters), Izd.Sovetskoe Radio, Moscow, 1971.
23. I.I.Sobel'man, Uspekhi Fiz.Nauk, 120, 85 (1976).
24. V.A.Vanke, V.M.Lopukhin, and V.L.Savvin, Uspekhi Fiz.Nauk, 123, 633 (1977).
25. "Bol'shaya Sovetskaya Entsiklopediya" (The Great Soviet Encyclopaedia), Vol.18, 1974, p.81.
26. "Bol'shaya Sovetskaya Entsiklopediya" (The Great Soviet Encyclopaedia), Vol.24, Pt.1, 1976, p.98.
27. F.Daniels and J.A.Duffie (Editors), "Solar Energy Research" (Translated into Russian), Inostr.Lit., Moscow, 1957.
28. V.A.Baum (Editor), "Ispol'zovanie Solnechnoi Energii Pri Kosmicheskikh Issledovaniyakh" (Use of Solar Energy in Cosmic Research), Izd.Mir, Moscow, 1964.
29. G.Ya.Umarov and A.A.Ershov, "Solnechnaya Energetika" (Solar Energetics), Izd.Znanie, Moscow, 1974.
30. M.Wolf, Science, 184, 382 (1974).
31. H.C.Hottel, Chem.Eng.Progress, 71, 53 (1975).
32. B.Sorensen, Science, 189, 255 (1975).
33. G.Zener, Science, 189, 294 (1975).
34. "Application of Solar Technology to Today's Energy Needs", Vols.1 and 2, Office of Technical Assessment of the US Congress, Washington, 1977.
35. N.L.Brown and J.W.Howe, Science, 199, 651 (1978).
36. Umschau in Wiss. und Technik, 75, 65 (1975).
37. I.Oshida, Butsuri, 30, 245 (1975).
38. B.J.Brinkworth, Chemistry in Britain, 11, 311 (1975).
39. M.M.Koltun, "Selektivnye Opticheskie Poverkhnosti Preobrazovatelei Solnechnoi Energii" (Selective Optical Surfaces for Solar Energy Converters), Izd. Nauka, Moscow, 1978.
40. A.L.Hammond, Science, 189, 538 (1975).
41. R.W.Harrigan, J.Solid State Chem., 22, 9 (1977).
42. J.G.Asbury and R.O.Mueller, Science, 195, 445 (1977).
43. K.D.Masterson, J.Solid State Chem., 22, 41 (1977).
44. A.L.Hammond and W.D.Metz, Science, 197, 241 (1977).
45. W.D.Metz, Science, 197, 353 (1977).
46. A.L.Hammond, Science, 197, 445 (1977).
47. W.D.Metz, Science, 197, 650 (1977).
48. A.L.Hammond, Science, 197, 623 (1977).
49. A.L.Hammond, Science, 197, 745 (1977).
50. E.S.Lipinsky, Science, 199, 644 (1978).
51. N.S.Lidorenko, V.M.Evdokimov, A.K.Zaitseva, M.M.Koltun, S.V.Ryabikov, and D.S.Skrebkov, Paper Presented to the World Electrotechnical Congress, Moscow, 1977, No.5A-01.
52. Zh.I.Alferov, V.M.Andreev, G.S.Daletskii, M.B.Kagan, N.S.Lidorenko, and V.M.Tuchkevich, Paper Presented to the World Electrotechnical Congress, Moscow, 1977, No.5A-04.
53. Zh.A.Alferov, Symposium "Budushchee Nauki" (Science: the Way Ahead), Izd.Znanie, Moscow, 1978, p.92.
54. H.Kelly, Science, 199, 634 (1978).
55. V.M.Evdokimov, Symposium "Preobrazovanie Solnechnoi Energii" (Solar Energy Conversion), Izd.Nauka, Moscow, 1980.
56. M.Calvin, Science, 184, 375 (1974).
57. J.O'M.Bockris, "Energy: the Solar Hydrogen Alternative", New York, 1975; Chem.Eng.News, 55, No.40, 27 (1977).
58. D.Haneman, Proc.Roy.Austral.Chem.Inst., 44, 37 (1977).
59. S.Claesson and L.Engström (Editors), "Solar Energy—Photochemical Conversion and Storage", National Swedish Board for Energy Source Development, 1977.
60. M.A.Leontovich, Uspekhi Fiz.Nauk, 114, 555 (1974).
61. Zh.I.Alferov, Vestnik Akad.Nauk SSSR, No.7, 28 (1976).
62. N.S.Lidorenko, Vestnik Akad.Nauk SSSR, No.9, 96 (1976).
63. H.Tributsch and H.Gerischer, Z.Elektrochem., 73, 251 (1969).
64. R.Memming, Photochem.Photobiol., 16, 325 (1972).
65. A.Marzin, Praxis Naturwiss, 22, 99 (1973).
66. R.Memming, Faraday Discuss.Chem.Soc., No.58, 261 (1974).
67. H.Gerischer, Faraday Discuss.Chem.Soc., No.58, 219 (1974).
68. W.W.Anderson and Y.G.Chai, Energy Conversion, 14, No.12, 10 (1975).
69. Y.G.Chai and W.W.Anderson, Appl.Phys.Letters, 27, 183 (1974).
70. H.Gerischer and J.Gobrecht, Z.Elektrochem., 80, 327 (1976).
71. A.B.Ellis, S.W.Kaiser, and M.S.Wrighton, J.Amer.Chem.Soc., 98, 1635 (1976).
72. A.B.Ellis, S.W.Kaiser, and M.S.Wrighton, J.Amer.Chem.Soc., 98, 6418 (1976).

73. J.M.Bolts, A.B.Ellis, K.D.Legg, and M.S.Wrighton, J.Amer.Chem.Soc., **99**, 4826 (1977).
74. H.Tributsch, Z.Elektrochem., **81**, 361 (1977).
75. H.Minoura, M.Tsuiki, and T.Oki, Z.Elektrochem., **81**, 588 (1977).
76. H.Minoura, H.Okada. and M.Tsuiki, Nippon Kagaku Kaishi, J.Chem.Soc.Japan, Chem.and Ind. Chem., **10**, 1443 (1977).
77. D.Hall, J.Electrochem.Soc., **124**, 804 (1977).
78. A.Heller, K.C.Chang, and B.Miller, J.Electrochem. Soc., **124**, 697 (1978).
79. T.Inoue, T.Watanabe, A.Fujishima, and K.Honda, J.Electrochem.Soc., **124**, 719 (1977).
80. M.Saito, T.Kishi, and T.Nagai, Denki Kagaku, **45**, 149 (1977).
81. K.C.Chang, A.Heller, B.Schwartz, S.Menezec, and B.Miller, Science, **196**, 1097 (1977).
82. H.Minoura, T.Nakamura, Y.Ueno, and M.Tsuiki, Chem.Letters, 913 (1977).
83. H.Meier, W.Albrecht, U.Tschirwitz, E.Zimmerhackl, and N.Geheeb, Z.Elektrochem., **81**, 592 (1977).
84. D.M.Tench and H.Gerischer, J.Electrochem.Soc., **124**, 1612 (1977).
85. H.Ikeda, M.Hara, K.Takahama, S.Murakami, and H.Tamura, Denki Kagaku, **45**, 587 (1977).
86. K.D.Legg, A.B.Ellis, J.M.Bolts, and M.S.Wrighton, Proc.Natl.Acad.Sci.USA, **74**, 4116 (1977).
87. A.J.Bard, J.Photochem., **10**, 59 (1979).
88. B.Miller, A.Heller, M.Robins, S.Menezes, K.G.Chang, and J.Thompson, J.Electrochem.Soc., **124**, 1019 (1977).
89. Y.Suda, Y.Shimoura, T.Sakata, and H.Tsubomura, J.Phys.Chem., **82**, 268 (1978).
90. V.A.Ilatovskii, I.B.Dmitrieva, and G.G.Komissarov, Zhur.Fiz.Khim., **52**, 121 (1978) [Russ.J.Phys. Chem., No.1 (1978)].
91. V.A.Ilatovskii, I.B.Dmitrieva, and G.G.Komissarov, Zhur.Fiz.Khim., **52**, 2551 (1978) [Russ.J.Phys. Chem., No.10 (1978)].
92. A.Heller, K.C.Chang, and B.Miller, J.Amer.Chem. Soc., **100**, 684 (1978).
93. J.M.Bolts and M.S.Wrighton, J.Amer.Chem.Soc., **100**, 5257 (1978).
94. E.Rabinowitch, J.Chem.Phys., **8**, 551 (1940).
95. A.W.Copeland, O.D.Black, and A.B.Garrett, Chem.Rev., **31**, 177 (1942).
96. M.Eisenberg and H.P.Silverman, Electrochim.Acta, **5**, 1 (1961).
97. T.Imura, S.Takagi, and K.Kawabe, Bull.Chem.Soc. Japan, **46**, 2075 (1973).
98. R.Gomer, Electrochim.Acta, **20**, 13 (1975).
99. M.I.C.Ferreira and A.Harriman, J.Chem.Soc., Faraday Trans.I, **73**, 1085 (1977).
100. T.Sakata, Y.Suda, J.Tanaka, and H.Tsubomura, J.Phys.Chem., **81**, 537 (1977).
101. A.Lottaz and A.Zalevsky, Chimia, **31**, 180 (1977).
102. W.J.Albery and M.D.Archer, Nature, **270**, 392 (1977).
103. W.J.Albery and A.W.Foulds, J.Photochem., **10**, 41 (1979).
104. W.J.Albery and M.D.Archer, Electrochim.Acta, **21**, 1155 (1977).
105. W.J.Albery and M.D.Archer, J.Electrochem.Soc., **124**, 688 (1977).
106. P.V.Kamat, M.D.Karkhanavala, and P.N.Moorthy, Indian J.Chem., **A15**, 342 (1977).
107. N.Kamitani, Shokubai, Catalyst, **19**, 171 (1977).
108. K.Shigehara, M.Nishimura, and E.Tsuchida, Bull. Chem.Soc. Japan, **50**, 3397 (1977).
109. A.Zeichner, J.R.Goldstein, and G.Stein, J.Phys. Chem., **82**, 1687 (1978).
110. A.Marzin, Prax.Naturwiss.Chem., 27, 68 (1978).
111. V.S.Bagotskii, Yu.M.Vol'fkovich, Yu.L.Golik, A.N.Suvorov, and Yu.S.Sherstobitov, Elektrokhimiya, **13**, 1611 (1977).
112. T.N.Veziroglu, UNESCO Courier, No.7, 32 (1978).
113. H.Ishikawa, M.Nakane, E.Ishii, T.Uehara, and G.Miyake, J.Chem.Soc.Japan, Chem.and Industry, **12**, 1817 (1977).
114. V.S.Bagotskii, Vestnik Akad.Nauk SSSR, No.7, 41 (1976).
115. T.Erdey-Gruz, "Chemical Sources of Energy" (Translated into Russian), Izd.Mir, Moscow, 1975.
116. K.V.Kordesch, J.Electrochem.Soc., 125, 77C (1978).
117. Yu.Ya.Gurevich, Yu.V.Pleskov, and Z.A.Rotenberg, "Fotoemissionnye Yavleniya na Granitse Metall–Rastvor" (Photo-emission Phenomena at the Metal–Solution Interface), Vol.1, Izd.VINITI, Moscow, 1978.
118. G.A.Korsunovskii, Symposium "Problemy Fotosinteza" (Problems in Photosynthesis), Izd.Akad.Nauk SSSR, Moscow, 1959, p.87.
119. K.Honda and T.Watanabe, Elektrokhimiya, **13**, 924 (1977).
120. D.M.Shub, A.A.Remnev, and V.I.Veselovskii, Elektrokhimiya, **11**, 1100 (1975).
121. Yu.S.Shumov and M.Heyrovsky, J.Electroanalyt. Chem., **65**, 469 (1975).
122. G.Stein, Israel J.Chem., **14**, 213 (1975).
123. H.Yoneyama, H.Sakamoto, and H.Tamura, Electrochim.Acta, **20**, 341 (1975).
124. H.Gerischer, J.Electroanalyt.Chem., **58**, 263 (1975).
125. J.Manassen, D.Cahen, G.Hodes, and A.Sofer, Nature, **263**, 97 (1976).
126. M.Miyake, H.Yoneyama, and H.Tamura, Electrochim. Acta, **21**, 1065 (1976).
127. H.Morisaki, T.Watanabe, M.Iwase, and K.Yazawa, Appl.Phys.Letters, **29**, 338 (1976).
128. T.Ohnishi, Y.Nakato, and H.Tsubomura, Z.Elektrochem., **79**, 523 (1975).
129. J.F.Houlihan, Chem.Eng.Progr., **54**, No.35, 6 (1976).
130. I.Nakato, K.Abe, and H.Tsubomura, Z.Elektrochem., **80**, 1002 (1976).
131. L.L.Larina and E.M.Trukhan, Trudy Moskov.Fiz.-tekh.Inst., Ser.Oschc.Molek.Fiz., No.9, 138 (1977).
132. V.B.Kireev and D.A.Filimonov, Trudy Moskov.Fiz.-tekh.Inst., Ser.Oschc.Molek.Fiz., No.9, 174 (1977).
133. F.Takahashi, Elektrokhimiya, **13**, 1674 (1977).
134. H.Tsubomura, I.Nakato, and T.Sakata, Elektrokhimiya, **13**, 1689 (1977).
135. M.Miyake and H.Tamura, Electrochim.Acta, **22**, 319 (1977).
136. M.Kazuo, Japan J.Appl.Phys., **16**, 1879 (1977).
137. W.D.K.Clark and N.Sutin, J.Amer.Chem.Soc., **99**, 4676 (1977).
138. S.Meshitsuka and K.Tamaru, J.Chem.Soc.Faraday Trans.I, **73**, 236 (1977).
139. K.L.Hardee and A.J.Bard, J.Electrochem.Soc., **124**, 215 (1977).
140. P.A.Kohl, S.N.Frank, and A.J.Bard, J.Electrochem. Soc., **124**, 225 (1977).
141. S.N.Frank and A.J.Bard, J.Amer.Chem.Soc., 99, 4667 (1977).
142. M.Tomkiewicz and J.M.Woodall, Science, **196**, 990 (1977).
143. A.L.Asatiani, T.V.Dzhavrishvili, and Z.A.Rotenberg, Elektrokhimiya, **13**, 309 (1977).
144. H.Tributsch, Z.Naturforsch., 32A, 972 (1977).

145. A.C.C.Tseung and S.Jasem, Electrochim.Acta, 22, 31 (1977).
146. L.S.R.Yeh and N.Hackerman, J.Electrochem.Soc., 124, 833 (1977).
147. A.N.Asanov, Dokl.Akad.Nauk SSSR, **225**, 836 (1975).
148. T.Yamamura and Y.Umezawa, Chem.Letters, 1286 (1977).
149. T.Takizawa, T.Watanabe, and K.Honda, J.Phys. Chem., 82, 1391 (1978).
150. P.Capelle, M.de Backer, O.de Witte, G.Feullade, and G.Lepoutre, Compt.rend., **C284**, 597 (1977).
151. K.Ohashi, J.McCann, and J.O'M.Bockris, Nature, 266, 610 (1977).
152. M.A.Butler and D.S.Ginley, Chem.Phys.Letters, 47, 319 (1977).
153. J.G.Mavroides, D.I.Tchernev, J.A.Kafalas, and D.F.Kolesar, US National Bureau of Standards Special Publication No.455, 1976, p.221.
154. G.Hodes, J.Manassen, and D.Cahen, J.Appl.Electrochem., 7, 181 (1977).
155. K.Nakatani and H.Tsubomura, Bull.Chem.Soc.Japan, 50, 783 (1977).
156. H.J.Danzmann, K.Hauffe, and Z.G.Szabo, Z.phys. Chem., 104, 95 (1977).
157. D.S.Ginley and M.A.Butler, J.Appl.Phys., **48**, 2019 (1977).
158. M.T.Spitler and M.Calvin, J.Chem.Phys., **66**, 4294 (1977).
159. H.Tsubomura and M.Matsumura, Kagaku, Chemistry, 32, 238 (1977).
160. K.Kohayakawa, A.Fujishima, K.Honda, Nippon Kagaku Kaishi, J.Chem.Soc.Japan, Chem.and Ind. Chem., 780 (1977).
161. M.A.Butler, J.Appl.Phys., **48**, 1914 (1977).
162. H.Minoura, M.Niwa, T.Oki, and M.Tsuiki, Nippon Kagaku Kaishi, J.Chem.Soc.Japan, Chem.and Ind. Chem., 487 (1977).
163. A.J.Nozik, Appl.Phys.Letters, **30**, 567 (1977).
164. H.H.Kung, H.S.Jarrett, A.W.Sleight, and A.Ferretti, J.Appl.Phys., 48, 2463 (1977).
165. M.Soma, Chem.Phys.Letters, **50**, 93 (1977).
166. J.O'M.Bockris and K.Uosaki, J.Electrochem.Soc., 124, 1348 (1977).
167. M.Matsumura, Y.Nomura, and H.Tsubomura, Bull. Chem.Soc.Japan, **50**, 2533 (1977).
168. M.Miyake, H.Yoneyama, and H.Tamura, Bull.Chem. Soc.Japan, 50, 1492 (1977).
169. T.Watanabe, T.Takizawa, and K.Honda, J.Phys. Chem., 81, 1845 (1977).
170. R.H.Wilson, L.A.Harris, and M.E.Gerstner, J.Electrochem.Soc., **124**, 1233 (1977).
171. M.Miyake, H.Yoneyama, and H.Tamura, Denki Kagaku, **45**, 411 (1977).
172. M.Fujihira, N.Onishi, and T.Osa, Nature, **268**, 226 (1977).
173. S.N.Frank and A.J.Bard, J.Phys.Chem., **81**, 1484 (1977).
174. M.S.Wrighton, P.T.Wolczanski, and A.B.Ellis, J.Solid State Chem., **22**, 17 (1977).
175. T.Inoue, T.Watanabe, A.Fujishima, and K.Honda, Chem.Letters, 1073 (1977).
176. A.Bourrase and G.Horowits, J.Phys.Lett.(France), 38, 291 (1977).
177. T.Miura, H.Shinoda, T.Kishi, and T.Nagai, Denki Kagaku, **45**, 223 (1977).
178. A.J.Nozik, Ann.Rev.Phys.Chem., **29**, 189 (1978).
179. A.W.Mau and W.H.F.Sasse, Proc.Roy.Austral.Chem. Inst., **44**, 89 (1977).
180. A.T.Vas'ko, P.P.Pogoretskii, and S.K.Kovach, Symposium "Elektronnye Protsessy v Vodnykh Rastvorakh" (Electronic Processes in Aqueous Solutions), Izd.Naukova Dumka, Kiev, 1979, p.20.
181. E.M.Trukhan and V.B.Kireev, Symposium "Preobrazovanie Solnechnoi Energii" (Solar Energy Conversion), Izd.Nauka, Moscow, 1980.
182. A.N.Asanov, Symposium "Materialy Tretego Vsesoyuznogo Soveshchaniya po Fotokhimii" (Papers Presented to the Third All-Union Photochemistry Conference), Rostov-on-Don, 1977, Izd.Moskov. Univ., p.42.
183. M.Tomkiewicz and H.Fay, Appl.Phys., **18**, 1 (1978).
184. J.R.Martin, R.Olier, and P.Clechet, J.Phys.Lett. (France), **38**, 271 (1977).
185. A.B.Bocarsly, J.M.Bolts, P.G.Gummins, and M.S.Wrighton, Appl.Phys.Letters, **31**, 568 (1977).
186. P.D.Fleischauer and J.K.Allen, J.Phys.Chem., 82, 432 (1978).
187. G.A.Korsunovskii, Zhur.Fiz.Khim., **52**, 2276 (1978) [Russ.J.Phys.Chem., No.9 (1978)].
188. S.O.Izidinov, V.P.Kuz'mina, and B.E.Aratovskaya, Zhur.Fiz.Khim., **52**, 2558 (1978) [Russ.J.Phys. Chem., No.10 (1978)].
189. E.I.Rabinowitch, "Photosynthesis and Related Processes" (Translated into Russian), Inostr.Lit., Moscow, Vol.1 (1951), Vol.2 (1953), Vol.3 (1959).
190. A.A.Krasnovskii, "Preobrazovanie Energii Sveta Pri Fotosinteze. Molekulyarnye Mekhanizmy" (The Conversion of Light Energy During Photosynthesis. Molecular Mechanisms), Izd.Nauka, Moscow, 1974.
191. B.A.Rubin and V.F.Gavrilenko, "Biokhimiya i Fiziologiya Fotosinteza" (Biochemistry and Physiology of Photosynthesis), Izd.Moskov.Univ., 1977.
192. E.Broda, Symposium "Nauka i Chelovechestvo" (Science and Mankind), Izd.Znanie, Moscow, 1978, p.170.
193. F.Daniels, Symposium "Studies on the Use of Solar Energy" (Translated into Russian), Inostr.Lit., Moscow, 1957, p.187.
194. J.A.Bassham, Science, **197**, 630 (1977).
195. J.R.Bolton, "International Conference on the Photochemical Conversion and Storage of Solar Energy", Ontario, Canada, 1976, p.A8.
196. K.Meyer, Symposium "Studies on the Use of Solar Energy" (Translated into Russian), Inostr.Lit., Moscow, 1957, p.191.
197. A.Fisher, Symposium "Studies on the Use of Solar Energy" (Translated into Russian), Inostr.Lit., Moscow, 1957, p.198.
198. E.Broda, Symposium "Budushchee Nauki" (Science: the Way Ahead), Izd.Znanie, Moscow, 1978, p.102.
199. L.V.M.la Rivière and E.J.da Silva, UNESCO Courier, No.7, 29 (1978).
200. I.V.Berezin, S.D.Varfolomeev, and P.P.Titov, Symposium "Voprosy Atomnoi Nauki i Tekhniki. Seriya Atomno-vodorodnaya Energetika" (Problems in Atomic Science and Technology. Atomic Hydrogen Energetics Series), Kurchatov Atomic Energy Institute, Moscow, 1977, p.26.
201. E.I.Rabinowitch, Symposium "Studies on the Use of Solar Energy" (Translated into Russian), Inostr. Lit., Moscow, 1957, p.209.
202. R.J.Marcus, Science, **123**, 399 (1956).
203. N.N.Lichtin (Editor), "The Current State of Knowledge of the Photochemical Formation of Fuel", NSF/RANN Workshop Report, Boston, 1974.

204. V.Balzani, L.Moggi. M.F.Manfrin, F.Bolletta, and M.Gleria, Science, **189**, 852 (1975).
205. J.R.Bolton, see Ref.195, Ontario, Canada, 1976, p.E11.
206. J.R.Bolton, J.Solid State Chem., **22**, 3 (1977).
207. D.M.Mattox, J.Solid State Chem., **22**, 31 (1977).
208. E.Schumacher, Chimia, **32**, 193 (1978).
209. S.Odile, "Quatorzième Semaine d'Études de Chimie organique", Nice, 1977.
210. N.J.Turro, V.Ramamurthy, and T.J.Katz, Nouv. J.Chim., 1, 363 (1977).
211. W.R.Bergmark, G.Lones, and T.E.Reinhard, see Ref.195, p.G4.
212. R.R.Hautala, J.Little, and E.Sweet, see Ref.195, p.G8.
213. W.H.F.Sasse, see Ref.195, p.G1.
214. N.J.Turro, W.R.Cherry, M.F.Mirbach, and M.J.Mirbach, J.Amer.Chem.Soc., **99**, 7388 (1977).
215. C.Kutal, P.Schwendiman, and P.Grutsch, Solar Energy, 19, 651 (1977).
216. T.Mikai and Y.Yamashita, Tetrahedron Letters, 357 (1978).
217. G.Ervin, J.Solid State Chem., **22**, 51 (1977).
218. R.K.Chan, see Ref.195, Ontario, Canada, 1976, p.D8.
219. J.C.Hemminger, R.Carr, and G.A.Somorjai, Chem.Phys.Letters, **57**, 100 (1978).
220. G.N.Schrauser and T.D.Guth, J.Amer.Chem.Soc., **99**, 7189 (1977).
221. H.Hennig, P.Thomas, R.Wagener, D.Renorek, and K.Jurdeczka, Z.Chemie, **17**, 241 (1977).
222. L.L.Basov and V.A.Kotel'nikov, Symposium "Spektroskopiya Fotoprevrashchenii v Molekulakh" (Spectroscopy of Photo-transitions in Molecules), Izd.Nauka, Leningrad, 1977, p.228.
223. D.Trivich and P.Flynn, Symposium "Studies on the Use of Solar Energy" (Translated into Russian), Inostr.Lit., Moscow, 1957, p.152.
224. I.V.Berezin, S.D.Varfolomeev, and S.V.Zaitsev, Dokl.Akad.Nauk SSSR, **229**, 94 (1976).
225. "Ekspress-informatsiya VINITI. Seriya Pryamoe Preobrazovanie Teplovoi i Khimicheskoi Energii v Elektrichestvo" (VINITI Express Information. Direct Conversion of Thermal and Chemical Energy into Electricity Series), No.33, 1978, p.1.
226. K.P.Mishchenko and A.A.Ravdel' (Editors), "Kratkii Spravochnik Fiziko-khimicheskikh Velichin" (Shorter Handbook of Physicochemical Constants), Izd.Khimiya, Leningrad, 1974.
227. G.V.Buxton, Coord.Chem.Rev., **22**, 195 (1977).
228. W.M.Latimer, "Oxidation States of the Elements and Their Potentials in Aqueous Solutions" (Translated into Russian), Inostr.Lit., Moscow, 1954.
229. B.P.Nikol'skii (Editor), "Spravochnik Khimika" (Chemist's Handbook), Vol.3, Izd.Khimiya, Moscow–Leningrad, 1974, p.742.
230. L.S.Lilich and M.K.Khripun, "Okislitel'no-vosstanovitel'nye i Drugie Donorno-Aktseptornye Reaktsii v Rastvorakh" (Redox and Other Donor–Acceptor Reactions in Solutions), Izd.Leningrad.Univ., 1978.
231. V.N.Kuznetsov, A.A.Lisachenko, and F.I.Vilesov, Khim.Vys.Energii, 7, 230 (1973).
232. V.I.Korotkov and V.E.Kholmogorov, Symposium "Fotosorbtsionnye i Fotokataliticheskie Yavleniya v Geterogennykh Sistemakh" (Photo-sorption and Photo-catalytic Phenomena in Heterogeneous Systems), Novosibirsk, 1977, p.96.
233. M.T.Macpherson and J.P.Simons, Chem.Phys. Letters, **51**, 261 (1977).
234. D.Yeager, V.McKoy, and G.A.Segal, J.Chem.Phys., **61**, 755 (1974).
235. V.M.Zolotarev and A.V.Demin, Optika i Spektrosk., **43**, 271 (1977).
236. V.Balzani and V.Carassiti, "The Photochemistry of Coordination Compounds", Academic Press, New York, 1970.
237. A.I.Oparin, "Vozniknovenie Zhizni na Zemle" (How Life Appeared on Earth), Izd.Akad.Nauk SSSR, Moscow, 1957.
238. V.B.Evstigneev, Symposium "Spektroskopiya Fotoprevrashchenii v Molekulakh" (Spectroscopy of Photo-transitions in Molecules), Izd.Nauka, Leningrad, 1977, p.131.
239. F.K.Fong and L.Galloway, J.Amer.Chem.Soc., **100**, 3594 (1978).
240. L.Galloway, J.Roettger, and D.R.Fruge, J.Amer. Chem.Soc., **100**, 4635 (1978).
241. T.Yamamura, Chem.Letters, 193 (1978).
242. M.Spiro and A.K.Ravnö, J.Chem.Soc., 78 (1965).
243. A.D.Nadezhdin, Yu.N.Kozlov, and A.P.Purmal', Zhur.Fiz.Khim., **49**, 2263 (1975) [Russ.J.Phys. Chem., No.9 (1975)].
244. A.Ya.Sychev, "Okislitel'no-vosstanovitel'nyi Kataliz Kompleksami Metallov" (Oxidation–Reduction Catalysis by Metal Complexes), Izd.Shtiintsa, Kishinev, 1976.
245. N.N.Semenov, A.E.Shilov, and G.I.Likhtenshtein, Dokl.Akad.Nauk SSSR, 221, 1374 (1975).
246. N.N.Semenov, Vestnik Akad.Nauk SSSR, No.10, 83 (1978).
247. J.Koryta, J.Dvořak, and V.Bohackova, "Elektrochemie" (Electrochemistry), Izd.Mir, Moscow, 1977.
248. A.Matsuda, R.Natoya, T.Okhmori, K.Kunimatsu, and T.Kushimoto, Elektrokhimiya, 13, 1659 (1977).
249. N.M.Bazhin and V.M.Berdnikov, Symposium "Svobodno-radikal'nye Sostoyaniya v Khimii" (Free-radical States in Chemistry), Izd.Nauka, Novosibirsk, 1972, p.129.
250. N.M.Bazhin and V.V.Korolev, Khim.Vys.Energii, 12, 425 (1978).
251. L.J.Heidt and A.F.McMillan, Science, 117, 75 (1953).
252. L.Heidt, Symposium "Studies on the Use of Solar Energy" (Translated into Russian), Inostr.Lit., Moscow, 1957, p.220.
253. D.D.Davis, K.L.Stevenson, and G.K.King, Inorg.Chem., 16, 670 (1974).
254. D.D.Davis, G.K.King, K.L.Stevenson, E.R.Birnbaum, and J.H.Hageman, J.Solid State Chem., 22, 63 (1977).
255. D.D.Davis, K.L.Stevenson, and C.R.Davis, J.Amer.Chem.Soc., **100**, 5344 (1978).
256. N.M.Bazhin, Chem.Phys.Letters, **43**, 469 (1976).
257. M.Brandis and G.Stein, J.Phys.Chem., **82**, 852 (1978).
258. D.K.Erwin, G.L.Geoffroy, H.B.Gray, G.S.Hammond, E.I.Solomon, W.C.Trogler, and A.A.Zagars, J.Amer.Chem.Soc., 99, 3620 (1977).
259. W.C.Trogler, D.K.Erwin, G.L.Geoffroy, and H.B.Gray, J.Amer.Chem.Soc., **100**, 1160 (1978).
260. A.W.Adamson and W.L.Walts, Chem.Rev., **68**, 541 (1968).
261. A.A.Poznyak, V.E.Stel'mashok, and V.K.Rumas, Khim.Vys.Energii, 11, 374 (1977).
262. H.Hada, Y.Yonezawa, A.Yoshida, and A.Kurakake, J.Chem.Phys., **80**, 2728 (1976).

263. G.V.Buxton, S.P.Wilford, and R.J.Williams, J.Chem.Soc., 4957 (1962).
264. C.H.Langford and J.H.Carey, Canad.J.Chem., **53**, 2430 (1975).
265. F.David and P.G.David, J.Phys.Chem., **80**, 579 (1976).
266. S.Hashimoto et al., Bull.Chem.Soc., Japan, **45**, 966 (1972).
267. A.V.El'tsov, O.P.Studzinskii, and V.M.Grebenkina, Uspekhi Khim., **46**, 185 (1977) [Russ.Chem.Rev., No.2 (1977)].
268. H.D.Burrows and T.J.Kemp, Chem.Soc.Rev., 3, 2 (1974).
269. M.Moriyasu, Y.Yokoyama, S.Ikeda, J.Inorg.Nuclear Chem., **39**, 2211 (1977).
270. B.V.Koryakin, T.S.Dzhabiev, and A.E.Shilov, Dokl.Akad.Nauk SSSR, **229**, 128 (1976).
271. I.S.Shchegoleva and A.I.Kryukov, Dokl.Akad.Nauk UkrSSR, B, 431 (1977).
272. S.Ya.Kuchmii, A.V.Korzhak, and A.I.Kryukov, Dokl.Akad.Nauk SSSR, **235**, 354 (1977).
273. A.I.Kryukov, S.Ya.Kuchmii, I.S.Shchegoleva, and A.V.Korzhak, Teor.Eksper.Khim., **13**, 135 (1977).
274. T.Donohue, J.Chem.Phys., 67, 5402 (1977).
275. I.S.Shchegoleva, Khim.Vys.Energii, **10**, 398 (1976).
276. N.I.Litsov, V.A.Voitenko, V.I.Nikolaevskaya, and A.A.Kachan, Khim.Vys.Energii, 12, 345 (1978).
277. B.N.Bandyopadhyay and A.Harriman, J.Chem.Soc. Faraday Trans.I, 73, 663 (1977).
278. J.A.Calvert and J.N.Pitts, "Photochemistry" (Translated into Russian), Izd.Mir, Moscow, 1967.
279. E.T.Denisov, "Konstanty Skorosti Gomoliticheskikh Zhidkofaznykh Reaktsii" (Rate Constants of Homolytic Liquid-phase Reactions), Izd.Nauka, Moscow, 1971.
280. O.Kalisky and M.Shirom, J.Photochem., 7, 215 (1977).
281. J.K.Thomas and P.Piciulo, J.Amer.Chem.Soc., 100, 3239 (1978).
282. D.Sandrini and V.Balzani, J.Amer.Chem.Soc., **99**, 4523 (1977).
283. M.D.Marcantonatos, Inorg.Chim.Acta, **24**, L37 (1977).
284. S.J.Formosinho, J.Chem.Soc., Faraday Trans.II, 73, 201 (1977).
285. P.J.Giordano, C.R.Bock, M.S.Wrighton, L.V.Interrante, and R.F.X.Williams, J.Amer.Chem. Soc., 99, 3187 (1977).
286. S.H.Peterson and J.N.Demas, J.Amer.Chem.Soc., **98**, 7880 (1976).
287. V.V.Korolev and N.M.Bazhin, Khim.Vys.Energii, 12, 421 (1978).
288. S.G.Schulman, in "Modern Fluorescence Spectroscopy", New York–London, 1976, Vol.2, p.239.
289. F.Celarsin, Z.phys.Chem., **106**, 25 (1977).
290. I.Yu.Martynov, A.B.Demyashkevich, B.M.Uzhinov, and M.G.Kuz'min, Uspekhi Khim., **46**, 3 (1977) [Russ.Chem.Rev., No.1 (1977)].
291. K.Durek, P.Schumacher, and R.N.Schindler, Z.Naturforsch., **A32**, 1157 (1977).
292. G.N.Schrauzer and T.D.Guth, J.Amer.Chem.Soc., **98**, 3508 (1976).
293. S.Leutwyler and E.Schumacher, Chimia, **31**, 475 (1977).
294. P.A.Jacobs, J.B.Uytterhoeven, and H.K.Beyer, Chem.Comm., 128 (1977).
295. P.H.Kasai and R.J.Bishop, J.Phys.Chem., **81**, 1527 (1977).
296. S.Markiewicz, M.S.Chan, R.H.Sparks, C.A.Evans, and J.R.Bolton, see Ref.195, p.E6.
297. D.J.Graves and J.D.Stramondo, Amer.Inst.Chem. Eng.Symp.Ser., 72, 43 (1976).
298. B.V.Koryakin, T.S.Dzhabiev, and A.E.Shilov, Dokl.Akad.Nauk SSSR, **233**, 620 (1977).
299. B.V.Koryakin, V.V.Rodin, and T.S.Dzhabiev, Izv.Akad.Nauk SSSR, Ser.Khim., 2788 (1977).
300. K.K.Rao, S.G.Reeves, L.Rosa, and D.O.Hall, see Ref.195, p.A6.
301. J.M.Lean and J.P.Sauvage, Nouv.J.Chim., 1, 449 (1977).
302. L.I.Boguslavskii, A.G.Volkov, M.D.Kandelaki, E.A.Nizhnikovskii, and M.A.Bibikova, Biofizika, 22, 223 (1977).
303. Y.Toyoshima, Nature, **265**, 187 (1977).
304. G.Sprintschnik, H.W.Sprintschnik, P.P.Kirsch, and D.G.Whitten, J.Amer.Chem.Soc., **98**, 2337 (1976).
305. G.Sprintschnik, H.W.Sprintschnik, P.P.Kirsch, and D.G.Whitten, J.Amer.Chem.Soc., **99**, 4947 (1977).
306. P.J.DeLaive, J.T.Lee, H,W.Sprintschnik, H.Abruna, T.J.Meyer, and D.G.Whitten, J.Amer.Chem.Soc., 99, 7094 (1977).
307. D.G.Whitten, F.R.Hopf, F.H.Quina, G.Sprintschnik, and H.Sprintschnik, Pure Appl.Chem., **49**, 379 (1977).
308. S.J.Valenty and G.L.Gaines, J.Amer.Chem.Soc., **99**, 1285 (1977).
309. A.Harriman, Chem.Comm., 777 (1977).
310. L.J.Yellowlees, R.G.Dickinson, C.S.Halliday, J.S.Bonham, and L.E.Lyons, Austral.J.Chem., **31**, 431 (1978).
311. N.Sutin, J.Photochem., **10**, 19 (1979).
312. V.Balzani, L.Moggi, M.F.Manfrin, F.Bolletta, and C.S.Laurence, Coord.Chem.Rev., **15**, 321 (1975).
313. N.E.Tokel and A.J.Bard, J.Amer.Chem.Soc., **94**, 2862 (1972).
314. N.E.Tokel-Takvoryan, R.E.Hemingway, and A.J.Bard, J.Amer.Chem.Soc., **95**, 6582 (1973).
315. J.N.Demas and A.W.Adamson, J.Amer.Chem.Soc., **95**, 5159 (1973).
316. W.Halper and M.K.De Armond, Chem.Phys.Letters, 24, 114 (1974).
317. G.S.Laurence and V.Balzani, Inorg.Chem., **13**, 2976 (1974).
318. G.A.Crosby, J.Amer.Chem.Soc., **97**, 7031 (1975).
319. C.T.Lin and N.Sutin, J.Amer.Chem.Soc., **97**, 3542 (1975).
320. C.T.Lin and N.Sutin, J.Phys.Chem., **80**, 97 (1976).
321. C.Creutz and N.Sutin, Inorg.Chem., **15**, 496 (1976).
322. C.T.Lin, W.Böttcher, M.Chou, C.Creutz, and N.Sutin, J.Amer.Chem.Soc., **98**, 6536 (1976).
323. C.Creutz and N.Sutin, J.Amer.Chem.Soc., **98**, 6384 (1976).
324. J.N.Demas and J.W.Addington, J.Amer.Chem.Soc., **98**, 5800 (1976).
325. J.N.Demas, J.W.Addington, S.H.Peterson, and E.W.Harris, J.Phys.Chem., **81**, 1039 (1977).
326. J.Van Houten and R.J.Watts, J.Amer.Chem.Soc., **97**, 3843 (1975).
327. J.Van Houten and R.J.Watts, J.Amer.Chem.Soc., **98**, 4853 (1976).
328. R.C.Young, T.J.Meyer, and D.G.Whitten, J.Amer. Chem.Soc., **97**, 4781 (1975).
329. A.Juris, M.T.Gandolfi, M.E.Manfrin, and V.Balzani, J.Amer.Chem.Soc., **98**, 1047 (1976).
330. R.Ballardini, G.Varani, F.Scandolo, and V.Balzani, J.Amer.Chem.Soc., **98**, 7432 (1976).

331. R.C.Young, T.J.Meyer, and D.G.Whitten, J.Amer. Chem.Soc., **98**, 286 (1976).
332. C.P.Anderson, D.J.Salmon, T.J.Meyer, and R.C.Young, J.Amer.Chem.Soc., **99**, 1980 (1977).
333. J.K.Nagle, R.C.Young, and T.J.Meyer, Inorg. Chem., **16**, 3366 (1977).
334. D.Meisel and M.S.Matheson, J.Amer.Chem.Soc., **99**, 6577 (1977).
335. D.Meisel, M.S.Matheson, and J.Rabani, J.Amer. Chem.Soc., **100**, 117 (1978).
336. R.J.Staniewicz, R.F.Sympson, and D.G.Hendricker, Inorg.Chem., 16, 2166 (1977).
337. R.J.Staniewicz and D.G.Hendricker, J.Amer.Chem. Soc., **99**, 6581 (1977).
338. J.F.Endicott and G.J.Ferrandi, J.Amer.Chem.Soc., 99, 5812 (1977).
339. M.Hinziker and A.Ludi, J.Amer.Chem.Soc., **99**, 7370 (1977).
340. T.J.Meyer, Israel J.Chem., **15**, 200 (1977).
341. K.Chandrasekaran and P.Natarajan, Chem.Comm., 774 (1977).
342. J.N.Demas, E.W.Harris, C.M.Flynn, and D.Diemente, J.Amer.Chem.Soc., 97, 3838 (1975).
343. E.Finkenberg, P.Fischer, S.Y.Huang, and H.D.Gafney, J.Phys.Chem., **82**, 526 (1978).
344. K.Ogura, H.Urabe, and T.Yosina, Electrochim. Acta, 22, 285 (1977).
345. K.Ogura, H.Urabe, and T.Yosina, Electrochim.Acta, 22, 1357 (1977).
346. J.Phillips and C.H.Langford, Electrochim.Acta, **23**, 143 (1978).
347. J.Phillips and C.H.Langford, J.Phys.Chem., **82**, 622 (1978).
348. M.Maestri, V.Balzani, and M.Z.Hoffman, J.Amer. Chem.Soc., **100**, 2694 (1978).
349. H.D.Burrows, J.Chem.Soc.Faraday Trans.I, 72, 163 (1976).
350. M.D.Marcantonatos, Inorg.Chim.Acta, **24**, L53 (1977).
351. M.Moriyasu, Y.Yokoyama, and S.Ikeda, J.Inorg. Nuclear Chem., **39**, 2205 (1977).
352. J.Rabani and M.S.Matheson, see Ref.195, p.E2.
353. C.Creutz and N.Sutin, Proc.Nat.Acad.Sci.USA, 72, 2858 (1975).
354. T.S.Glikman and M.E.Podlinyaeva, Ukrain.Khim. Zhur., **21**, 211 (1955).
355. G.Nord and O.Wernberg, J.Chem.Soc., Dalton Trans., 866 (1972).
356. G.Nord and O.Wernberg, J.Chem.Soc., Dalton Trans., 845 (1975).
357. A.A.Schilt, "Analytical Applications of 1,10-Phenanthroline and Related Compounds", Internat.Series of Monographs in Analytical Chemistry, Vol.32. Illinois, 1969.
358. V.Ya.Shafirovich, A.P.Moravskii, and T.S.Dzhabiev, Kinetika i Kataliz, **18**, 509 (1977).
359. W.W.Clark, "Oxidation-Reduction Potentials of Organic Systems", Baltimore, 1960.
360. B.Ke, S.Demeter, K.I.Zamarev, and R.F.Khairutdinov, Biochim.Biophys.Acta, **545**, 265 (1979).
361. K.I.Zamaraev and R.F.Khairutdinov, Uspekhi Khim., **47**, 992 (1978) [Russ.Chem.Rev., No.6 (1978)].
362. D.S.Chernavskii, N.M.Chernavskaya, and Ya.N.Grigorov, Symposium "Problemy Biofotokhimii" (Problems in Bio-photochemistry), Izd.Nauka, Moscow, 1973, p.191.
363. N.M.Chernavskaya and D.S.Chernavskii, "Tunnel'nyi Transport Elektronov v Fotosinteze" (Tunnelling Electron Transport in Photosynthesis), Izd.Moskov.Univ., 1977.
364. R.W.Callahan and T.J.Meyer, Chem.Phys.Letters, **39**, 82 (1976).
365. M.J.Powers, R.W.Callahan, D.J.Salmon, and T.J.Meyer, Inorg.Chem., **15**, 894 (1976).
366. M.J.Powers, D.J.Salmon, R.W.Callahan, and T.J.Meyer, J.Amer.Chem.Soc., **98**, 6731 (1976).
367. R.W.Callahan, F.R.Keene, T.J.Meyer, and D.J.Salmon, J.Amer.Chem.Soc., **99**, 1064 (1977).
368. H.Fischer, G.M.Tom, and H.Taube, J.Amer.Chem. Soc., **98**, 5512 (1976).
369. J.K.Farr, L.G.Hulett, R.H.Lane, and J.K.Hurst, J.Amer.Chem.Soc., **97**, 2654 (1975).
370. V.A.Durante and P.C.Ford, J.Amer.Chem.Soc., **97**, 6898 (1975).
371. D.A.Piering and J.M.Malin, J.Amer.Chem.Soc., **98**, 6045 (1976).
372. R.D.Cannon, Chem.Phys.Letters, **19**, 299 (1977).
373. K.Mutai, K.Kobayashi, T.Kobayashi, and C.Utsunomiya, Chem.Letters, 1047 (1977).
374. R.Foster, J.Chem.Soc., Perkin Trans.II, 507 (1975).
375. H.Masuhara, K.Kaji, and N.Mataga, Bull.Chem.Soc. Japan, **50**, 2084 (1977).
376. H.E.Toma and P.S.Santos, Canad.J.Chem., **55**, 3549 (1977).
377. K.Rieder and H.Taube, J.Amer.Chem.Soc., **99**, 7891 (1977).
378. Y.Hatano, M.Yamamoto, and Y.Nishijima, J.Phys. Chem., **82**, 367 (1978).
379. P.N.Chatz, S.B.Piepho, and E.R.Krauz, Chem.Phys. Letters, **55**, 539 (1978).
380. M.J.Powers and T.J.Meyer, J.Amer.Chem.Soc., **100**, 4993 (1978).
381. B.C.Bunker, R.S.Drago, and D.N.Hendrickson, J.Amer.Chem.Soc., **100**, 3805 (1978).
382. M.Maestri and M.Grätzel, Z.Elektrochem., 81, 504 (1977).
383. K.G.Mathai and E.Rabinowitch, J.Phys.Chem., **66**, 663 (1962).
384. R.N.Tarafdar and K.K.Rohatgi-Mukherjee, see Ref.195, p.D3.
385. D.Stigter, J.Phys.Chem., **68**, 3603 (1964).
386. A.L.Loeb, T.G.Overbeck, and P.H.Wiersema, "The Electrical Double Layer Around a Special Colloid Particle", M.I.T.Press, Cambridge, 1961.
387. D.W.Breck, "Zeolite Molecular Sieves: Structure, Chemistry and Use" (Translated into Russian), Izd.Mir, Moscow, 1976.
388. I.V.Berezin, K.Martinek, and A.K.Yatsimirskii, Uspekhi Khim., **42**, 1729 (1973) [Russ.Chem.Rev., No.10 (1973)].
389. C.A.Brenton, Pure Appl.Chem., **49**, 969 (1977).
390. J.Kiwi and M.Grätzel, Angew.Chem., **90**, 900 (1978).
391. J.M.Lehn, J.P.Sauvage, and R.Liessel, Nouv.J. Chim., **3**, 423 (1979).
392. G.I.Likhtenshtein, "Mnogoyadernye Okislitel'no-vosstanovital'nye Metallofermenty" (Polynuclear Oxidation–Reduction Metal Enzymes), Izd.Nauka, Moscow, 1979.
393. G.L.Elizarova, L.G.Matvienko, V.N.Parmon, and K.I.Zamaraev, Dokl.Akad.Nauk SSSR, **249**, 863 (1979).
394. V.Ya.Shafirovich and V.V.Strelets, Nouv.J.Chim., **2**, 199 (1978).
395. M.R.Tarasevich and K.A.Radyushkina, Uspekhi Khim., **49**, 1498 (1980) [Russ.Chem.Rev., No.8 (1980)].
396. S.Mandal and B.R.Sant, Nuclear Chem., **39**, 2273 (1977).

397. V.Ya.Shafirovich, N.K.Khannanov, and A.E.Shilov, Kinetika i Kataliz, **19**, 877, 1498, 1502, 1591 (1978).
398. V.V.Strelets, O.N.Efimov, and V.Ya.Shafirovich, Kinetika i Kataliz, **18**, 646 (1977).
399. M.M.Morrison and D.T.Sawyer, Inorg.Chem., **17**, 333 (1978).
400. A.Harriman, Coord.Chem.Rev., **28**, 147 (1979).
401. K.R.Mann, N.S.Lewis, V.M.Miskowski, D.K.Erwin, G.S.Hammond, and H.B.Gray, J.Amer.Chem.Soc., **99**, 5525 (1977).
402. V.M.Miskowski, G.L.Nobinger, D.S.Kliger, G.S.Hammond, N.S.Lewis, K.R.Mann, and H.B.Gray, J.Amer.Chem.Soc., **100**, 485 (1978).
403. G.L.Geoffroy and M.G.Bradley, J.Organomet.Chem., **134**, C27 (1977).
404. J.A.Labinger and S.Madhavan, J.Organomet.Chem., **134**, 381 (1977).
405. V.F.Kiselev, A.S.Petrov, and R.V.Prudnikov, Kinetika i Kataliz, **19**, 1593 (1978).
406. V.F.Kiselev, A.S.Petrov, and R.V.Prudnikov, Dokl.Akad.Nauk SSSR, **245**, 1146 (1979).
407. A.J.Renouprez, P.Fouilloux, J.P.Candy, and J.Tomkinson, Surface Sci., **83**, 285 (1979).
408. M.Watanabe, Nippon Kagaku Kaishi, 1762 (1977).

Siberian Section of the USSR Academy of Sciences, Institute of Catalysis, Novosibirsk

Translated from *Uspekhi Khimii*, 49, 1498 - 1522 (1980) U.D.C. 541.138.3 : 546

Electrocatalysis on Metalloporphyrins

M.R.Tarasevich and K.A.Radyushkina

Results of theoretical and applied research on electrocatalytic reactions—the cathodic reduction of oxygen, hydrogen peroxide, and carbon dioxide and the anodic oxidation of organic and inorganic substances—on metalloporphyrins are analysed with a list of 132 references.

CONTENTS

I. Introduction 718
II. Electrophysical and catalytic properties of metalloporphyrins 718
III. Kinetics and mechanism of the electroreduction of oxygen on metalloporphyrins 720
IV. Use of organic complexes of metals to produce gas-diffusion electrodes 725
V. Electrochemical reactions of hydrogen peroxide and other electrocatalytic reactions 726

I. INTRODUCTION

Organic complexes of metals constitute a novel and extremely promising class of electrocatalysts. Among them compounds containing as ligands various porphyrin derivatives (metal phthalocyanines, tetra-arylporphyrins) attract especial attention. The possibility of using these compounds as electrode materials is due to three main factors—great activity in various heterogeneous redox reactions, semiconductor properties, and high chemical and thermal stability—and would provide a method for replacing catalysts based on precious metals. Enlargement of the scale of application of new technical electrochemical processes, e.g. in sources of current, the photoelectrochemical transformation of solar energy, etc., will largely depend on solving this problem.

Investigation of the mechanism and the kinetics of chemical and electrochemical reactions on organic metal complexes is also of considerable theoretical interest, as it helps to reveal the role of collective and local effects in electrocatalysis and to establish the relation between chemical structure and catalytic activity. These results may be useful also for understanding several aspects of enzymic catalysis. Molecular complexes containing a porphyrin group serve as active centres in protein macromolecules—enzymes and electron-carriers in respiratory chains in living organisms—and play a decisive part in photosynthesis.

The most important task of current research on electrocatalysis is to establish rules for the selection of catalytically active systems. The importance of this problem is increasing especially as a consequence of the almost unlimited number of possible organic compounds.

The present Review, covering the literature to January 1977, examines in the greatest detail published information on the mechanism and the kinetics of the electroreduction of molecular oxygen. Other electrocatalytic and photocatalytic reactions, whose investigation is only beginning, are considered in less detail.

II. ELECTROPHYSICAL AND CATALYTIC PROPERTIES OF METALLOPORPHYRINS

Among organic metal complexes possessing semiconductor properties compounds of the porphyrin series occupy an important place in electrocatalytic investigations. Results on their chemical, electrophysical, and catalytic characteristics have been summarised in several monographs[1-4] and reviews[5-8]. In the present Review, therefore, we shall very briefly consider only those properties that are necessary for an interpretation of the electrocatalytic phenomena.

The two hydrogen atoms attached to nitrogen in the porphyrin molecule can be replaced by a metal to form coordination complexes. The three main groups of porphyrin derivatives are—(i) reduced porphyrins, (ii) porphyrins with substituents at positions 5, 10, 15, and 20, e.g. tetraphenylporphyrin (TPhP), and (iii) porphyrins with benzene rings attached at outer bonds, e.g. tetrabenzoporphyrin (TBP).

Among tetra-azaporphyrin derivatives phthalocyanines (Phth) are especially well known. X-Ray structural investigations have established[1,9] that phthalocyanines of bivalent metals (copper, nickel, iron, cobalt) belong to the monoclinic system, symmetry group D_4h; such high symmetry is a consequence of conjugation effects. Several polymeric metal phthalocyanines are known[1]. Polyphthalocyanines ($Phth_i$) are compounds of high molecular weight having a strip, network, or three-dimensional structure and containing tetra-azaporphyrin macrorings C_8N_8 alternating in a definite sequence. The joining of monomer units into a polymer can occur either through benzene rings (without disruption of conjugation) or through bridging groups (methylene, oxygen, nitrogen, etc.), which are either isolators or weak transmitters of conjugation. The unbroken chain of conjugation in polyphthalocyanines is short (4–6 units).

Monomeric phthalocyanines can exist in more than one modification differing in crystal structure and electrical properties[1]. The monoclinic unit cell comprises two molecules, and the distance between parallel molecules (e.g. in a crystal of copper phthalocyanine) is 3.38 Å; the area occupied by one molecule is 123 Å^2. The α-form has a tetragonal structure and is formed by precipitation from concentrated sulphuric acid or sublimation at high vapour pressures; the β-form can be obtained by heating the α-form above 300 °C. The transition occurs more rapidly and at a lower temperature in a vacuum than in air[1]. In the β-form the phthalocyanine molecules are more densely packed, which leads to stronger interplanar interactions than in the α-modification. For example, the interplanar spacings are 11.8 and 9.8 Å, while the size of the crystals increases from 100–200 Å to 1 μm for the α- and β-modifications of copper phthalocyanine respectively[1].

Porphyrin and its derivatives are characterised by a developed system of conjugated double bonds covering the whole molecule. The changes occurring in metal porphyrins during chemical reactions are associated with electronic transitions in the conjugated system of the ligand and in the electron system of the central metal ion. Therefore an understanding of the nature of catalytic and electrocatalytic processes on organic metal complexes requires a detailed study of their electronic structure.

Quantum-chemical calculations on porphyrin complexes of transition metals have shown[9-14] that the orbitals of the metal, other than those of copper and zinc, interact weakly with the π-system of porphyrin. Zinc and nickel porphyrins are diamagnetic, and those of copper and cobalt are paramagnetic; with iron and manganese several variants of the spin state are possible, because the energies of their obitals are so close to that of the $a_{2u}(\pi)$ molecular orbital. Similar results were obtained[12] for the phthalocyanines of bivalent nickel, cobalt, and iron; a somewhat different electronic configuration was found for manganese phthalocyanine.

The appearance of excited states in the visible and the ultraviolet was attributed[11] to the orbital transitions

$$a_{2u}(\pi)\rightarrow e_g^*(\pi) \qquad a_{1u}\rightarrow e_g^*(\pi).$$

The strong degeneracy and mixing of these energy levels leads to a low-energy state *Q* in the visible and a high-energy state in the region of the Soret band. The *Q*-bands approximate to a one-electron transition in the sequence

porphyrin > tetra-azoporphyrin > tetrabenzoporphyrin > > phthalocyanine.

The results of quantum-chemical calculations correlate satisfactorily with the electronic absorption spectra of porphyrin and its derivatives, although the participation of a large number of orbitals of the ligand system and perhaps *d*-orbitals of the metal must be taken into account in order to intepret the fine structure of these spectra[11,14].

The electronic absorption spectra of polyphthalocyanines on the whole are similar to the spectra of the monomers[15], but the less intense bands become flattened on polymerisation. The invariability of the long-wavelength band, representing the energy levels of the ground and lowest excited states of phthalocyanine, indicates that polymerisation does not affect the character of the π-electron interaction of the benzene and tetra-azaporphyrin rings of phthalocyanine.

A more detailed analysis of the electronic structure of metal derivatives of porphyrin, in particular of the spin state of the central metal ion, is made by comparing theoretical calculations[9,11,12] with experimental results obtained by electron spin resonance[4,5,16-18], Mössbauer spectroscopy[19,20], and measurements of magnetic susceptibility[21,22]. The e.s.r. data show that the unpaired electron in copper and cobalt phthalocyanines is located in $d_{x^2-y^2}$ [16] and d_{z^2} [17] orbitals respectively, which is consistent with the above results of quantum-chemical calculations.

An especially large number of studies have been made on the electronic state of iron ions in porphyrin complexes. However, this question has not yet been clarified. Thus some workers[19] have found the electronic configuration

$$(d_{xy})^2(d_{yz}d_{xz})^3(d_{z^2})^1,$$

but others[21] have found

$$(d_{xy,\ xz})^4(d_{xy})^1(d_{z^2})^1.$$

Calculations[11] indicate that the energy of the orbitals usually increases in the sequence

$$d_{xy}<d_\pi<d_{z^2}<d_{x^2-y^2}.$$

However, experimental and calculated positions for the band corresponding to electron transfer from metal to ligand have suggested[13,14] the alternative sequence

$$d_{z^2}<a_{xy}<d_\pi<d_{x^2-y^2}.$$

In view of the peculiarities of the electronic structure of manganese and iron porphyrins the distribution of d-electrons in these central ions is probably strongly dependent on the mode of preparation and the specific experimental conditions[20,23].

The porphyrin ring is amphoteric: in acid medium the lone pairs of the nitrogen atoms enable it to add one or two protons to form singly or doubly charged cations, and in alkaline medium singly and doubly charged anions can be formed[2]. Protons add to the central nitrogen atoms even at pH 2–3, and the excess charges are uniformly distributed throughout the whole π-electron system of the molecule[24]. In phthalocyanine the first proton is added at considerably lower pH values ($pK \cong 1.8$), probably at a bridging nitrogen atom[25]. The number and positions of protons added to phthalocyanines are still matters of controversy.

Important features of metalloporphyrins, of great value for the interpretation of their catalyic and electrocatalytic properties, are their ability to add additional ligands (extra coordination) and to exist in ionic forms. Possible participation of the latter in catalysis and electrocatalysis makes it necessary to establish the redox potentials of the ring and of the central ions in non-aqueous and aqueous solutions and to identify the path of electronic transfers (ring, metal). The two problems are solved respectively by polarography and by combined study of electron spin resonance[17,18,26,27], electronic[17,18,27-29], and infrared[27,30] spectra. The general approach to these questions and a comprehensive bibliography will be found in Refs.27 and 31.

In contrast to metalloporphyrins, which form singly and doubly charged anions, the molecules of most metal phthalocyanines are capable of adding up to four electrons[12]. Porphyrin complexes in which the metal ion cannot be oxidised (zinc, magnesium, cadmium, copper) undergo oxidation in two one-electron stages[26] with formation of singly and doubly charged cations. In cobalt and iron complexes an electron is probably first detached from the metal, after which the porphyrin ring is oxidised[17,18]. Localisation of the charge depends substantially on the nature of the central metal ion: in singly charged anions of metal-free phthalocyanine and tetraphenylporphyrin the excess charge is localised on the ligand; in both of the cobalt complexes the electron is localised on the central atom[5,28,31]; and in the anions $[FePhth]^-$ and $[FePhth]^{2-}$ the negative charge is shared between the iron atom and the ligand[5,28].

The coordination of additional ligands by planar-coordinated metal porphyrins, termed "extra coordination", is their important property. In relation to heterogeneous catalysis and electrocatalysis it consists merely in the reversible adsorption interaction of reactants and components of the medium with the active centre of the catalyst. For specific aspects of catalysis and electrocatalysis it is of the greatest interest to examine the axial bonding of several simple electrochemically active molecules—oxygen, carbon monoxide, nitric oxide, sulphur dioxide, water—and also component ions of the electrolyte.

Nitric oxide is coordinated to iron, cobalt, and manganese porphyrins in the presence of axially bound ligands containing nitrogen[32-37]. The complex of cobalt porphyrin with nitric oxide can be regarded formally as Co^{III}–NO^- with charge transfer from the $3d_{xz}$ or $3d_{yz}$ orbitals of cobalt to anti-bonding $2p\pi^*$ molecular orbitals of the nitrosyl ligand. π-Interaction of these metalloporphyrins with nitric oxide weakens from manganese to iron and then to cobalt. The same porphyrins form mono- and di-adducts with carbon monoxide[38-41]. Adsorption of the latter gas is more stable than that of oxygen: if they are present together, oxygen is coordinated first, and is then displaced by carbon monoxide. The coordinating power for carbon monoxide falls in the sequence[38]

protoporphyrin > tetraphenylporphyrin > tetrabenzoporphyrin > phthalocyanine.

Electron spin resonance indicates the fully reversible formation of an almost axially symmetric complex by sulphur dioxide with cobalt tetraphenylporphyrin in toluene solution[42].

Optical and e.s.r. measurements have shown that cobalt phthalocyanines, tetraphenylporphyrins, and tetra-*p*-methoxyphenylporphyrins in anhydrous medium (e.g. toluene) at low temperatures (−80 °C) form equimolecular oxygen adducts reversibly[43–47]. In the presence of a strong donor (e.g. imidazole) a mononuclear adduct is formed even at room temperature. The e.s.r. spectra indicate that the oxygen complex of cobalt tetraphenylporphyrin has the electronic configuration $Co^{III}...O_2^-$: i.e. considerable delocalisation of the unpaired electron and partial charge transfer to the oxygen atom take place.

Two models—parallel and unsymmetrical or bent (the Griffiths and Pauling models respectively)—have been used in a quantum-chemical calculation[11] of the coordination of an oxygen molecule with iron porphyrins. With parallel orientation the π_x-orbital of oxygen will overlap the d_{z^2}-orbital of the metal, and the anti-bonding π_x^*-orbital of oxygen the $d_{xz}d_{yz}$-orbitals of the metal. The calculation showed that such coordination should be accompanied by transfer of negative charge (−0.53) from iron to oxygen, which should result in formation of the O_2^- ion in a vibrationally excited state. According to the Pauling version, on formation of a bond between oxygen and iron porphyrin the bent orientation is stabilised by formation of a σ-bond with the d_{z^2}-orbital. Maximum σ-bonding is achieved with an M–O–O angle of 120°. An approximation to this structure is found in oxyhaemoglobin.

A considerable quantity of experimental information has now accumulated on the heterogeneous catalysis of several reactions on metalloporphyrins, detailed accounts of which will be found in reviews[6–8,48]. The range of reactions activated by these complexes is extraordinarily wide; most of the studies have been made on the oxidation of organic compounds—mild oxidation of hydrocarbons (cumene[6,7,49–51], propene[48], mesitylene[52]), oxidative dehydrogenation (of alcohols[8,32,53–55] and cyclohexadiene[56–59])—and on decarboxylation[6,8], processes probably involving a stage of activated adsorption of molecular oxygen on the catalyst with formation of O_2^- or O^- ions. They are therefore of interest for predicting electrocatalytic activity in the cathodic reduction of molecular oxygen, as well as in other electrode reactions involving the adsorption of oxygen as an intermediate stage.

The main effects on the rate and the selectivity of redox reactions are attributed to the nature of the central metal ion[6,8,49,51,55–59], the chemical structure of the organic complex (effect of substituents in the ligand[56–59], polymerisation[6,7,48]), and the crystal structure[6,8,60]. The catalytic activities of phthalocyanines and tetraphenylporphyrins of transition metals—iron, cobalt, manganese, copper, nickel—in the oxidative dehydrogenation of cyclohexadiene have been compared[56–59] with the first oxidation potentials of the catalyst[17]. The catalytic activity of a phthalocyanine complex is greater the lower the first oxidation potential:

manganese > iron > cobalt > nickel, copper.

However, such comparison may well be ambiguous, since the localisation of charge accompanying the oxidation takes place in different regions of the complex—in the electronic system of the central ion in the iron, cobalt, and manganese complexes, or in the ligand in the copper and nickel complexes.

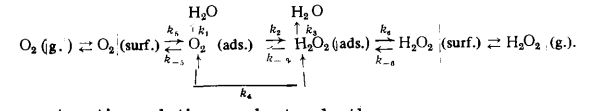
Such correlation is not observed at all for the catalytic properties of tetraphenylporphyrin complexes: the cobalt complex is more active than the iron complex, although their first oxidation potentials are respectively 0.52 and −0.32 V. This is probably connected with the complicated interrelated effects of organic ligand and metal on redox processes, and may indicate that not only the central atom but also the ligand is catalytically active. The latter has recently been convincingly shown[8] for the oxidation of isopropyl alcohol and the decomposition of oxalic acid. It must also be borne in mind that chemisorption bonds may differ in different redox processes, e.g. not only a π-bond with transition-metal ions of a chelate complex but also a bond using unpaired electrons. In the latter case the catalytic activity may correlate with the concentration of paramagnetic centres, as was found[61] for the ortho–para conversion of hydrogen on copper phthalocyanines.

The decomposition of hydrogen peroxide is very often used as model in investigations of the catalytic properties of organic semiconductors. This reaction is especially interesting for electrocatalysis, since in many cases hydrogen peroxide is formed as intermediate in the electroreduction of oxygen. Studies of the decomposition of hydrogen peroxide on phthalocyanines of various metals (iron, cobalt, nickel, copper, manganese, platinum, palladium, ruthenium, osmium, rhodium, and iridium)[6,7,48,62–64] have shown that monomeric ruthenium, osmium, and iron phthalocyanines[62] and polymeric copper phthalocyanine[7,48] are most active. They show also that neither the presence of unpaired *d*-electrons in the central atom nor oxidisability of the latter is a condition of catalase activity by metallophthalocyanines, which is probably due to the ability of certain such compounds to form intermediate complexes with hydrogen peroxide. The activity of a powdered metal (cobalt, copper, nickel) coated with a thin (10^{-5}–10^{-6} cm) continuous film of a phthalocyanine of the same metal far exceeds those of the individual components towards the decomposition of hydrogen peroxide[63]. This can be explained, in terms of the electronic theory of catalysis[65], by injection of electrons from the metal into the phthalocyanine film (when the thickness of the latter does not exceed the depth of shielding) with a consequent displacement of the Fermi level on the phthalocyanine surface.

This example is evidence of the contribution by collective electronic properties to the catalytic activity of organic metal complexes. However, most of the experimental results that have accumulated indicate a definite role for local electron transfers determined by the chemical properties of the catalytic complex organometallic molecule and its electronic structure. In organic semiconductors the interaction between separate molecules is considerably weaker than that between component parts of the same molecule, and every molecule in the crystal lattice is able to retain its individuality. This must probably be taken into account in the first place when catalytic and electrocatalytic research results are examined.

III. KINETICS AND MECHANISM OF THE ELECTROREDUCTION OF OXYGEN ON METALLOPORPHYRINS

The electroreduction of molecular oxygen, studied in the greatest detail with organic metal complexes, takes place on air or oxygen cathodes in chemical sources of current. Reduction of oxygen can follow different paths depending on the nature of the electrocatalyst[66]:



On the most active platinum electrode the process goes mainly via dissociative adsorption of oxygen directly to water (with rate constant k_1).[67,68] Hydrogen peroxide can be formed only in a parallel reaction (k_2). On a carbon electrode molecularly adsorbed oxygen undergoes reduction[69]. Hydrogen peroxide is formed in a two-electron reaction, and

its further transformation occurs at considerably more negative potentials, since $k_3 \ll k_2$. On several electrode materials hydrogen peroxide can be catalytically decomposed (k_4),[67,70] and oxidised by a reverse reaction (k_{-2}). The adsorption and desorption of oxygen (k_5 and k_{-5}) or of hydrogen peroxide (k_6 and k_{-6}) can also be slow stages[71,72]. Electrocatalysis can in principle consist in the acceleration of any stage of this process.

In view of the many-electron character of the electroreduction of molecular oxygen a study of this process should include two main stages—(i) elucidation of the mechanism or path of the process, i.e. establishment of the relation between the partial reactions in the overall process, and (ii) kinetic analysis of the most important partial reactions with the aim of elucidating the nature of the slow stage.

1. Model Systems

Organic metal complexes have low conductance, and are therefore deposited as a thin film on an electrically conducting carrier for the study of their electrocatalytic reactions. Several model systems have been designed for investigations under purely kinetic or strictly defined hydrodynamic conditions.

1. Thin films (10^2–10^4 Å) of organic metal complexes on a smooth, electrically conducting support, which are applied from solution[73–75] or by vacuum sputtering[20,76,77]. Gold or pyrographite is most often used as the support.

2. Extremely thin layers of catalysts comprising a highly dispersed (usually carbon) carrier coated with the organic metal complexes[78–88]. This system is more active than the first and is often used in investigations using a disc electrode with a ring. This method makes it possible to fix on the annular electrode an intermediate product (in the present case hydrogen peroxide) in the reaction occurring on the disc, and is most informative with respect to separation of the process into partial reactions and determination of kinetic parameters for each of the latter[89].

3. Suspension electrodes[82–86], enabling diffusion restraints to be eliminated and electrocatalytic activities of organic metal complexes deposited on a dispersed carrier to be compared under kinetic conditions. A disadvantage is the complicated character of the transfer of charge from particles of the suspension to the current leads[90], a stage which under certain conditions may become rate-determining.

4. Porous gas-diffusion electrodes promoted by organic complexes[58,88,91]. Comparisons of catalytic activity by this method are qualitative, since the characteristics of such electrodes depend significantly on several macrokinetic parameters[92].

Kinetic analysis of electrochemical reactions on organic metal complexes must take into account structural features of the electrical double layer on semiconducting materials, specifically the possible distribution of electrode potential between the Helmholtz layer in the electrolyte and the space charge in the semiconductor[93]. The potential distribution depends on the concentration and mobility of free charge carriers, the concentration of surface states, etc. If the thickness of the semiconductor film is less than the depth of shielding (for organic metal complexes it is 10^{-6}–10^{-5} cm), additional effects are possible as a consequence of injection of charge carriers from the conductor (support) into the semiconductor (catalyst)[65]. This requires investigation of the structure of the complex–electrolyte interface for the above specific systems.

Measurements of differential capacitance on cobalt, iron, and metal-free phthalocyanine films sputtered on to pyrographite have shown that the presence of the film lowers the electrode capacitance to some 10% of that of the support, to ~0.5–0.7 μF cm^{-2} (Fig. 1c).[78,93] The capacitance depends significantly on the a.c. frequency, which probably indicates that the measured capacitance is determined not by the charge of the depleted layer in the semiconductor but by rapid surface states. This suggests that migration of charge in a film is a rapid process.

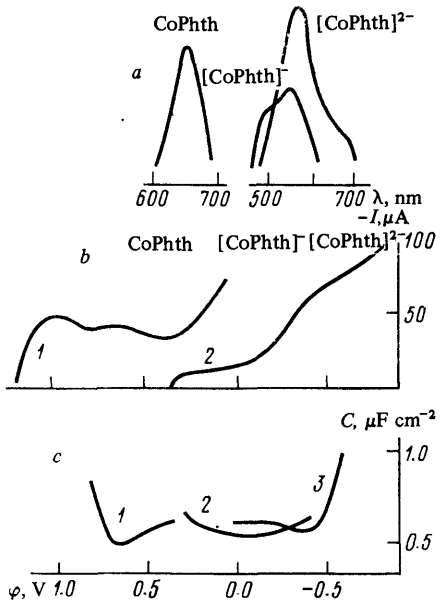


Figure 1. Investigation of cobalt phthalocyanine films at various pH.[78,93]
(*a*) Specular reflectance spectra.
(*b*) Potentiodynamic I–ϕ curves determined on film at pH: 1) 0.3; 2) 14.
(*c*) Dependence of differential capacitance of CoPhth on potential at pH: 1) 0.3; 2) 6.8; 3) 14.

The electronic structure of the neutral state of organic complexes is considered when the nature of catalytic and electrocatalytic activities is discussed. Under the conditions of electrochemical reactions, however, the charge on the complexes may vary (with formation of ionic modifications) as the pH and the electrode potential change. Interesting conclusions follow from a study of the surface state of cobalt phthalocyanine based on comparison of electrochemical and spectral measurements in aqueous solutions at pH 0.3 and 14 (Figs. 1*a* and 1*b*): independently of the pH the potentiodynamic current–potential (I–ϕ) curves of the complex contain several plateaux or maxima, from which to a first approximation three can be isolated in the potential ϕ_r ranges 1.2–0.75, 0.75–0.4, and 0.4–0 V†.

† Here ϕ_r is the potential relative to a hydrogen electrode in the same solution and ϕ the potential relative to a normal hydrogen electrode.

In order to identify electrochemical changes undergone by cobalt phthalocyanine in aqueous solution spectral studies have been made[93] by specular reflectance directly under conditions of electrochemical polarisation. A film of this complex, like all neutral metal phthalocyanines, has an absorption band in the range 600–670 nm. On cathodic polarisation ($\phi < -0.4$ V) the band due to the neutral molecule becomes weaker, and a double band appears at 400–500 nm (Fig. 1*a*). This indicates formation of a singly charged anion of cobalt phthalocyanine with the charge localised on the central cobalt ion. At large negative potentials ($\phi < -0.8$ V) in alkaline aqueous solution a broad band appears representing a doubly charged anion with the second electron localised on the ligand. The reflectance spectrum of iron phthalocyanines undergoes reversible changes under the influence of an electrolyte[94]. A qualitative correlation has been established[20] between the position of the main absorption peak and the spin state of the iron atom in phthalocyanines prepared by different methods. Thus over the potential range of electroreduction of the oxygen molecule the phthalocyanine molecule may be present in various electronic states depending on the pH and the nature of the central ion.

At present information on the structure of the interface between organic metal complex and electrolyte is extremely limited and is related only to a few specific systems used in studying the electroreduction of oxygen. From these results it can be suggested that the potential drop is mainly located in the electrolyte and that charge transfer in the semiconducting film is rapid[20].

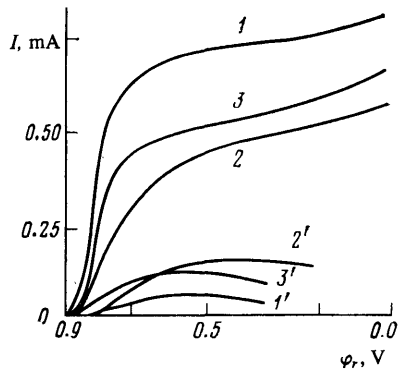


Figure 2. Polarisation curves for the reduction in 0.1 *N* KOH of oxygen on: 1) $CoPhth_i$; 2) CoTPhP; 3) CoTMPhP; 1′–3′) corresponding curves for the oxidation of hydrogen peroxide on a platinised platinum ring ($m = 680$ rev/min).

2. Mechanism of the Electroreduction of Oxygen

Published work reveals the effect of the structure of organic metal complex catalysts, their crystal structure, and the composition of the solution on the mechanism and the rate of the electroreduction of molecular oxygen. The most important factor is the chemical structure of the catalyst molecule—the type of ligand and substituents and the degree of polymerisation on the one hand, and the nature of the central ion on the other.

Macrocyclic complexes containing a system of conjugated π-electrons—phthalocyanines[73–88,95], tetraphenylporphyrins [58,80,81,83–85], dibenzotetra-aza-annulenes (DBTAA)[86,87]—exhibit greater or less activity in the electroreduction of oxygen both in acid and in alkaline solutions. (The number of π-electrons in the inner conjugated system of these complexes is roughly the same at ~18.) Polarisation curves for the reduction of oxygen at a rotating disc electrode coated with a thin layer of polymeric cobalt phthalocyanine, of cobalt tetraphenylporphyrin, or of cobalt tetrakismethoxyphenylporphyrin (CoTMPhP) in alkaline solution have a single wave (Fig. 2),[80,81] in contrast to those of pyrographite[69] or carbon black[96]. Fig. 2 includes for the above compounds the variation of the limiting currents for the oxidation of hydrogen peroxide on the ring. Numerical calculations applied to the results by the method of Ref. 89 have shown that the mechanism of the reduction of molecular oxygen on these organic metal complexes is different: on cobalt tetraphenylporphyrin reaction takes place only with intermediate formation of hydrogen peroxide ($k_1 = 0$);[80,81] on polymeric cobalt phthalocyanine and on cobalt tetrakismethoxyphenylporphyrin parallel direct reduction to water takes place, its contribution to the total process being respectively 50% and 30%.[80,81]

In acid solution only the reaction involving intermediate formation of hydrogen peroxide occurs on all the complexes investigated. The constant k_2 decreases in the sequence[80,81]

$$CoTMPhP > CoTPhP > CoPhth_i > CoPhth.$$

Phthalocyanines are less active in acid solutions than are tetraphenylporphyrin complexes[58,80,81,83–85]. The introduction of electron-donors into the phenyl groups increases the activity of cobalt tetraphenylporphyrin in the sequence[85]

$$-OCH_3 > \langle\bigcirc\rangle > H\ .$$

However, the method of preparation of the chelate is probably quite important. For example, the catalytic activity of cobalt tetraphenylporphyrin was unaffected[58] by the introduction of *p*-methoxy- and *p*-nitro-substituents. Electron-acceptors, e.g. the fluoride ion, do not influence the electrocatalytic activity of cobalt phthalocyanine[58], but lower that of iron phthalocyanine[58,82]. Cobalt dibenzotetra-aza-annulene is more active than the tetraphenylporphyrin chelate in acid solutions[86,87], and neither donor nor acceptor substitutents affect the rate of electroreduction of oxygen on this complex.

Thus, in relation to the electroreduction of molecular oxygen, the organic ligands investigated form the sequences

Phth > TPhP > DBTAA in alkaline solutions
DBTAA > TPhP > Phth in acid solutions.

The nature of the central metal ion has a still more substantial influence on the rate and the mechanism of the ionisation of molecular oxygen on the organic complexes[75–88,95]. In relation to the rate of electroreduction of molecular oxygen (independently of pH) the activity of the metal phthalocyanines varies in the seqence

$$Fe\ (II),\ Fe\ (III) > Co\ (II),\ Mn\ (II) > Ni\ (II) \geqslant Cu\ (II) > 2H\ .$$

With tetraphenylporphyrins at all pH [58,80,81,83–85] and with dibenzotetra-aza-annulenes in acid and alkaline solutions[86,87] the bivalent cobalt complexes are more active than the bi- and ter-valent iron complexes:

$$Co\ (II) > Fe\ (II,\ III) > Ni\ (II),\ Cu\ (II)\ \text{(on TPhP)}\ ,$$
$$Co\ (II) > Mn\ (II) > Fe\ (II,\ III) > Ni\ (II),\ Cu\ (II)\ \text{(on DBTAA)}\ .$$

Systematic investigations using a disc electrode with a ring[75,78–81] have established which reactions in the complicated reduction of molecular oxygen are catalysed by organic metal complexes and how their relative rates vary with the chemical structure of the catalyst. In acid solutions the reaction yielding hydrogen peroxide is accelerated in the presence of metal complexes of phthalocyanine, tetraphenylporphyrin, and tetrakismethoxyphenylporphyrin. In alkaline solutions this is accompanied, in the presence of monomeric and polymeric iron and manganese phthalocyanines, polymeric cobalt phthalocyanine, and cobalt tetrakismethoxyphenylporphyrin, by the direct reaction involving rupture of the O–O bond. Reduction of oxygen to water without intermediate formation of hydrogen peroxide[79] diverges significantly from conclusions reached by other workers[73,74,76,77,82–87], who accept that in all cases reaction occurs only via this intermediate stage.

A correlation has been found[97] between the electrocatalytic activity of metal phthalocyanines and their magnetic properties determined by the spin state of the central ion. In the view of other workers[91], however, no direct relation exists between magnetic moment and electrocatalytic activity. It should be noted that the latter workers[91] use results obtained on porous gas-diffusion electrodes, which diminishes the reliability of the conclusions because of possible distortion by macrokinetic effects.

The nature of the carrier has a considerable effect on the electrocatalytic activity of metal chelates. The greatest activity is achieved by the use of various forms of carbon, with the maximum effect when alkaline groups are present on the carbon surface[82]. The mechanism of these phenomena is still obscure. The electrocatalytic activity of the α-modification of iron(II) phthalocyanine is greater than that of the β-form[76,94]. The electronic spectra of transmitted and reflected light show a ~15 000-cm^{-1} shift of the band to longer wavelengths on passing from the β- to the α-modification, which is attributed[76,94], in agreement with Ref.13, to a greater concentration of high-spin iron(III) phthalocyanine in the latter form. This is due to adsorption of oxygen in the bulk of the α-form and transition of the greater part of the iron(II) complex into a high-spin form. Cathodic polarisation of a specimen of the α-modification leads to an irreversible loss of activity. The enhanced electrochemical activity is attributed to a complex $Fe^{III}Phth-O_2^-$, on which occurs secondary adsorption of the oxygen molecule involved in the electrochemical reaction[76,94].

Detailed investigations of the effect of the method of preparation of monomeric and polymeric iron phthalocyanines on their electrocatalytic activity and the spin state of the central ion have established[20] that a polymer formed on a carrier and containing iron(III) of intermediate spin is the most active; the least active is the iron(II) monomer in the triplet state. However, the state of iron phthalocyanine at the interface with the electrolyte and the mechanism of adsorption of molecular oxygen remain obscure.

The above discussion shows that the main factor in electrocatalysis of the oxygen reaction is local interaction between an oxygen molecule and a catalyst molecule: collective interaction effects may be of secondary importance, at least in the above specific model systems. This conclusion is supported[88] by the lack of correlation between the electrocatalytic activity of phthalocyanines of several metals and their electrical conductivity.

Thus the reaction path of the cathodic reduction of oxygen on organic complexes of metals is now in general clear. On all the metal porphyrins investigated at all pH molecular oxygen is reduced by a consecutive mechanism involving intermediate formation of hydrogen peroxide. On several organic complexes in alkaline solutions (pH 10–14) this is accompanied by simultaneous reduction of oxygen directly to water without intermediate formation of hydrogen peroxide, i.e. involving rupture of the oxygen–oxygen bond either in an oxygen molecule or more probably in the molecular ion O_2^-. In the case of iron phthalocyanine direct formation of water is the main reaction.

3. Kinetics of the Reduction of Oxygen

Investigation of the kinetics of the reduction of oxygen over a wide pH range is necessary in order to ascertain the nature of the slow stage, which has been undertaken for metal-free phthalocyanine, monomeric and polymeric cobalt phthalocyanines, and cobalt tetraphenylporphyrin (Fig.3).[80,81] Table 1 gives typical variations in the kinetic parameters $\partial\phi/\partial \lg i$ and $\partial\phi/\partial$pH for the catalysts under different experimental conditions. Throughout the pH range 0–14 the rate of reduction of molecular oxygen to hydrogen peroxide is higher in the presence of the organic complexes than with carbon black as carrier. With the exception of cobalt tetraphenylporphyrin in acid medium the kinetic parameters of the reduction on the various catalysts are closely similar to those on carbon black. Such coincidence indicates a similar mechanism for the slow stage. Investigations on carbon black[96] and other carbonaceous materials[69,98] have shown that the cathodic reduction of oxygen is governed by the slowness of transfer of the first electron to an adsorbed oxygen molecule (or from an O_2^- ion in the reverse anodic oxidation of hydrogen peroxide):

$$(ML) + O_2 \rightarrow (ML)O_2,$$
$$(ML)O_2 + e \rightarrow (ML)O_2^- \text{ (slow stage)},$$
$$(ML)O_2^- + H_2O \rightarrow (ML)HO_2 + OH^-,$$
$$(ML)HO_2 + e \rightarrow (ML)HO_2^-,$$
$$[(ML)HO_2^- + H_2O \rightarrow (ML) + H_2O_2 + OH^-].$$

The remaining stages, leading to formation of hydrogen peroxide or HO_2^- in acid or alkaline solution respectively, are rapid. In acid and neutral solutions the reaction is irreversible, with $(\partial\phi/\partial\,\text{pH})_{i=\text{const}} = 0$, $\partial\phi/\partial \lg i = 120$ mV, and the transmission or Brønsted coefficient $\alpha = 0.5$. With rise in pH the rate of the reverse reaction increases, and the O_2–$H_2O_2(HO_2^-)$ system approaches reversibility, with a consequent negative shift in potential and decrease in $\partial\phi/\partial \lg i$. It can quite justifiably be assumed that the reduction of oxygen has a similar mechanism on the organic complexes (except for cobalt tetraphenylporphyrin in acid solutions)[80,81].

The behaviour of cobalt tetraphenylporphyrin departs completely from the above scheme, a very interesting phenomenon that merits special attention. A formal explanation can be based on the hypothetical slow stage

$$(ML)O_2 + H^+ + e \rightarrow (ML)HO_2$$

with $\partial\phi/\partial \lg i = \partial\phi/\partial\,\text{pH} = 120$ mV when $\alpha = 0.5$. The change in the mechanism of the reduction of oxygen on cobalt tetraphenylporphyrin and tetrakismethoxyphenylporphyrin in acid solutions may exist because their protonation may differ in character from that of the phthalocyanines.

The kinetics of the reduction of oxygen at various pH has been investigated also on monomeric and polymeric cobalt and iron phthalocyanines[20,94]. Detailed comparison of these results with those of other workers[75,79–81] shows a certain parallelism: in both cases the reaction is of first order with respect to molecular oxygen, the derivative $\partial\phi/\partial \lg i$ decreases with increase in pH to reach ~40 mV at pH > 13, in alkaline solutions the potential becomes more negative with increase in pH, and the slopes of the polarisation curves on promoted

and unpromoted carbonaceous materials coincide. However, it is concluded[20], in contrast to the other workers[75,79–81], that in alkaline solutions chemical cleavage of the O–O bond

$$HO_2^- \text{ (ads.)} + H_2O \rightarrow 2OH + OH^-$$

is the slow stage. This mechanism is clearly of limited value, since it does not explain all the experimental results, especially in non-alkaline media.

Table 1. Kinetic parameters of the reduction of oxygen to hydrogen peroxide on carbon black in the presence of organic complexes*.[80,81]

pH	$\partial\varphi/\partial$ pH, mV	$\partial\varphi/\partial \lg i$, mV
	carbon black	
2—10	0	—90—120
10—14	—60—30	—40—50
	cobalt phthalocyanine	
2—10	0	—100—120
10—14	—60—30	—40—50
	cobalt tetraphenylporphyrin	
0—4	—110	—100—120
4—10	0—10	—100—120
10—14	—60	—40—60

*Closely similar values of the kinetic parameters were observed on films of the phthalocyanines 500–1000 Å thick sputtered on a pyrographite electrode.

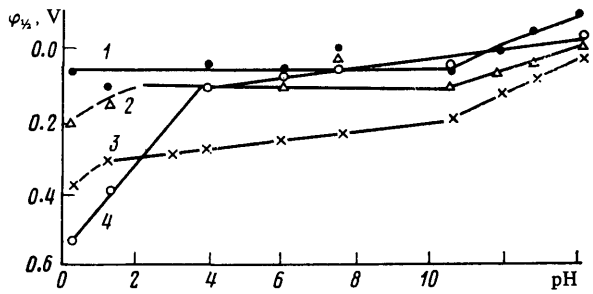


Figure 3. Dependence of half-wave potential on pH for the reduction of oxygen[80,81] on: 1) carbon black; 2) metal-free and cobalt phthalocyanine monomers; 3) cobalt phthalocyanine polymer; 4) cobalt tetraphenylporphyrin.

Several attempts have been made to explain the electrocatalytic action of metal porphyrins on the cathodic reduction of oxygen. The simplest approach is to establish a correlation between electrocatalytic activity and oxidisability[58], the latter measured by the first oxidation potential of the complex. Indeed, if the slow stage is electron transfer from the central ion, these reactions are similar. Good correlation between electrocatalytic activity and oxidation potential actually exists for monomeric iron, cobalt, and copper phthalocyanines, but the situation is considerably impaired with other ligands.

In the mechanism of "redox catalysis"[86,87] the activity of the complexes is related to the tendency of the central metal ion to pass into a higher valency state, i.e. to the third ionisation potential. The metal chelate is oxidised chemically by oxygen or an intermediate product to the cation, which then undergoes the electrochemical stage of cathodic reduction to the original compound. Such an approach does not actually consider the reduction of oxygen. Furthermore, it ignores the mutual influence of ligand and metal ion, which is evident e.g. in the difference in the activity series for phthalocyanines and tetraphenylporphyrins.

The effect of the central ion on the rate of the electroreduction of oxygen has been explained[20,77,78,84,85,94] on the basis of the quantum-chemical calculations of the electronic structure of metalloporphyrins and their oxygen complexes briefly considered in Section II. Stable complexes of oxygen with metal (e.g. iron) porphyrins are formed[11] by adsorption of the oxygen in a lateral position. The d_{z^2} orbital of the cobalt ion is most favourable for bonding an oxygen molecule, since its symmetry ensures the necessary overlap of orbitals[85]. It is assumed that the adsorption of an oxygen molecule on a metal phthalocyanine (tetraphenylporphyrin) is accompanied by formation of a $\sigma-\pi$ double bond between the $d_{xz}d_{yz}$ and d_{z^2} orbitals of the central ion and the π^* molecular orbital of the oxygen molecule. Partial electron transfer from the central metal ion to the antibonding π^* orbitals of the oxygen atom weakens the O–O bond in the molecule. This tends to accelerate the cathodic reduction of oxygen.

Since formation of a donor–acceptor bond requires interaction of filled oxygen orbitals with vacant d_{z^2} metal orbitals, iron(II, III), cobalt(II), and manganese(II) complexes should exhibit the greatest activity, whereas only weak or completely absent catalytic activity can be expected for nickel(II) and copper(II) complexes#. Augmenting the number of delocalised π electrons (polymerising phthalocyanines or introducing donor groups into tetraphenylporphyrin) increases the electron density on the central ion, which facilitates electron transfer to the oxygen molecule and accelerates its reduction. On the other hand, increasing the degree of localisation of the electron on the adsorbed oxygen molecule weakens the O–O bond until it ruptures with direct formation of water. To explain the change in the activity sequence of ligands on passing from acid to alkaline solutions account must be taken of the possible occurrence of reaction on charged forms of the organic complexes (anions, cations), which may be present on the electrode surface within certain pH and potential ranges, as shown at the beginning of this Section.

Discussion of the nature of the electrocatalytic effects on the basis of approximate quantum-chemical calculations is, of course, only qualitative and leaves aside many experimental factors, e.g. the effects of the support or carrier[58,74,82], the crystalline modification[76,94], and the mode of preparation of the organic metal complex[58,78,80]. Their explanation requires a more profound (both theoretical and experimental) study of the adsorption interaction of such complexes with the reactants and investigation of the structure of the catalyst–electrolyte interface and the electronic structure of the adsorbed state.

The validity of this deduction depends on the adequacy of the quantum-chemical calculations in relation to the experimental results. Several discrepancies between them have been mentioned in Section II.

IV. USE OF ORGANIC COMPLEXES OF METALS TO PRODUCE GAS-DIFFUSION ELECTRODES

The great activity of several organic complexes of metals in the electroreduction of molecular oxygen has enabled them to be used to activate oxygen (air) electrodes in electrochemical sources of current[82,88,91,99–114], transducers[115], and other electrochemical devices. The production of active and stable gas-diffusion electrodes requires the solution of several macrokinetic problems in the optimum distribution of catalyst, electrolyte, and gas in a porous electrically conducting matrix with the aim of maximum development of the surface available for the electrochemical reaction[92]. Only results bearing directly on the use of organic metal complexes will be considered here.

Because of the low electrical conductivity of organic metal complexes they are used in combination with a highly dispersed carrier (a carbonaceous material or nickel powder). The catalyst is introduced into the carrier either by mechanical mixing[99,100] or by impregnating the carrier with a solution of the organic complex in concentrated sulphuric acid or other appropriate solvent (pyridine, dimethylformamide, etc.)[101–114]. The latter method is the most usual, since it will give a uniform distribution of the catalyst on the carrier surface. Another method is to form the organic metal complex directly on the carrier surface[91,108,116]. The chief design feature of the electrodes employed in work with these complexes is their water-repellancy, with a stable interface between gas and electrolyte achieved by introducing into the active mass a water-repellant agent (polyethylene or fluoroplastic), which is also a binder. The active mass is applied to a wire-gauze or porous metal base serving as current lead. Other details of the design and technique of preparation of the electrodes will be found in the literature[99–114].

Table 2. Electrochemical activity of oxygen electrodes comprising carbon black promoted with 20% of monomeric metal phthalocyanines in 12 *N* potassium hydroxide at 90 °C.[102]

Catalyst	–	H_2Phth	NiPhth	CuPhth	MoO_2Phth	CoPhth	FePhth	MnPhth	PtPhth	PdPhth
i, mA cm^{-2}, at φ_r = 0.80 V	40	60	8	60	70	130	120	140	110	140

Many monomeric phthalocyanines display extremely high electrochemical activity in porous gas-diffusion electrodes in an alkaline electrolyte. The rates of the electroreduction of oxygen on iron, cobalt, manganese, platinum, and palladium phthalocyanines are several times higher than that on pure carbon black. It is interesting that the introduction of metal-free phthalocyanine into carbon black increases the reaction velocity by ~50%. In the case of cobalt, molybdenyl, and copper phthalocyanines the change from monomer to polymer increases the current density by 100–200% (Fig.4).[102] A similar effect has been observed[108] with polymeric iron phthalocyanine. The influence of method of preparation on the activity of gas-diffusion electrodes has been investigated[102] for polymeric cobalt phthalocyanine.

The activity and the stability of gas-diffusion electrodes depend significantly also on their macrokinetic parameters, which are determined by the porous structure of the water-repellent active layer and the distribution of electrolyte and gas in the latter. These aspects have been investigated in the greatest detail[117,118] on water-repellent electrodes based on carbon black promoted with polymeric cobalt phthalocyanine. Mercury porosimetry indicates that contents of the polymer up to 10 mass % have no effect on the electrode structure; 20 mass % increases the total porosity; and up to 40 mass % some of the narrow pores become blocked. Application of this method to a frozen electrolyte has shown[119] that introduction of the polymer with the same fluoroplastic content leads to a considerable growth of liquid porosity.

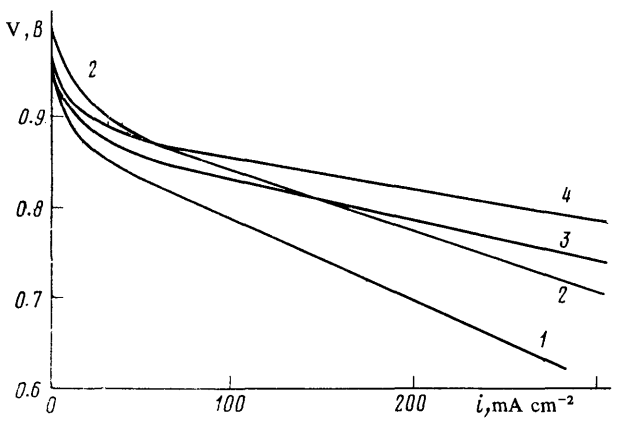


Figure 4. Polarisation curves for the reduction of oxygen, in 12 *N* KOH at 90 °C, on porous carbon electrodes promoted with polyphthalocyanines[102]: 1) $MnPhth_i$; 2) $CuPhth_i$; 3) MoO_2Phth_i; 4) $CoPhth_i$.

The correlation between current density at a gas-diffusion electrode and liquid porosity indicates a direct relation between the structure and the electrochemical activity of an electrode. Optimisation of the structure of the active layer [102,118] has enabled current to be generated under conditions close to optimum, i.e. inner kinetic[92]. The apparent activation energy for porous electrodes promoted with iron and polymeric cobalt phthalocyanines at $\phi_r = 0.83$ V is 4–5 kcal mole^{-1}, which confirms the predominantly kinetic character of the process. Carbon electrodes promoted with a cobalt phthalocyanine polymer have the highest electrochemical parameters in an alkaline electrolyte (0.3 A cm^{-2} at ϕ_r = 0.80 V).

An urgent problem in connection with electrochemical current sources is to develop an oxygen (air) cathode for acid media that does not contain scarce metals, which would avoid the complications associated with the carbonisation of alkaline electrolytes involved in the use of organic fuels or contaminated hydrogen with atmospheric oxygen as oxidant. However, no inorganic catalysts not containing precious metals and sufficiently stable in acid media have yet been reported. Certain organic metal complexes are very promising in this respect.

Table 3 compares the electrochemical characteristics of carbon–oxygen electrodes promoted with organic metal complexes (for acid media)[82,85,103–107,109,111–114,120,121]. The potential of such an electrode promoted with polymeric iron phthalocyanine is 0.85 V at a current density of 10 mA cm^{-2}, but the electrodes are unstable[82]. Some stabilisation of their

functioning could be achieved by varying the mode of preparation of the iron polyphthalocyanine[88,106,107]. The instability in acid solution of the electrochemical characteristics of carbon–oxygen electrodes containing phthalocyanines is probably due to partial dissociation of tetrabenzotetra-aza-porphyrin complexes in acid solutions. Hydrogen peroxide, formed in acid solutions as intermediate in the reduction of oxygen, may also have an adverse effect[80,81]. It oxidises metal phthalocyanines with cleavage of the macroring[1]. This probably limits the direct use of metal-containing porphyrin complexes in acid electrolytes.

Table 3. Electrochemical characteristics of carbon electrodes promoted with organic metal complexes in 3–6 *N* H_2SO_4 at 25–30 °C (τ = duration of functioning).

Active layer	φ_r, V, at i, mA cm^{-2}				τ, h	Ref.
	10	20	40	50		
Carbon black + $CoPhth_f$ + polyethylene	0.70	0.60	0.50	0.43	—	82
Carbon black + $FePhth_f$ + polyethylene	0.85	0.78	0.72	0.70	—	82
Norit BRX + 50% $FePhth_f$ + fluoroplastic	—	0.80	0.75	—	400	88, 106
Carbon + $FePhth_f$ + fluoroplastic	0.78	0.71	0.60	0.56	1000	107
Norit BRX + $CoPhth_f$ + fluoroplastic	0.72	0.69	0.64	—	150	103, 104
Norit FNX + CoTMPhP + fluoroplastic	0.75	0.70	0.65	0.63	300	85
Carbon AG-3 + macromolecular cpd. based on CoTMPhP	0.82	0.79	0.76	0.75	10000	120, 121

Heat-treatment of organic semiconductors at temperatures up to 1200 °C yields pyropolymers characterised by a narrow forbidden gap and significantly higher conductivity. The polymers are probably formed from highly unsaturated aromatic molecules[122] and possess great chemical stability. This group of polymeric compounds is extremely promising for electrolcatalysis.

Table 4. Effect of heat-treatment temperature t on durability τ of oxygen–carbon electrodes containing 5 mass % CoTMPhP in 4.5 *N* H_2SO_4 at 10 mA cm^{-2}.

t, °C	400	600	700	800	900	1000
τ, h	150	350	500	10000	10000	10000

Polyacrylonitrile pyrolysed at 600–1000 °C has been used[123] to activate an oxygen electrode in an acid electrolyte. At current densities of 50–80 mA cm^{-2} the potential of such an electrode was 0.7 V, but in durability tests it fell appreciably.

A method has been proposed[121] for preparing a catalyst based on carbon promoted with organic cobalt complexes (tetraphenylporphyrin, tetrakismethoxyphenylporphyrin, phthalocyanine) to ensure prolonged (>10 000 h) stable functioning of oxygen (air) electrodes in an acid electrolyte (4.5 *N* sulphuric acid). A mixture of carbon and the organic complex (e.g. cobalt tetrakismethoxyphenylporphyrin) is subjected to heat-treatment in an inert gas (helium) at 800° to 900 °C, which does not affect the initial activity of the catalysts, but has a substantial effect on the stability of their operation [Table 4].[120] X-Ray structural examination and elementary analyses have shown that the heat-treatment of cobalt chelates yields new macromolecular compounds whose chemical stability in sulphuric acid exceeds considerably that of the original compounds.

These investigations have shown that the principal parameters of the porous active layer—the total porosity and also the ratio of liquid and gas pores—are not affected by heat-treatment. Results obtained by means of a disc electrode with a ring indicate that microkinetic factors have a decisive role in stabilising the electrochemical characteristics of electrodes having heat-treated catalysts. The rate of conversion of hydrogen peroxide in the presence of thermally stabilised catalysts is increased some tenfold in comparison with the initial organic complexes, which lowers its concentration in the pores of the active layer and stabilises the working of oxygen electrodes in an acid electrolyte.

V. ELECTROCHEMICAL REACTIONS OF HYDROGEN PEROXIDE AND OTHER ELECTROCATALYTIC REACTIONS

Other electrocatalytic reactions on organic metal complexes have been studied in less detail than the electroreduction of molecular oxygen.

1. Reactions of Hydrogen Peroxide

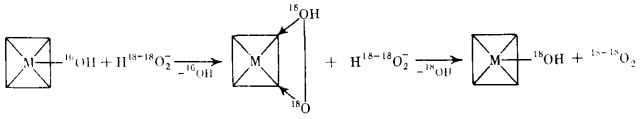
It is of interest from various points of view to investigate the electrode behaviour of hydrogen peroxide. As shown above, in several cases this compound is formed as intermediate in the reduction of oxygen, and its subsequent transformation determines the efficiency of operation of the oxygen (air) cathode. On the other hand, the decomposition of hydrogen peroxide is used as a model in investigations of heterogeneous catalysis on organic complexes. The possibility that it may undergo electrochemical reactions on complexes possessing semiconductor properties is usually ignored§.

Qualitative studies have been made of the cathodic reduction of hydrogen peroxide on phthalocyanines of several metals[73,88,106]. Comparisons have been made[88,106] between the catalytic activity and the conductivity of polymeric cobalt and iron phthalocyanines. The lack of correlation between these parameters led to the catalase activity of phthalocyanines being attributed to acceptor sites, assumed to be defects, dislocations, etc.

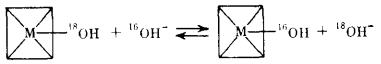
A combination of polarisation measurements, gasometry, and isotopic analysis of the oxygen evolved by the decomposition of hydrogen peroxide labelled with oxygen-18 has permitted[124] separate examination of the chemical and the electrochemical reactions of hydrogen peroxide on monomeric iron and cobalt phthalocyanines. Typical polarisation and gasometric curves are shown in Fig. 5 for cobalt phthalocyanine. Cathodic polarisation of the electrode entails reduction of the peroxide, and anodic polarisation its oxidation with evolution of molecular oxygen (curves *1* and *2*). Decomposition occurs also by a chemical mechanism, as is indicated by the maximum in the potential dependence of gas evolution, in the region of which the decomposition is bimolecular. At more anodic and more cathodic potentials the

§ The work of Roginskii and his colleagues[7] forms an exception.

order of the reaction decreases to unity. The oxygen evolved on decomposition of the labelled peroxide indicates that the peroxy-bond remains unbroken. These results suggest that the mechanism of the breakdown of hydrogen peroxide (e.g. in alkaline solutions) at a steady potential is



which is followed by rapid isotope exchange



so that the evolved oxygen has the same isotopic composition as the original hydrogen peroxide. The phthalocyanine molecule can function only after the chain is complete. Intermediate compounds—complexes of phthalocyanine with one or two adsorbed molecules (ions) of hydrogen peroxide—are essentially the Chance–Ogura complexes formed in the decomposition of hydrogen peroxide by catalase.

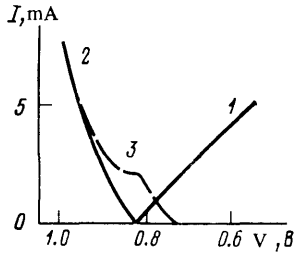


Figure 5. Curves obtained on a pyrographite electrode coated with CoPhth in 1 *N* KOH + 0.005 *N* H_2O_2:[80] 1, 2) polarisation; 3) gasometric.

On the application of electrochemical polarisation the central metal ion becomes able either to donate or to accept electrons, which permits the occurrence of a stationary electrochemical reaction with a consequent change in the order of the reaction to unity. A mechanism for the anodic oxidation and the cathodic reduction of hydrogen peroxide on cobalt and iron phthalocyanines has been suggested[124] on the basis of kinetic results. The pH dependence of the kinetics of the cathodic process enables two regions to be distinguished: $\partial\phi_C/\partial pH \cong 0$ or 120 mV according as the pH is below or above 12. This indicates that the cathodic reaction is controlled by the slowness of the stage

$$H_2O_2 + e \rightarrow OH + OH^- .$$

With respect both to chemical (catalase) and to electrochemical activity the phthalocyanines investigated form the sequence

polymeric cobalt > monomeric iron > monomeric cobalt phthalocyanines.

2. Photocatalytic Reactions

As noted in Section II, phthalocyanines are photoconductors. When thin layers are illuminated in the wavelength range 0.5–0.8 μm, free charge carriers are formed: an internal photoeffect arises. The concentration of free carriers may increase more than hundredfold[1,65] in metal-free phthalocyanine. Recently the effect of illumination on the electroreduction of oxygen has been studied on metalfree, copper, cobalt, and iron phthalocyanines either sputtered on to a support (pyrographite, gold, platinum, etc.)[125,126,128] or deposited from solution on the surface of a mercury drop[127]. Both photoactivity and dark activity are greatly influenced by the nature of the central ion[125,127], the material of the support[125–128], and the solution pH.[125]

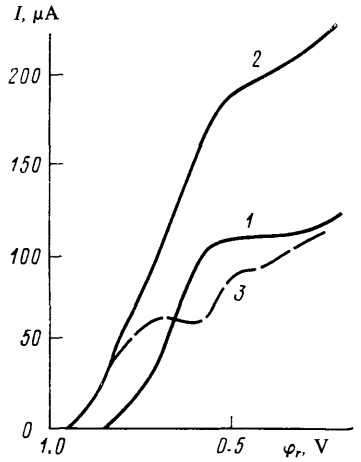


Figure 6. Polarisation curves for the reduction of oxygen on an H_2Phth film (100 Å) in 0.1 *N* KOH: 1) without illumination; 2) illumination with white light; 3) photocurrent[80].

Light has the greatest effect on the rate of the electroreduction of oxygen on metal-free phthalocyanine, the photoelectrochemical activity diminishing in the sequence of phthalocyanines

metal-free > copper > cobalt, iron.

Thus the sequence of electrocatalytic activity of phthalocyanines in the reduction of oxygen with the electrode illuminated has been opposite to that observed under dark conditions. It has been suggested[125,126,128] that light increases the concentration of O_2^- ions without changing the mechanism of the electroreduction of oxygen. According to other workers[127] it increases the rate of cathodic reduction of hydrogen peroxide. Fig.6 shows polarisation curves obtained in 0.1 *N* aqueous potassium hydroxide for the reduction of oxygen on a thin film of metal-free phthalocyanine sputtered on pyrographite. The photocurrent (curve 3) exceeds or equals the dark current, which probably indicates a change in reaction mechanism on illumination of the phthalocyanine—occurrence of the direct reaction to water.

3. Other Reactions

According to the patent literature organic complexes of metals are beginning to be used for activation of the electrooxidation of carbon monoxide[129], hydrogen[110,130], hydrazine [129,130], and several organic compounds (methanol[130], and

formic[129,131] and oxalic[129] acids) and of the electroreduction of carbon dioxide[132] (Table 5). As in the electroreduction of oxygen, phthalocyanines, tetraphenylporphyrins, and dibenzotetra-aza-annulenes of several metals are used. The oxidation of organic and inorganic compounds is catalysed by metal-free, copper, palladium, chromium, and vanadyl phthalocyanines and by nickel, zinc, and platinum tetraphenylporphyrins, i.e. by compounds that are relatively inactive towards the electroreduction of oxygen. Monomeric cobalt, nickel, manganese, palladium, copper, and iron phthalocyanines have been investigated for the electroreduction of carbon dioxide[132]. A high rate of electroreduction to oxalic and gluconic acids was observed only in the presence of cobalt and nickel phthalocyanines. The mechanism of these reactions was not investigated, but this work is evidently promising and will be developed both theoretically and by extending the ranges of electrochemical reactions and catalytically active organic compounds.

Table 5. Electrochemical activities of organic complexes towards oxidation.

Cpd.	Catalyst	Rate of oxidation	Ref.
HCOOH	CoDBTAA	11.0 mA mg^{-1} (φ_r = 0.5 V), 2 *N* H_2SO_4	129
	CoDBTAA, heat-treated	6.8 mA mg^{-1} (φ_r = 0.35 V), 2 *N* H_2SO_4	131
N_2H_4	CoDBTAA	7.5 mA mg^{-1} (φ_r = 0.5 V), 2 *N* H_2SO_4	129
	Co bis-1-hydroxy-anthraquinone	10 mA cm^{-2} ($\Delta\varphi$ = 0.1 V), KOH	130
H_2	PdPhth	500 mA cm^{-2} (φ_r = 0.5 V), 2 M H_2SO_4	130

---o0o---

Intensive reserach on electrocatalysis by organic complexes of metals has been undertaken during the past five years, but appreciable progress has already been made during this short period, both in understanding the nature of electrocatalytic activity and in elucidating the possible practical application of organic catalysts for the activation of electrochemical reactions. Local interaction of the electrochemical reactants with the catalyst molecule is shown to play the chief part. In the electroreduction of oxygen the direction and the rate are determined by the nature of the central metal ion in the organic complex and hence by the character of the adsorption interaction of an oxygen molecule with it. Detailed kinetic investigations have suggested phenomenological schemes for electrode reactions. Several metalloporphyrins are promising electrocatalysts for alkaline electrolytes. New possibilities, especially in acid media, are opened up by the use of thermally stabilised macromolecular compounds.

The task of future research is to extend the range of electrocatalytically active systems and electrocatalytic reactions. A more profound theoretical study is required of the adsorption interaction of reactants and catalyst, which governs the main effects of electrocatalysis. This needs the development of combined physical and electrochemical methods for determining the structure of the interface between organic catalyst and electrolyte.

REFERENCES

1. F.H.Moser and A.L.Thomas, "Phthalocyanine Compounds", Reinhold, New York, 1963.
2. J.E.Falk, "Porphyrins and Metalloporphyrins", Elsevier, New York, 1964.
3. F.Gutmann and L.E.Lyons, "Organic Semiconductors" (Wiley, New York, 1967) (Translated into Russian), Nauka, Moscow, 1970.
4. L.P.Kayushin, Z.P.Gribova, and O.A.Azizova, "Elektronnyi Paramagnitnyi Rezonans Fotoprotsessov Biologicheskikh Soedinenii" (Electron Spin Resonance of Photoprocesses of Biological Compounds), Nauka, Moscow, 1973.
5. A.N.Sidorov and V.G.Maslov, Uspekhi Khim., **44**, 577 (1975) [Russ.Chem.Rev., No.4 (1975)].
6. W.Hanke, Z.Chem., **9**, 1 (1969).
7. S.Z.Roginskii, "Elektronnye Yavleniya v Geterogennom Katalize" (Electronic Phenomena in Heterogeneous Cata-Catalysis), Nauka, Moscow, 1975.
8. S.A.Borisenkova and A.P.Rudenko, Vestnik Moskov. Univ., **17**, 3 (1976).
9. Y.Niwa, H.Kobayashi, and T.Tsuchiya, J.Chem.Phys., **60**, 799 (1974).
10. A.M.Schaffer and M.Gourterman, Theor.Chim.Acta, **25**, 63 (1972).
11. M.Zerner, M.Gouterman, and H.Kobayashi, Theor. Chim.Acta, **6**, 363 (1966).
12. R.Taube, Z.Chem., **6**, 6 (1966).
13. S.C.Mathur and J.Singh, Internat.J.Quant.Chem., **6**, 57 (1972).
14. M.J.Stillman and A.J.Thomson, J.Chem.Soc., Faraday Trans.II, **70**, 805 (1974).
15. B.D.Berezin and L.P.Shormanova, Vysokomol.Soed., **10A**, 384 (1968).
16. D.J.E.Ingram, "Biological and Biochemical Applications of Electron Spin Resonance" (Hilger, London, 1969) (Translated into Russian), Mir, Moscow, 1972.
17. A.Wolberg and J.Manassen, J.Amer.Chem.Soc., **92**, 2982 (1970).
18. F.A.Walker, J.Amer.Chem.Soc., 92, 4235 (1970).
19. B.W.Dale, R.J.P.Williams, P.R.Edwards, and C.E.Johnson, J.Chem.Phys., **49**, 3445 (1968).
20. A.J.Appleby, J.Fleisch, and M.Savy, J.Catalysis, **44**, 281 (1976).
21. C.G.Barraclough, R.L.Martin, S.Mitra, and R.S.Sherwood, J.Chem.Phys., **53**, 1638 (1970).
22. C.G.Barraclough, R.L.Martin, S.Mitra, and R.S.Sherwood, J.Chem.Phys., **53**, 1643 (1970).
23. D.C.Grenoble and H.D.Drickamer, J.Chem.Phys., **55**, 1624 (1971).
24. V.M.Mamaev, G.V.Ponomarev, S.Z.Zenin, and R.P.Evstigneeva, Teor.Eksper.Khim., 6, 40 (1970).
25. B.D.Berezin, Izv.Vys.Ucheb.Zaved., Khim.i Khim. Tekhnol., **14**, 336 (1971).
26. J.Fajer, D.C.Borg, A.Forman, D.Dolphin, and R.H.Felton, J.Amer.Chem.Soc., **92**, 3451 (1970).
27. J.-H.Fuhrhop, K.M.Kadish, and D.G.Davis, J.Amer. Chem.Soc., **95**, 5140 (1973).
28. D.W.Clack and J.R.Yandle, Inorg.Chem., 11, 1738 (1972).
29. A.P.Bobrovskii and A.N.Sidorov, Zhur.Strukt.Khim., **17**, 63 (1976).
30. M.J.Stillman and A.J.Thomson, J.Chem.Soc., Faraday Trans.II, **70**, 790 (1974).
31. L.D.Rollman and R.T.Iwamoto, J.Amer.Chem.Soc., **90**, 1455 (1968).
32. C.Ercolani and C.Neri, Chem.Comm., 1715 (1967).

33. C.Ercolani, C.Neri, and G.Sartori, J.Chem.Soc.A, 2123 (1968).
34. P.K.Picuilo, G.Rupprecht, and W.Schedit, J.Amer. Chem.Soc., **96**, 5293 (1974).
35. B.B.Wayland and L.W.Olson, J.Amer.Chem.Soc., **96**, 6037 (1974).
36. W.R.Scheidt and M.E.Frisse, J.Amer.Chem.Soc., **97**, 17 (1975).
37. W.R.Scheidt and P.L.Picuilo, J.Amer.Chem.Soc., **98**, 1913 (1976).
38. C.J.Welchler, D.L.Anderson, and F.Basolo, J.Amer. Chem.Soc., **97**, 6707 (1975).
39. V.Stynes and B.R.James, J.Amer.Chem.Soc., **96**, 2733 (1975).
40. Shie-Ming Peng and J.A.Ibers, J.Amer.Chem.Soc., **98**, 8032 (1976).
41. I.Collamati, C.Elcolani, and G.Rossi, Inorg.Nuclear Chem.Letters, 12, 799 (1976).
42. B.B.Wayland and D.Mohajer, Chem.Comm., 776 (1972).
43. Y.Iwamoto and T.Kwan, J.Catalysis, **18**, 354 (1970).
44. D.W.Wagnerowa, E.Schwertnerova, and J.Veprek-Siska, Coll.Czech.Chem.Comm., **39**, 1980 (1974).
45. D.V.Stynes, B.R.James, and J.A.Ibers, J.Amer. Chem.Soc., **95**, 1796 (1973).
46. F.A.Walker, J.Amer.Chem.Soc., **95**, 1154 (1973).
47. K.M.Kadish and M.M.Morrison, Third International Symposium Biochemistry, Jülich, 1975, p.100.
48. S.Z.Roginskii, Problemy Kinetiki i Kataliza, **15**, 12 (1973).
49. B.D.Berezin and L.N.Shlyapova, Izv.Vys.Ucheb Zaved., Khim.i Khim.Tekhnol., **14**, 1665 (1971).
50. T.I.Andrianova, A.I.Sherle, and A.A.Berlin, Izv. Akad.Nauk SSSR, Ser.Khim., No.3, 531 (1973).
51. F.Steinbach, Kinetika i Kataliz, **16**, 1094 (1975).
52. E.Kwaskowska-Chec, K.Fried, H.Przywarska-Boniecka, and J.J.Ziolkowski, React.Kinetics Catalysis Letters, 2, 425 (1975).
53. F.Steinbach and K.Hiltner, Z.phys.Chem.(Frankfurt), **83**, 128 (1973).
54. H.Kropf and O.J.Witt, Z.phys.Chem.(Frankfurt), **76**, 331 (1971).
55. N.N.Ionescu, R.H.Schuster, D.Trestianu, and A.Mikhailescu, Z.Chem., **15**, 496 (1975).
56. J.Manassen and A.Bar-Ilan, J.Catalysis, 17, 86 (1970).
57. A.Bar-Ilan and J.Manassen, Intra-Sci.Chem.Reports, 6, 65 (1972).
58. J.Manassen, J.Catalysis, **33**, 133 (1973).
59. A.Bar-Ilan and J.Manassen, J.Catalysis, **33**, 68 (1974) [sic].
60. A.D.Simonova, N.P.Keier, N.N.Kundo, E.K.Mamaeva, and G.V.Glazneva, Kinetika i Kataliz, **14**, 988 (1973).
61. J.K.Acres and D.D.Eley, Trans.Faraday Soc., **60**, 1157 (1964).
62. B.D.Berezin and A.N.Shlyapova, Izv.Vys.Ucheb. Zaved., Khim.i Khim.Tekhnol., **12**, 1641 (1968).
63. S.D.Levina, T.I.Andrianova, M.M.Sakharov, O.A.Golovina, K.P.Lobanova, and Z.A.Rotenberg, Zhur.Fiz.Khim., **40**, 1229 (1966) [Russ.J.Phys.Chem., No.6 (1966)].
64. P.Waldmeier and H.Sigel, Chimia, **24**, 196 (1970).
65. F.F.Vol'kenshtein, "Fizikokhimiya Poverkhnosti Poluprovodnikov" (Physical Chemistry of the Surface of Semiconductors), Nauka, Moscow, 1973.
66. M.R.Tarasevich, Elektrokhimiya, **9**, 599 (1973).
67. M.R.Tarasevich and K.A.Radyushkina, Elektrokhimiya, 6, 376, 372 (1970).
68. M.R.Tarasevich and V.S.Vilinskaya, Elektrokhimiya, 8, 1489 (1972).
69. M.R.Tarasevich, F.Z.Sabirov, and R.Kh.Burshtein, Elektrokhimiya, **7**, 404 (1971).
70. A.M.Khutornoi, G.I.Zakharkin, and M.R.Tarasevich, Zhur.Fiz.Khim., **7**, 404 (1971) [Russ.J.Phys.Chem., No.2 (1971)].
71. M.R.Tarasevich, K.A.Radyushkina, V.Yu.Filinovskii, and R.Kh.Burshtein, Elektrokhimiya, **6**, 1522 (1970).
72. H.S.Wroblowa, Yen-Chi Pan, and G.Razumney, J. Electroanalyt.Chem., **69**, 195 (1976).
73. A.Kozawa, V.E.Zilionis, and R.J.Brodd, J.Electrochem. Soc., **117**, 1470, 1474 (1970).
74. A.Kozawa, V.E.Zilionis, and R.J.Brodd, J.Electrochem. Soc., **118**, 1705 (1971).
75. M.R.Tarasevich and V.A.Bogdanovskaya, Bioelectrochem.Bioenerg., **2**, 69 (1975).
76. M.Savy, G.Magner, and G.Perslerbe, Compt.rend., **275**, 163 (1972).
77. M.Savy, C.Bernard, and G.Magner, Electrochim.Acta, **20**, 383 (1975).
78. V.E.Kazarinov, M.R.Tarasevich, K.A.Radyushkina, and V.N.Andreev, J.Electroanalyt.Chem., **100**, 225 (1979).
79. K.A.Radyushkina, M.R.Tarasevich, and S.I.Andruseva, Elektrokhimiya, **11**, 1079 (1975).
80. M.R.Tarasevich and K.A.Radyushkina, Izv.Vys.Ucheb. Zaved., Khim.i Khim.Tekhnol., **19**, 1639 (1976).
81. M.R.Tarasevich, K.A.Radyushkina, and S.I.Andruseva, Bioelectrochem.Bioenergy., **4**, 3 (1977).
82. H.Jahnke and M.Schönborn, Cómptes rendus des Troisièmes Journées internationales d'Etude des Piles à Combustible, 1969, Presses academiques Européennes, Bruxelles, p.60.
83. H.Alt, H.Binder, W.Lindner, and G.Sandstede, J. Electroanalyt.Chem., **31**, Appl.19 (1971).
84. H.Alt, H.Binder, A.Köhling, and G.Sandstede, Electrochim.Acta, **17**, 873 (1972).
85. H.Alt, H.Binder, and G.Sandstede, J.Catalysis, **28**, 8 (1973).
86. F.Beck, W.Dammert, J.Heiss, H.Hiller, and R.Polster, Z.Naturforsch., **28a**, 1009 (1973).
87. F.Beck, J.Appl.Electrochem., **7**, 239 (1977).
88. H.Meier, W.Albrecht, U.Tschirwitz, and E.Zimmerhackl, Ber.Bunsengesellschaft phys,Chem., **77**, 843 (1973).
89. V.S.Bagotskii, M.R.Tarasevich, and V.Yu.Filinovskii, Elektrokhimiya, **6**, 84 (1972).
90. G.Ya.Slaidin', V.S.Bagotskii, M.R.Tarsevich, L.Yu.Balode, Ya.B.Shimshelevich, G.V.Shteinberg, and Ya.E.Chakste, in "Materialy IV Vsesoyuznoi Konferentsii po Kataliticheskim Reaktsiyam v Zhidkoi Faze" (Proceedings of the Fourth All-Union Conference on Catalytic Reactions in the Liquid Phase), Alma-Ata, 1974, p.346.
91. R.Dabrowski, M.Matysiak, and Z.Witkiewicz, "Electrochemical Power Sources", Prague, 1975, p.178.
92. Yu.A.Chizmadzhev, V.S.Markin, M.R.Tarasevich, and Yu.G.Chirkov, "Makrokinetika Protsessov v Poristykh Sredakh" (Macrokinetics of Processes in Porous Media), Nauka, Moscow, 1971.
93. K.A.Radyushkina, M.R.Tarasevich, and S.I.Andruseva, Zhur.Fiz.Khim., **52**, 1311 (1978) [Russ.J.Phys. Chem., No.5 (1979)].
94. M.Savy, P.Andro, G.Bernard, and G.Magner, Electrochim.Acta, **18**, 191 (1973).
95. W.Beyer and F.Sturm, Angew.Chem., **84**, 154 (1972).
96. S.I.Andruseva, M.R.Tarasevich, and K.A.Radyushkina, Elektrokhimiya, **13**, 253 (1977).
97. J.P.Randin, Electrochim.Acta, **19**, 83 (1974).

98. R.J.Taylor and A.A.Humffray, J.Electroanalyt.Chem., **64**, 63 (1975).
99. R.Jasinski, J.Electrochem.Soc., **112**, 526 (1965).
100. H.Tanaka, A.O.Negishi, and J.Ono, Denki Kagaku, **39**, 596 (1971).
101. K.A.Radyushkina, R.Kh.Burshtein, B.D.Berezin, M.R.Tarasevich, and S.D.Levina, Elektrokhimiya, **9**, 410 (1973).
102. K.A.Radyushkina, O.A.Levina, M.R.Tarasevich, R.Kh.Burshtein, B.D.Berezin, O.A.Kofman, and L.P.Shormanova, Elektrokhimiya, **11**, 989 (1975).
103. M.Musilova, J.Mrha, and J.Jindra, J.Appl.Electrochem., **3**, 213 (1973).
104. L.J.Johansson, J.Mrha, and R.Larsson, Electrochim. Acta, **18**, 255 (1973).
105. J.A.S.Bett and J.T.Lemquist, Amer.Chem.Soc., Div. Fuel Chem.Progr., **13**, 44 (1969).
106. H.Meier, W.Albrecht, U.Tschirwitz, and E.Zimmerhackl, Ber.Bunsengesellschaft phys.Chem., **76**, 1104 (1972).
107. C.Kretzschmar and K.Wiesener, Z.phys.Chem.(Leipzig), **257**, 39 (1976).
108. A.J.Appleby and M.Savy, Electrochim.Acta, **21**, 567 (1976).
109. French P.1 582 905 (1969); Chem.Abs., **73**, 5165 (1970).
110. US P.3 585 079 (1971); Chem.Abs., **77**, 13 245 (1972).
111. BRD P.Application 2 046 354 (1972); Chem.Abs., **77**, 69 412 (1972).
112. BRD P.Application 2 049 008 (1973); Chem.Abs., **78**, 91 840 (1973).
113. French P.2 100 585 (1972); Chem.Abs., **78**, 51 860 (1973).
114. BRD P.Application 2 549 083 (1977); Chem.Abs., **87**, 104 469 (1977).
115. S.J.Yao, M.Michuda, F.Markley, and S.K.Wolfson, "Direct Conversion of Thermal into Electrical Energy and Fuel Cells", Inf.Byull., **4**, 141 (1974).
116. S.N.Pobedinskii, A.A.Trofimenko, M.I.Bazanov, A.N.Aleksandrova, K.N.Belongov, and M.I.Al'yanov, in "III Vsesoyuznyi Simpozium po Kinetike i Mekhanizmu Reaktsii s Uchastiem Kompleksnykh Soedinenii" (Third All-Union Symposium on the Kinetics and Mechanism of Reactions Involving Complex Compounds), Ivanovo, 1974, p.102.
117. A.V.Dribinskii, M.R.Tarasevich, R.Kh.Burshtein, N.N.Lezhnev, K.A.Radyushkina, O.A.Levina, and R.I.Zusman, Elektrokhimiya, **14**, 22 (1978).
118. A.V.Dribinskii, M.R.Tarasevich, R.Kh.Burshtein, K.A.Radyushkina, and O.A.Levina, Elektrokhimiya, **13**, 1631 (1977).
119. A.V.Dribinskii, M.R.Tarasevich, and R.Kh.Burshtein, Elektrokhimiya, 7, 1144 (1971).
120. V.S.Bagotskii, M.R.Tarasevich, K.A.Radyushkina, O.A.Levina, and S.I.Andruseva, Dokl.Akad.Nauk SSSR, **233**, 889 (1977).
121. O.A.Levina and K.A.Radyushkina, USSR P.542 416 (1975); Byull.Izobr., No.27, 205 (1977).
122. A.A.Berlin, Uspekhi Khim., 44, 502 (1975) [Russ. Chem.Rev., No.3 (1975)].
123. G.Richter and G.Luft, Ber.Bunsengesellschaft.phys. Chem., **76**, 1105 (1972).
124. G.I.Zakharkin and M.R.Tarasevich, Elektrokhimiya, **11**, 1019 (1975).
125. G.A.Alferov and V.I.Sevast'yanov, Elektrokhimiya, **11**, 827 (1975).
126. V.I.Sevast'yanov, G.A.Alferov, A.N.Asanov, and G.G.Komissarov, Biofizika, **20**, 1004 (1975).
127. Yu.S.Schumov and M.Heyrovsky, J.Electroanalyt. Chem., **65**, 469 (1975).
128. B.Schreiber and M.Savy, Compt.rend., **282**, 787 (1976).
129. BRD P.Application 2 128 842 (1972); Chem.Abs., **78**, 79 028 (1973).
130. US P.3 617 388 (1971).
131. H.Jahnke, M.Schönborn, and G.Zimmermann, Topics Cur.Chem., **61**, 133 (1976).
132. S.Meshitsuka, M.Ichikawa, and K.Tamaru, Chem. Comm., **5**, 158 (1974).

Institute of Electrochemistry,
USSR Academy of Sciences,
Moscow

Translated from *Uspekhi Khimii*, **49**, 1523-1553 (1980) U.D.C. 541.64:539.3

Determination of the Useful Lifetime of a Polymeric Material as a Physicochemical Problem

O.N.Karpukhin

The principal problems of the determination of the useful lifetime of a polymeric material under various operating conditions in a given article are formulated, the disadvantages of the traditional simplified empirical approaches to solutions of problems of this kind are analysed, and the principal trends in physicochemical research, which lead to success in solving the given problem, are discussed.
The bibliography includes 50 references.

CONTENTS

I.	Introduction	731
II.	Formulation of the problem	731
III.	Extrapolation of the results of tests on the polymeric material to operating conditions	733
IV.	The "change in the mechanism" of the ageing of a polymeric material on passing from test conditions to operating conditions	736
V.	Allowance for the variability of operating conditions	740
VI.	Initial data for the formulation of the problem of the prediction of the useful lifetime	743
VII.	Kinetic classification of ageing mechanisms	744

I. INTRODUCTION

The quality of a material consists of the set of its properties which are important in practice. However, not only the properties of the material at a given instant, as it were, its instantaneous properties, but also the way in which the properties of the material vary under different operating conditions are of practical importance; this characteristic of the quality of the polymeric material (PM) in fact determines its useful lifetime.

The instantaneous properties of the material can be measured in different ways and the number of such methods is large and they have been thoroughly developed. At the present time one can characterise quantitatively virtually any instantaneous property of the material, it is possible to determine any of its mechanical or rheological characteristics, its spectrum of mechanical or dielectric losses or its absorption or luminescence spectra can be characterised, the composition of the material and that of its impurities can be determined, and it is even possible to determine the composition of the active species formed in the material under any conditions.

Unfortunately however, apparatus for measuring one extremely important property of the material, which determines the kinetics of the variation of its instantaneous properties under any conditions and hence its useful lifetime under these conditions, does not and apparently cannot exist. The solution of this problem, which requires investigation, is sometimes simple and sometimes fairly complex. The present review is devoted to problems of the methodology of such investigations. They are of urgent importance at the present time by virtue of two causes of different kinds.

On the one hand, the assortment of polymeric materials with different properties, materials which are either already produced industrially or whose industrial production can be achieved, has increased. In this connection the problem arises of the optimum application of the given material or the optimum material for a given article, and not simply the problem of the determination of the useful lifetime of the given material. Materials with enhanced stability are not always best for a given article, since an increase of stability usually entails also an increased cost of the material and excessive stability of the material creates the additional problem of the disposal of the residue after the given article has failed. Therefore if, as commonly occurs, the predicted useful lifetime of the material is too short, the result may be large unnecessary expenditure on excessive stabilisation of the material or reinforcement of the constructions produced from the material.

On the other hand, the present state of the theory of the ageing of polymeric materials makes it possible to pose the question of a more rigorous formulation of problems associated with the determination of their useful lifetime. More than ten years ago the principal problems of the fundamental research into the question of the ageing of polymeric materials were formulated[1,2] and a long series of studies on these lines was initiated. Considerable experience in work with polymeric materials has now accumulated, extensive experimental studies have been carried out, the foundations have been created for a theory of the ageing of polymeric materials, methods have been developed for the determination of the quantitative characteristics of this process, and the first successes have been achieved in the description of the kinetics of the variation of properties of polymeric materials of practical importance in the course of ageing on the basis of data on the mechanisms of the processes occurring in polymeric materials[3]. All these factors suggest that it is already possible to pose the question of the replacement of what is actually an empirical method of forecasting generally used at the present time by a scientific approach to the problem based on the understanding of the fundamental features of the mechanisms of the processes occurring in the ageing of polymeric materials.

II. FORMULATION OF THE PROBLEM

1. The Necessary Initial Data

The instantaneous properties of the material can be characterised quantitatively by a point in the multidimensional space of properties or by a vector **Y** directed to this point. The components of vector **Y** are quantitative characteristics of the instantaneous properties of the material, its composition, strength (σ), dielectric losses tan δ, optical density, etc.

The polymeric material should possess a set of properties in order to be suitable for use in a given article. This means that in the space of the instantaneous properties of the material there exists a region of operational suitability of the material S_0. If the vertex of the vector **Y** falls within this region, then such a material can fulfill its necessary functions in the given article at the given instant.

However, the condition that the vector Y falls within the region S_0 is itself insufficient for the material to be used in the given article. It is necessary that throughout the entire useful lifetime of the article the vertex of the vector **Y** does not leave the region of the operational suitability of the material. In the course of use and storage the properties of the material Y gradually change as a result of the ageing processes occurring in it. The vertex of the vector Y gradually shifts in the space of properties (Fig.1). The way in which it shifts depends not only on the properties of the material, but is also determined by the conditions under which the material is used. In the course of ageing the relative contributions of the properties change and the vertex of the vector Y shifts along different trajectories, which depend on the process conditions.

In the general case these conditions can be characterised by another vector **X** in the space of operating conditions. Its components will be, for example, temperature, stress, intensity and spectral composition of the incident radiation, humidity, oxygen pressure, etc. Thus the problem of the determination of the useful lifetime of the polymeric material is a special case of the more general problem of the determination of the kinetics of the variation of the properties of such a material under any conditions, i.e. the problem is to find the function

$$\mathbf{Y}=\mathrm{f}(\mathbf{X}, t). \qquad (1)$$

In this treatment the breakdown of the polymeric material in a given article is characterised by the time during which the vertex of the vector Y reaches the limit of the region of the operating suitability S_0 under conditions **X**.

Consequently the useful lifetime of the polymeric material is determined by (1) the properties of the material, (2) the operating conditions **X**, and (3) the requirements which the material must meet or the region of its operating suitability S_0.

Accordingly, the accuracy of the determination of the useful lifetime of the polymeric material depends not only on the extent to which the characteristics of the instantaneous properties of different specimens of a given material are uniform, but also on the accuracy of the determination of its operating conditions and of the characteristics of its operating suitability.

2. The Purpose of Prediction

When the question of the prediction of the useful lifetime of a material is considered, one usually examines two different problems: the problem of determining the useful lifetime of the given material under specified conditions of its use and storage and the problem of determining the guaranteed lifetime of the material in articles of a particular type.

The solution of the first problem is directed towards the determination of the most probable useful lifetime of the material under operating conditions which are known beforehand and have been determined accurately. This is in essence a physicochemical problem which must be solved on the basis of current ideas concerning the physicochemical ageing processes in the material and on the basis of the results of accelerated tests of the material carried out under rigorously controlled conditions.

The determination of the guaranteed lifetime of the material is a qualitatively different problem. In the course of the guaranteed lifetime the material can exist in a certain range of operating conditions and it is necessary that the probability of the loss of its operating suitability under these conditions should not exceed a certain quantity corresponding to a specified coefficient of reliability of the article made from this material[4,5]. In solving this problem, one must take into account the possible variability of the properties of different batches of the material or of the material in different articles, the possible differences in their operating conditions, and even the possible differences in the requirements which must be met by different articles of a given type.

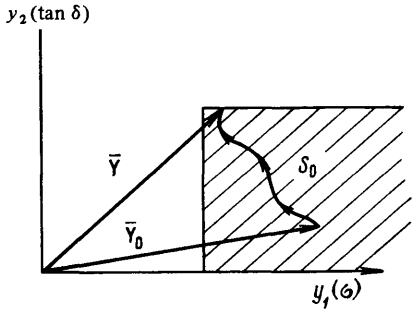


Figure 1. Trajectory of the variation of the properties of the polymeric material. For the significance of the notation, see text.

The basis of the problem is statistical and belongs to the theory of reliability. If the first problem has been solved, then the second can also be solved by statistical mathematical methods, provided that the distributions of the properties of the material, its operating conditions, and its operating suitability have been specified.

This review deals mainly with questions associated with the solution of the first problem. Problems of reliability are involved only in connection with the experimental error in the measurement of the rate of change of the properties of the material and in connection with the problem of averaging the time-variable operating conditions of the material.

3. Principal Ways of Determining the Useful Lifetime of a Polymeric Material

There exist two idealised ways of determining the useful lifetime of a polymeric material.

1. Modelling of the operating conditions of the polymeric material in the laboratory, i.e. laboratory tests on the material under conditions identical with its operating conditions in the given article.

2. The study of the detailed mechanisms of all the processes occurring in the material and calculation from these data of the useful lifetime of the material under any conditions.

Neither of these procedures can be recommended in the pure form as a realistic method for the solution of the problem of prediction.

Modelling cannot in essence be regarded as a method for the prediction of the useful lifetime of the material. With the aid of modelling, one can really only determine the useful lifetime of the material under the given conditions and one need know nothing about the processes which lead to an alteration of the properties of the material. It is sufficient to reproduce satisfactorily the operating conditions of the material in the laboratory, to place the material under these conditions, and to measure its useful lifetime. The accuracy of the determination of the useful lifetime depends in this case only on the accuracy with which the operating conditions are simulated.

However, not all operating conditions can be modelled in the laboratory and in choosing the material for a given article one can hardly seriously entertain the procedure involving the preparation of the article from all possible combinations of materials. Therefore modelling is usually employed in the last stages of the investigation when the material for the article has been chosen by some other methods and it only remains to refine its useful lifetime. In essence, the procedure involving the modelling of the operating conditions in the laboratory or the determination of the useful lifetime by interpolating the results of laboratory tests does not constitute prediction—with its aid one can only conclude what the result of the test is. This method in essence lacks any predictive power.

Nevertheless prediction is necessary, since one must know how all the properties of materials, which must be used for many years or under unique conditions, will vary. The question of the prediction of the stability of a polymeric material arises when one must decide whether a given material is or is not to be manufactured, or whether or not a given article is to be made from this material. A number of examples of problems the solution of which require the prediction of the useful lifetime of the polymeric material are listed below.

1. Determination of the useful lifetime of articles to be stored and used for a long time:
   (a) Constructional materials (medicine, building industry);
   (b) Specialised engineering applications (photographic materials, electronics);
   (c) Conservation of articles (spare parts, stock of spare articles).
2. Construction of articles:
   (a) Optimum materials for articles;
   (b) Optimum applications for the material.
3. New materials:
   (a) The search for applications of given materials;
   (b) Estimation of the scale of manufacture.
4. Mass applications of materials:
   (a) Estimation of the relative scales of industrial manufacture;
   (b) Elucidation of the time and extent of repairs;
   (c) Utilisation of waste.

In all these cases extrapolation of the results of preliminary tests to conditions under which the material has never been tested is required and not the interpolation of the results of tests on polymeric materials. In essence, the difference between the problem of the prediction of the useful lifetime of a polymeric material and the problem of the modelling of the operating conditions in the laboratory is the same as the difference between the problems of extrapolation and interpolation.

The second idealised method for the solution of the problem is also unrealistic. Evidently, a detailed study of the mechanism of ageing leads to the solution of the problem and ultimately makes it possible to determine the useful lifetime of the given material under any conditions, and usually with any degree of accuracy. However, this procedure is known to be laborious and long. Despite the fact that polymer chemistry has already existed for several decades, there are only a few materials whose useful lifetime can be predicted from the knowledge of the mechanism of their ageing and only under certain conditions. Nevertheless, this way of solving the problem is in fact used in the leading laboratories in the world in which fundamental research is being carried out, and this research actually determines the level of our knowledge about the mechanisms of the ageing processes in the polymeric material and makes it possible to cover the entire wide variety of materials, the methods for their synthesis, and the ways in which they can be modified and adapted to the solution of particular problems. The second method of solution therefore predominates in the initial stages of the study and in choosing the material.

Most of the work on the determination of the useful lifetime of polymeric materials is performed by methods which lie somewhere between these two idealised procedures. In real prediction both empirical methods involving the extrapolation of the results of laboratory tests on the material and the available information about the ageing mechanism are widely used. If the prediction is based largely on the results of tests on the given material, then one speaks of empirical and semiempirical methods of prediction; on the other hand, if information about the fundamental features of the mechanism of the ageing of the material predominates, then one speaks of describing the kinetics of the variation of the properties of the material on the basis of complete or incomplete knowledge of the process mechanism[6].

In both cases the prediction is based on the extrapolation of the results of laboratory tests on the material to its operating conditions, but extrapolation and laboratory tests are understood to have the same broad significance. The result of a test on the polymeric material includes not only the results of its study but also the set of all the accumulated experimental and theoretical information about the given material as well as any of its analogues, while extrapolation includes the development of methods of adjusting the results of tests for any operating conditions, which are as fully characterised as is possible.

III. EXTRAPOLATION OF THE RESULTS OF TESTS ON THE POLYMERIC MATERIAL TO OPERATING CONDITIONS

1. Mathematical Difficulties

In predicting the useful lifetime of the polymeric material one must solve the following problem. There exists a region Z_0 in the conditions governing the tests on the material. In this region of conditions the tests are carried out. On their basis, one obtains in some way, for example, by interpolation, a mathematical description of the kinetics of the change in the properties of the material $\mathbf{Y}(\mathbf{X}, t)$. It is necessary to extrapolate this relation outside the limits of the region Z_0.

In this formulation of the tast, problems of a mathematical nature immediately arise. In mathematics the task formulated in this way is invalid[7]. In the general case any problem of extrapolation is invalid because one can always select a function which describes adequately all the available experimental data and which behaves arbitrarily outside the region of the tests.

On the other hand, common sense suggests that such absolute invalidity of the extrapolation problem is probably too extreme. In the vicinity of the region in which the tests are carried out there is bound to be a region in which extrapolation is possible. The problem formulated must not

concern the existence or non-existence of such a region and must deal with the information required to extend this region and to increase the accuracy of a well-founded extrapolation within this region.

The possibility of validating the problem which is invalid from the mathematical point of view by relatively straightforward methods can be seen from the following simplest example. Suppose that it is necessary to extrapolate over a long time interval the decreasing relation $Y(t)$ illustrated in Fig.2. The conditions are constant throughout the process and the extrapolation must be carried out on the basis of the results of tests indicated by points in Fig.2.

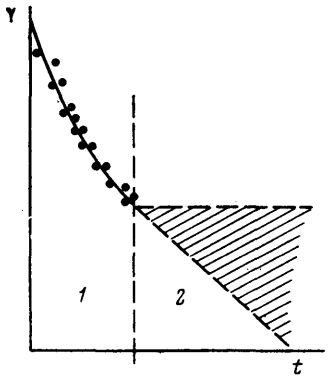


Figure 2. Example of the simplest extrapolation: 1) region of tests Z_0; 2) region of extrapolation. The shaded region represents the possible extrapolation in accordance with Eqn.(3).

If no limitations are imposed on the extrapolated relation, then, outside the range of measurements, it can vary arbitrarily. Indeed, the relation can be continued through any point outside the range of measurements, using, for example, a polynomial function containing more parameters than the number of experimental points. However, even a simple limitation, which is natural for many chemical processes, namely

$$Y<Y(0),\ \frac{dY}{dt}<0,\ \frac{d^2Y}{dt^2}>0, \tag{2}$$

and which postulates that the relation must decrease monotonically and must have no points of inflection, makes it possible to produce a well-founded prediction for virtually any time.

When $t>t_0$, any solution can be found between two straight lines:

$$f_1(t)=f(t_0);$$
$$f_2(t)=f(t_0)+(t-t_0)\left(\frac{df}{dt}\right)_{t=t_0}. \tag{3}$$

It appears that, when one specifies a narrower class of functions which can describe the given relation, then the accuracy of the extrapolation can be increased compared with Eqn.(3), and it is also possible to obtain data concerning the possible distribution of the error of the extrapolation for any t.

Thus the introduction of a series of such very simple constraints made the invalid extrapolation problem entirely valid and susceptible to solution by methods of modern mathematical statistics and computer techniques.

Unfortunately the region where such problems can be solved has so far been poorly worked out. Only problems in which the form of the $Y(X, t)$ relation is known exactly are solved. It is then possible to find not only the most probable extrapolation and the distribution of the expected error, but also to specify the optimum plan of tests whereby one can carry out the extrapolation with the minimum error[8].

When the mechanism of the ageing of the given material has not been established, it is usually impossible to predict exactly the form of the kinetic curve. However, the general understanding of the essential features of the processes occurring during ageing frequently makes it possible to specify the general characteristics of the expected relation. In some cases one may expect a monotonically decreasing relation analogous to that illustrated in Fig.2, while in others one can postulate a curve with a point of inflection or a relation with a characteristic induction period, etc. One can hardly assume that the $Y(X, t)$ relation will undergo a large number of oscillations for time-invariant external conditions X. All this qualitative information makes the problem of extrapolation valid from the mathematical point of view.

The greater the amount of the information available about the ageing mechanism, the more fully and more accurately can one describe the form of the kinetic curve and the greater the accuracy of the useful lifetime predicted by extrapolation.

This general consideration of the extrapolation problem shows that the problem of the characteristics of the form of the kinetic curves for the variation of the properties of the polymeric material under various conditions, i.e. the problem of the classification of the mechanisms of the ageing of polymeric materials and the characteristic features of each class of mechanisms, is particularly important for the prediction of the useful lifetime of polymeric materials. On the other hand, the mathematical problem reduces to ensuring that in the course of extrapolation there is the smallest possible loss of information accumulated both in the tests on the polymeric material and in the compilation of the *a priori* information about it.

2. Traditional Predictive Methods

For the majority of materials, the ageing mechanism has not yet been established. Therefore in predicting the useful lifetimes of such materials one frequently (see, for example Elizavetin[9]) uses methods based on the simplest hypothesis that the ageing of the polymeric material can be formally described as an elementary chemical reaction. The rate of this reaction is determined by a rate constant, which varies with temperature according to the Arrhenius law and which varies under the influence of mechanical stresses in accordance with Zhurkov's equation; in the presence of radiation, the constant increases in proportion to the intensity of the latter:

$$k=k_0 I e^{-(E-\gamma\sigma)/RT}, \tag{4}$$

where E is the activation energy for the process, σ the mechanical stress, I the intensity of light, and γ and k_0 are proportionality coefficients. The majority of methods for the useful lifetimes of polymeric materials used at present have been based on this hypothesis.

According to a USSR Government Standard (GOST),[10,11] it is recommended that the temperature dependence of the useful lifetime of the polymeric material be described in terms of the Arrhenius equation. The lifetime of the polymeric material under mechanical forces is described by the Zhurkov equation:

$$\tau = \tau_0 \exp\left(\frac{E - \gamma\sigma}{RT}\right). \quad (5)$$

The principle of the summation of the faults arising in the course of the ageing in the polymeric material, otherwise known as the principle of superposition, is widely used[12,13]. The mathematical expression of this principle is Bailey's equation[14], according to which, under the conditions of a time-variable influence on the polymer, its useful lifetime τ is defined by the equation

$$\int_0^\tau \frac{dt}{\tau_0(\mathbf{X}(t))} = 1, \quad (6)$$

where $\tau_0(\mathbf{X})$ is a function characterising the relation between the useful lifetime of the material and its operating conditions for constant $\mathbf{X}$ and $\tau_0\mathbf{X}(t)$ is the same function where the time-variable characteristic of the operating conditions $\mathbf{X}(t)$ has been substituted as the argument. On the other hand, the useful lifetime τ to be determined is involved in this equation as the integration limit.

Combination of the Arrhenius equation with Bailey's equation leads to the familiar principle of the temperature–time superposition, which establishes the equivalence of the influence of temperature and the duration of that influence. Thus in the field of mechanical stresses the useful lifetime of a polymeric material should be defined by the equation

$$\int_0^\tau k_0 e^{-[E-\gamma\sigma(t)]/RT(t)}\, dt = 1. \quad (7)$$

The superposition principle is valid when the change in the properties of the material is irreversible and when these properties vary in the space of properties along a single trajectory whatever the operating conditions. This also shows that the ageing of the material proceeds to the same extent whatever the sequence in which the operating conditions are altered.

A corollary of the superposition principle is that constant conditions, equivalent to variable operating conditions exist. Thus Eqns.(4) and (7) show that the time of accelerated tests (τ_{equiv}), at the chosen temperature T_0 and under the conditions of a stress σ_0, which is equivalent to operation during a period τ at an arbitrary temperature $T(t)$ and stress $\sigma(t)$, is determined by the relation

$$\tau_{equiv} = \int_0^\tau e^{-\left(\frac{E-\gamma\sigma(t)}{RT(t)} - \frac{E-\gamma\sigma_0}{RT_0}\right)} dt. \quad (8)$$

By means of simple rearrangements, it is possible to obtain from Eqn.(8) the familiar equation for the equivalent temperature[15–17]

$$T_{equiv} = \frac{E}{R \ln\left(\frac{1}{\tau}\int_0^\tau e^{-E/RT(t)}\, dt\right)}, \quad (9)$$

at which the properties of the material change would change by the same amount during the period τ as they do with a variable temperature $T(t)$.

All these principles and equations are valid for the determination of the useful lifetime of materials whose ageing can be described as a single elementary chemical reaction of any order. Even in the presence of two parallel stages one may expect the breakdown of the Arrhenius law and the failure of Bailey's equation. These questions will be examined in greater detail in the following Sections.

Nevertheless the principles discussed above have been used successfully to describe the kinetics of the variation of the strength and viscoelastic characteristic of polymeric materials under conditions such that the mechanical stress is the principal factor responsible for the change in the properties of the material. For example, Zhurkov's equation describes the lifetime of many polymeric materials acted upon by mechanical loads[18]. However, over a wide range of stresses, particularly under conditions such that, apart from the stress, the ageing process is influenced also by other factors (such as oxygen, light, ozone, etc.), Eqn.(6) does not hold. Even the "fatigue" characteristics of the material are very difficult to describe by these methods, let alone the "static fatigue" which causes the material to break down regardless of the applied stress. This is apparently due to the fact that the "fatigue" of the polymeric material, i.e. its breakdown when acted upon by small stresses, is determined mainly by the irreversible physicochemical transformations of the material, induced by other causes such as oxidation, photochemical transformation, interaction with a corrosive medium, etc., and not by stresses. The mechanism of these processes is usually fairly complex and cannot be described at the level of empirical functions of the susceptibility of the material to damage, which vary with time in the same way as in a pseudoelementary nth order reaction and it is therefore necessary to take into account the influence of the stress on each elementary step of the complex ageing process. A relatively wide range of studies has now been carried out[20,21] in which an attempt has been made to predict the useful lifetime of polymeric materials while retaining the principles of the above methods. For example, the breakdown of the linearity of the plot of the logarithm of the lifetime against the reciprocal of temperature is treated as the variation of the activation energy for a process, and the physical causes of this variation are sought. The so-called pole in Zhurkov's equation is displaced and the physical nature of this displacement is elucidated. The essence of these phenomena is probably associated with the non-elementary nature of the ageing of polymeric materials under these conditions. It is hardly possible to solve successfully the problems arising by assuming that the ageing process of the polymeric material and hence the kinetics of the variation of its properties can be formally regarded as a single chemical reaction.

A radical-chain mechanism of the mechanothermal degradation of a polymer, including a chain initiation stage involving the rupture of strained bonds in the macromolecules, depolymerisation, chain transfer with formation of a central radical, the decomposition of this radical under the influence of stresses, the migration of the free valence along the central radical, and chain termination, has been examined[22]:

$$\begin{aligned}
&\text{Polymer} \xrightarrow{k_1\sigma} 2\dot{R}_t \text{ (initiation)},\\
&\dot{R}_t \xrightarrow{k_2} \dot{R}_t + \text{monomer (depolymerisation)},\\
&\dot{R}_t + \text{polymer} \xrightarrow{k_3} \text{polymer} + \dot{R}_c \text{ (chain transfer)},\\
&\dot{R}_c \xrightarrow{k_4(\sigma)} \dot{R}_t + \text{polymer (radical decomposition)},\\
&\dot{R}_c \xrightarrow{k_5(\sigma)} \dot{R}_t \text{ (migration of free valence)},\\
&2\dot{R}_c \xrightarrow{k_6} \text{polymer (chain termination)}.
\end{aligned} \quad (10)$$

The stress has the most significant influence on the constants k_1, k_4, and k_5.

Analysis of the corresponding kinetic equations shows that, over relatively narrow ranges of variation of the stresses, the Zhurkov equation holds formally, but τ_0, E, and γ are effective quantities which do not characterise a single elementary reaction but refer to a complex combination of several rate constants for different elementary reactions. Consequently, for an arbitrary material, it is impossible to relate τ_0 to the vibration period of any bonds in the molecule and E cannot be related to the activation energy for any one elementary step of the chemical process. These quantities do not characterise the elementary step, but refer to decomposition of the material as a whole. Accordingly, these quantities are not constant and depend on the process conditions. When the mechanism of the ageing of the material is unknown, the terminology frequently employed[17,20] becomes only a jargon. There is no more point in speaking of the activation energy for the ageing process than there would be in speaking of the activation energy for thermal expansion.

Thus calculation shows that, for the example under consideration, over a wide range of stresses, the semilogarithmic form of the relation between the lifetime of polypropylene and the stress should be concave. Fig.3 shows that the results of the calculation using the rate constants for the mechanothermal degradation of polypropylene obtained independently agree satisfatorily with the experimental values[23]. These results have been examined in greater detail elsewhere[24].

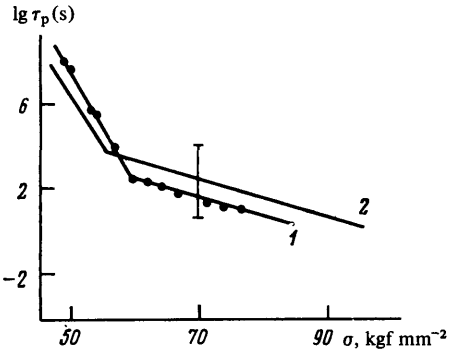


Figure 3. The influence of stresses on the useful lifetime of polypropylene: 1) experimental data[23]; 2) calculation[22] based on mechanism (10) with indication of the error of the calculation.

Analogous breaks in the semilogarithmic relations between the lifetime and the stress can be observed under the conditions of the joint action of oxygen and the stress, light and the stress, etc. In this case the relations become convex[25], since the polymer acted upon by small stresses breaks down almost independently of the kind of stress it is subjected to.

Over a wide range of temperatures, Eqn.(6) also does not hold. For example[26], E for many polymers varies sharply in the vicinity of their brittle temperatures T_{br}, which is due to the fact that the relaxation processes at $T > T_{br}$ become capable of competing with the mechanical dissociation of the macromolecule.

IV. THE "CHANGE IN THE MECHANISM" OF THE AGEING OF A POLYMERIC MATERIAL ON PASSING FROM TEST CONDITIONS TO OPERATING CONDITIONS

1. The Causes of the "Change in Mechanism"

In the determination of the useful lifetime of a polymeric material by extrapolation from the more severe conditions of accelerated tests to the milder operating conditions, the greatest difficulties do not arise from the extrapolation itself but from the fact that the ageing mechanism changes along the extrapolation path. Strictly speaking there is usually no actual "change in the mechanism" along the extrapolation path. Critical changes in the mechanism are extremely rare. They are normally observed probably only in the liquid–crystal phase transition, which is hardly ever observed in a pure form in polymeric materials. Even after crystallisation of polymers, the chemical changes usually involve the same mechanism as in the melt and in the remaining amorphous phase of the polymeric material.

There is usually a change not in the ageing mechanism but merely in the rate-limiting stage of the ageing process. For example, in a study[27] of the kinetics of the thermal oxidation of polyethylene at elevated temperatures the effective activation energy for the process was found, and on the basis of these data it was predicted that the insulation made of this polyethylene on pipes at 60 °C would be suitable for use over a period of approximately 15 years. However, in this prediction, no account was taken of the fact that at high temperatures the kinetics of the consumption of the thermal stabiliser are determined by its involvement in the oxidation process, while at a low temperature, where the oxidation process, which has a relatively high activation energy is sharply retarded, the thermal stabiliser begins to be consumed mainly by its diffusion from the specimen, which is a low activation energy process, and not due to the chemical transformation. As a result, it was found that the insulation of pipes breaks down after only $1\frac{1}{2}$ years, and not after 15 years.

An analogous effect was observed in a study of the lifetime of polymeric materials subjected to low stresses[25]. Under the conditions of high stresses, the rate of the process is limited by the step involving the dissociation of the macromolecules under the influence of the mechanical stress. Under these conditions, Zhurkov's equation holds satisfactorily and the logarithm of the lifetime of the material τ is linearly related to the stress σ and the parameter E/RT of the Arrhenius equation. For low stresses, the rate of this process becomes insignificant and other processes determine the variation of the properties of the material, for example, its chain oxidation. As a result, a sharp break is observed in the $\lg \tau - \sigma$ relation in the region of low stresses.

In neither case was there any change in the ageing mechanism either at low temperatures or under the conditions of low stresses. The thermal stabiliser diffused with an unchanged activation energy over the entire temperature range and also at higher temperatures, but under the latter conditions the rate of the process was negligible compared with the rate of oxidation and therefore could not be taken into account in the prediction. Similarly, for high stresses, the oxidation of the polymer proceeds in the same way as for low stresses, but in the former case the rate of the process can be neglected compared with the rate of dissociation of the strained molecules. Both effects described are associated with the usual phenomenon involving the competition of several elementary chemical or physical processes constituting the essential feature of the ageing mechanism,

the rate constants for these reactions varying monotonically along the extrapolation section in conformity with the Arrhenius or Zhurkov equations.

A somewhat more complex situation arises when there is a sharp change in the conditions for the elementary steps of either the chemical transformation of the substance or if there is a physical alteration in the structure of the material along the extrapolation section. This difficulty can be sometimes overcome when the features of the variation of quantitative characteristics of the elementary step are known for this change of conditions.

Thus it is known that the rate constants for bimolecular reactions are to a large extent determined by the nature of the molecular mobility in the medium. Molecular mobility influences both the transport of the reactants towards one another and the probability of the chemical interaction at the site where the reactants meet. It has been shown[28] that, on passing from liquid-phase systems to vitreous polymeric matrices, there is the so-called levelling of reactivity for series of molecules with different chemical structure participating in isotypical chemical reactions. Molecules whose reactivity in the liquid phase differs by 2–4 orders of magnitude have reactivities differing by only 1–2 orders of magnitude in the solid polymer. This phenomenon is associated with the sharp alteration of the molecular mobility in the medium and is independent of the chemical structure of the molecules of the latter.

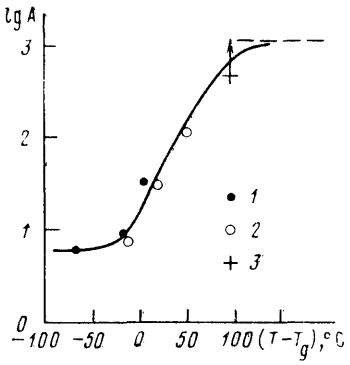


Figure 4. The influence of the molecular mobility of the medium on the relative rate constant (A) for the quenching of singlet oxygen. Polymeric matrices: 1) polystyrene; 2) butyl methacrylate–methacrylic acid copolymer (BMK-5, $T_g \approx 35$ °C); 3) polybutadiene. The dashed straight line corresponds to the liquid phase[29].

Fig.4 shows that the relative reactivity of the reactants in different polymeric matrices is determined by the difference between the experimental temperature and the glass point of the medium T_g, which is known[30] to be a measure of the molecular mobility of the medium over a wide temperature range. With the aid of a model taking into account the relative movement of the reactants in the cage where they meet, it has been shown[31] that the levelling phenomenon can be described quantitatively by the relation

$$\left(\frac{k_1}{k_2}\right)_S = \sqrt{\left(\frac{k_1}{k_2}\right)_L}, \qquad (11)$$

where k_1 and k_2 are the probabilities of the chemical transformation of two different substances in an isotypical chemical reaction when the transport of the reactants towards one another and the activation energy for the process can be neglected. The subscripts show that the process takes place in the solid polymer at $T < Tg$ or in the liquid phase.

Using Eqn.(11) and the data for the variation of the diffusion coefficients of the reactants and the molecular mobilities of the medium, it is possible to calculate the change in the reaction rate constant along the extrapolation path and to estimate the ratio of the rates of different processes under operating conditions. However, one should not forget here that Eqn.(11) refers to the elementary step of the chemical reaction and not to the ageing process as a whole and similar relations can therefore be applied in a real process when the kinetic mechanism of the ageing of polymeric material is known.

Not only chemical reactions in the polymeric material are responsible for its ageing. The change in its properties can be caused by physical processes which do not alter the chemical nature of the polymeric material. For example, a distinctive feature of the polymeric material is that it is frequently used in a thermodynamically non-equilibrium state. The great length of the polymer molecule sharply retards the occurrence of many physical processes, which makes it possible to use for a long time polymers in a state far from equilibrium from the physical point of view. Thus crystallising polymers are used in a partially amorphous state, the preliminary orientation of the polymer persisting for many years and the stresses arising in the polymer sometimes relaxing in the course of the entire useful lifetime of the material[27,32].

During the ageing of the polymeric material, chemical reactions are accompanied by its physical rearrangement and both processes can proceed at comparable rates. The change in the ratio of these rates can be one of the causes of the apparent "change in the mechanism" of the ageing of the polymeric material. Thus, when the polymer is used in the vitreous state, then owing to the non-uniformity of the chemical process in the bulk of the specimen local internal stresses arise which alter in their turn the rate constants for the elementary reactions. At higher temperatures the relaxation of stresses can be significantly faster than the chemical reaction of the substance, while in accelerated tests of the polymeric material this phenomenon could not be observed at all.

The solution of the problem of the possible occurrence of such phenomena along the extrapolation section is determined by the state of research into the problem of the influence of mechanical stresses on the kinetics of the ageing of polymeric materials, which is an important fundamental problem in chemical kinetics, as well as the question of the mechanism of the generation of internal stresses and the kinetics of their alteration in the course of the ageing of the polymeric material. Whereas relatively much attention has been devoted to the first problem at the present time[33], particularly in connection with the use of polymeric materials under load, only few studies have been undertaken on the second problem, despite its undoubted importance[34].

As a second example, complicating the influence of physical kinetics on the solution of the problem of the prediction of the useful lifetime of a polymeric material, one may examine the physical disorientation of the amorphous component of the half-crystallised polymer. Under operating conditions, the physical disorientation of the polymer filament proceeds at a negligibly low rate. Nevertheless it has been shown[35,36] that the chemical ageing process in such a highly oriented filament frequently differs qualitatively from the ageing of an isotropic non-oriented polymer. At the same time any

increase of temperature leads not only to the acceleration of the chemical process but also to the acceleration of the physical disorientation of the amorphous phase of the polymer and hence to a real qualitative change in the chemical mechanism of the ageing process. Thus, in accelerated tests processes whose role under operating conditions is negligible can begin to affect the ageing process.

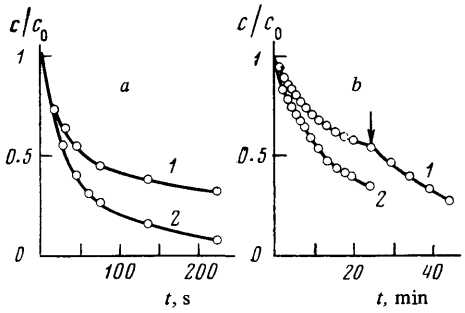


Figure 5. Kinetics of the photochemical oxidation of naphthacene (0.025%) (*a*) and anthracene (0.5%) (*b*) in polystyrene films in air under irradiation: 1) without intermediate heating; 2) with intermediate 15 min heating at 90 °C at instants indicated by circles. Intermediate heating was also applied at the instant designated by an arrow[37].

Fig.5 presents another example of a process in the polymer matrix in which the chemical transformation of the substance and the physical rearrangement of the local environment of the reactive species compete. The photochemical reaction of hydrocarbons with condensed nuclei within a vitreous polymer is inhibited sharply under conditions where the concentration of the reactants has altered relatively little—the so-called kinetic process arrest has occurred[37,38]. The reason for this phenomenon is that the photochemical process is significantly faster than the physical rearrangement of the local environment of the reacting species, the molecules existing under conditions favourable for the chemical reaction are rapidly consumed, and the photochemical process is retarded, since only molecules existing under conditions unfavourable for reaction remain in the specimen.

Under the real conditions of the employment of a polymeric material in which hydrocarbons with condensed nuclei have been introduced as special additives, for example, in photochromic materials or carriers of information, photochemically active light is less intense than in accelerated tests and does not operate all the time, while the physical rearrangement of the matrix proceeds continuously at the same rate and does not therefore limit the photochemical decomposition of the additive. As a result, no kinetic arrest is observed and the process is significantly faster than might have been expected on the basis of a formal inspection of the results of accelerated tests[39].

Thus at least three causes of the "change of the mechanism" of the ageing of polymeric materials when the ageing conditions are altered can be specified.

1. Competition between different elementary reactions constituting the ageing mechanism. A change in conditions can direct the ageing process via another pathway.

2. The influence of the physical structure of the polymer matrix on the elementary step of the chemical reaction. A change in this structure under different conditions can alter significantly the ratio of the rate constants for the elementary reactions.

3. Competition between the chemical transformation of the polymeric material and the physical change in its temperature.

In all the instances examined there is no actual change in the process mechanism and there is only change in its rate-limiting stage. Fundamental study of the ageing of the material might in fact render greatest assistance in the observation of such possible changes in the rate-limiting change of the process.

Even qualitative ideas about the process mechanism can sometimes help to solve the problem of a well-founded prediction. There is a possibility of a multistage extrapolation of different elementary processes proceeding independently in the polymer. For example, in the thermal oxidation of a stabilised polymer one must take into account not only the consumption of the thermal stabiliser in the oxidation reaction, but also its consumption as a result of its diffusion from the polymer. On the other hand, the rate of diffusion can be measured by independent methods. On comparing subsequently the results of the extrapolation of both rates to the operating conditions, it is possible to discover the process which determines the rate of consumption of the stabiliser. If there is a kinetic arrest in the photochemical process, the rates of rearrangement of the local environment of the species can also be obtained by an independent method[40] and hence one can estimate the role of this process under operating conditions.

Thus even a qualitative understanding of the principal stages of the ageing of a polymeric material significantly facilitates the solution of the problem of the prediction of the useful lifetime of the material.

2. Prediction of the Useful Lifetime of Polymeric Materials as a Kinetic Study

The possibility of "a change in the mechanism" of the ageing of a polymeric material makes the solution of the problem of the prediction of its useful lifetime extremely indefinite. One can actually claim that there should exist instances where a well-founded prediction is altogether impossible and in many cases the degree of risk cannot apparently be characterised quantitatively; nevertheless, since the problem of the determination of the useful lifetime exists, one must seek ways for its optimum solution.

The problem reduces in fact to the observation of a possible "change in the mechanism" of ageing already during tests on the polymeric material. A trivial procedure consists in carrying out tests under conditions as close as possible to the operating conditions. Naturally, all the possibilities of this procedure must be utilised but the method does not solve the problem of prediction, but merely reduces it to the modelling of the operating conditions in the laboratory, which is not always possible, as mentioned previously.

There remains a single method—the derivation of maximum possible information from the results of tests on the polymeric material.

A characteristic feature of the polymeric material is that in the latter there are virtually no abrupt changes in structure, characteristic of, for example, phase transitions in low-molecular-weight compounds. This gives rise to the hope that the "change in the mechanism" of the ageing of a polymeric material does not take place abruptly either. However, the "change in mechanism" can occur not only by virtue of a change in external conditions, but also as the ageing process proceeds and at different stages of the transformation of the material the process will be limited by different

steps. Therefore the study of the kinetics of the change in the properties of the polymeric material up to advanced stages of the transformation yields much more information than a simple determination of the useful lifetime of the material, since it can reveal signs of a "change in the ageing mechanism" under conditions where this change still does not determine the useful lifetime of the material.

We shall consider the advantages of the kinetic approach in relation to this formal example. Suppose that the kinetics of the change in the properties of the material can be described by the sum of two exponential functions:

$$U/U_0 = \gamma e^{-k_1 t} + (1-\gamma) e^{-k_2 t}, \qquad (12)$$

the constants k_1 and k_2 varying with temperature in accordance with the Arrhenius law with different activation energies, while the coefficient γ is independent of temperature. For example, γ can characterise the fraction of one of the components of a composite material when the quantitative characteristic of the property of the material U is a result of the additive effect of the two components which exhibit different thermal stabilities.

If the useful lifetime of such a material is characterised in terms of the time taken for the decrease of U to a certain limite U^0, then evidently the effect of activation energy for the useful lifetime measured in this way will depend on U^0 (Fig.6). Fig.6*a* shows how the effective activation energy E_{eff} for the useful lifetime of such a material varies for different values of U^0. Evidently, depending on the ratio of the activation energies and the pre-exponential factors for the constants k_1 and k_2, the quantity E_{eff} can both increase and decrease as U^0 varies.

Fig.6*b* shows how accurately the Arrhenius law holds under these conditions. The difference between the calculated activation energies δE at 360 and 400 K was adopted as a measure of its validity. Evidently, appreciable deviations from the Arrhenius law, for example $\delta E = 1$ kcal, are observed over relatively narrow ranges of values of U^0, while for the remaining values of U^0 the Arrhenius law holds satisfactorily and it is virtually impossible to observe the complex variation of the useful lifetime of the material as a function of temperature.

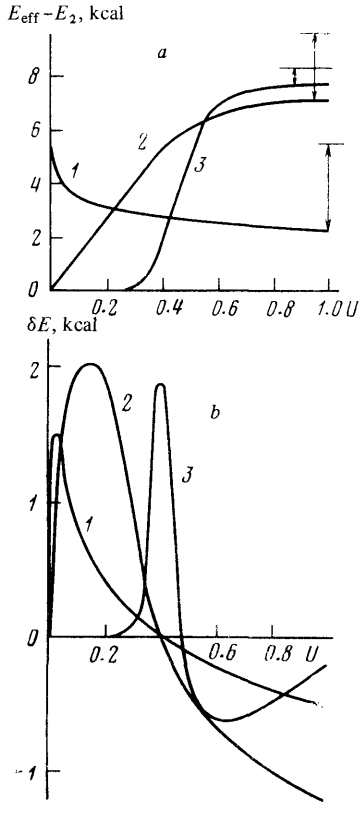


Figure 6. *a*) Variation of the effective activation energy for the attainment of a quantity U^0, the kinetics of the variation of which are described by Eqn.(13); temperature range 360–400 K; *b*) deviation from the Arrhenius law. The calculation was performed for $E_1 - E_2 = 5.5$ (curve *1*), 9.6 (curve *2*), and 8.3 kcal mol^{-1} (curve *3*) and $\chi = (k_1/k_2)\exp(E_1 - E_2)/400R = 10^3$ (curve *1*) and 10^6 (curves *2* and *3*). The values of the quantity $E_1 - E_2$ are indicated by arrows next to the corresponding curves.

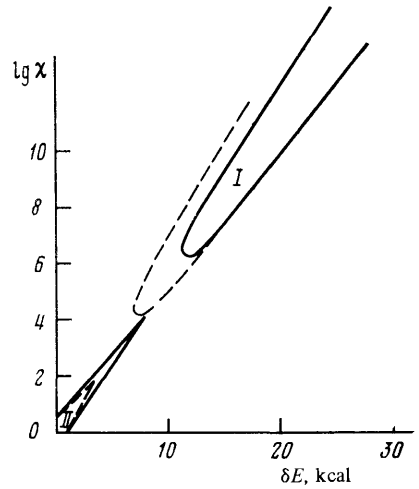


Figure 7. Conditions governing the observation of deviations from the Arrhenius law for process kinetics described by Eqn.(13); $\chi = (k_1/k_2)\exp(E_1 - E_2)/400R$; I is the region where $\delta E > 0.8$ kcal mol^{-1} in the measurement of the initial rates; II is the region where deviations from the exponential law governing the variation of U are not observed. The continuous lines correspond to the temperature range 360–400 K and the dashed lines correspond to 320–400 K; $\gamma = 0.5$.

If only the initial rates of change of U are measured, then deviations from the Arrhenius law can be observed only when the rates of change of both terms in Eqn.(12) are comparable. Fig.7 presents the results of the numerical calculations, showing that, even over a fairly wide temperature range of the measurements in the coordinate plane $\chi - \delta E$, where $\chi = (k_1/k_2)e^{\delta E/RT}$ and $\delta E = E_1 - E_2$, there is only a small region in which it is possible to observe deviations from the Arrhenius law (the shaded region in Fig.7, where $\delta E > 1$ kcal mol^{-1} in the temperature range 360–400 K). If the process kinetics are followed up to a degree of conversion of only 75%, then $\gamma = 0.5$ and, for a 5% accuracy of the

measurement, deviations from the exponential law governing the variation of U (and hence the deviations from the Arrhenius law) can be observed for almost all ratios of the constants. An exception is a small region of low values of δE and χ.

The above example shows how much more information can be derived from kinetic measurements compared with "point" measurements of the useful lifetime of the material. Therefore prediction of the useful lifetime of materials should be based on extrapolation of the parameters which describe the kinetics of the variation of the properties of the material under different conditions and not on extrapolation of the dependence of the useful lifetime of the material on the conditions of the tests. It is desirable to have data not only for the small "permissible" changes in the properties of the material but also for the kinetics of the variation of these properties up to stages which are as advanced as possible.

It may be that such measurements of the rate of change of the properties of a polymer subject to mechanical forces would make it possible to observe the features of the influence of mechanical stresses on the ageing of the polymer for small loads and of the oxidation process for high loads and there would be no question of a change in the process mechanism. It may also be that a study of, for example, the kinetics of the consumption of the thermal stabiliser in the high-temperature oxidation of polyethylene would make it possible to observe the diffusional component of its consumption and to make a correct prediction of the thermal stability of polyethylene under operating conditions.

V. ALLOWANCE FOR THE VARIABILITY OF OPERATING CONDITIONS

1. Formulation of the Problem

Extrapolation of the results of severe, forced, and accelerated tests on the polymeric material to mild conditions under which it is used, i.e. transition from high to low temperatures and from high irradiation intensities or high loads to low values of these parameters—all these constitute only one aspect of the problem of the prediction of the useful lifetime of the polymeric material. It is no less difficult to take into account the fact that during use the material usually exists under continuously varying conditions, and not simply the change in the operating conditions compared with accelerated tests. Day changes to night, a moist period is replaced by a dry one, intensive use is followed by a period of storage, etc.

Usually in accelerated tests the material is tested under conditions which remain constant throughout the test. By carrying out such tests under various conditions, it is possible to obtain a mathematical description of the process under any conditions. If the operating conditions are within the range of the conditions of the tests, then the problem of prediction is apparently solved, since, in contrast to extrapolation, interpolation can be carried out with any degree of accuracy and it is only necessary to have a sufficient amount of experimental data. However, this is true only if one predicts the variation of the properties of the material under constant conditions, as in the tests. On the other hand, the problem of the way in which the properties of the material should vary under variable conditions remains in essence open.

We shall assume that the kinetics of the variation of a property of the material Y are described by the following equation under constant conditions:

$$Y = k_1(1 - e^{-k_2 t}), \tag{13}$$

where k_1 and k_2 are effective constants, which vary with temperature in accordance with the Arrhenius equation. We shall examine the problem of the description of this process under variable conditions—at a variable temperature. There is hardly any point in substituting the time-variable values of k_1 and k_2 in Eqn.(14), since a decrease of temperature, resulting in a decrease of k_2, usually does not lead to the same decrease in Y and conversely the process kinetics at high temperatures are usually independent of the time during which the specimen remains at a low temperature, where k_2 is close to zero. It is not always possible to substitute an average temperature in Eqn.(13). For example, the question arises of an average temperature which must be invoked if it is necessary to discover how the properties of the polymeric material vary when the latter cools or conversely when it is heated at a constant rate.

The problem is complicated still further when the polymeric material is acted upon by several factors. For example[25], in the initial stage of the photochemical oxidation of polyolefins the kinetics of the variation of their mechanical properties are determined by the parameter

$$\Omega = kI^2 t^3, \tag{14}$$

where k is a constant which varies with temperature in accordance with the Arrhenius law and I is a quantity proportional to the intensity of the light incident on the specimen.

It is also not permissible to substitute the average temperature and light intensity in Eqn.(14), since one must take into account, on the one hand, the fact that the temperature and light intensity are usually strongly correlated and, on the other hand, it is evident that one can neglect the time intervals during which the light intensity and temperature are sufficiently small.

Some workers[6] suggest that Eqns.(13) and (14) be differentiated with respect to time and that time be subsequently eliminated from the resulting expression or that one seek from the very beginning a mathematical description of the process not in the form of a dependence of the rate of change of the properties on time but in the form of the dependence of the rate of the process on the current properties of the material, i.e. that one carry out transformations of the type

$$\begin{gathered}\mathbf{Y} = \mathrm{f}(\mathbf{X}, t),\ \mathbf{X} = \text{const},\ t = \varphi(\mathbf{X}, t);\\ \frac{\partial \mathbf{Y}}{\partial t} = \frac{\partial \mathrm{f}}{\partial t}(\mathbf{X}, \varphi(\mathbf{X}, \mathbf{Y})) = \psi(\mathbf{X}, \mathbf{Y}).\end{gathered} \tag{15}$$

We may replace the partial derivative by the total derivative, and obtain

$$\frac{\mathrm{d}\mathbf{Y}}{\mathrm{d}t} = \psi(\mathbf{X}(t), \mathbf{Y}). \tag{16}$$

Thus, instead of Eqns.(14) and (15), we obtain the expressions

$$\frac{\mathrm{d}Y}{\mathrm{d}t} = k_2(k_1 - Y), \tag{17}$$

$$\frac{\mathrm{d}\Omega}{\mathrm{d}t} = 3(kI^2\Omega^2)^{1/3}. \tag{18}$$

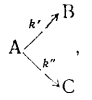
On solving similar equations under variable conditions, it is possible to find a mathematical description of the variation of the properties Y and Ω with time:

$$Y = \mathrm{e}^{-\int_0^\tau k_2\,\mathrm{d}t} \int_0^\tau k_1 k_2\, \mathrm{e}^{\int_0^\tau k_2\,\mathrm{d}t}\,\mathrm{d}t, \tag{19}$$

$$\Omega = \left(\int_0^\tau (kI^2)^{1/3}\,\mathrm{d}t\right)^3. \tag{20}$$

In the general case, in the description of the kinetics of the variation of the properties of the polymeric material, one cannot arbitrarily apply any one of the procedures described. In essence, in this case one is faced with the same problem as the cybernetic problem of the prediction of the behaviour of a "black box", which cannot be solved when data for its behaviour are available only under constant conditions. Thus Eqn.(14) discussed above can describe the kinetics of the accumulation of the reaction product formed via two different kinetic mechanisms.

1. The accumulation of the reaction product of one of two parallel reactions:



(21)

$$[B] = \frac{k'}{k'+k''}[A]_0(1-e^{-(k'+k'')t}). \quad (22)$$

The kinetic mechanism (22) can model the ageing process initiated by radicals formed in the decomposition of some initiator. In this case C are the products of the interaction of active centres within the cage which do not alter the properties of the material.

2. The accumulation of an unstable product in a zero-order reaction:

$$\xrightarrow{w_i} B \xrightarrow{k_d}, \quad (23)$$

$$[B] = \frac{w_i}{k_d}(1-e^{-k_d t}). \quad (24)$$

The kinetic mechanism (23) can also model the ageing process, B being an unstable reaction product capable of reverting to the initial state.

Thus two qualitatively different kinetic mechanisms lead to formally the same description of the process kinetics under constant conditions. However, under variable conditions, mechanisms (21) and (23) lead to different solutions. We obtain from Eqn.(21)

$$[B] = \int_0^\tau k'[A]_0 e^{-\int_0^t (k'+k'')dt} dt, \quad (25)$$

or, on converting to the notation defined by Eqn.(14), we have

$$[B] = \int_0^\tau k_1 k_2 e^{-\int_0^t k_a dt} dt. \quad (26)$$

We obtain from Eqn.(23)

$$[B] = e^{-\int_0^\tau k_d dt} \int_0^\tau w_i e^{\int_0^t k_d dt} dt = e^{-\int_0^\tau k_a dt} \int_0^\tau k_1 k_2 e^{\int_0^t k_a dt} dt. \quad (27)$$

Evidently there is also a qualitative difference in the kinetics of the variation of the quantity [B] under variable conditions. According to mechanism (21), the concentration of B under any conditions can only increase irreversibly. On the other hand, the establishment of a steady-state concentration of B under constant conditions according to Eqn.(23) is a consequence of the equality of the rates of formation and consumption of this product, so that under variable conditions the concentration of B can both increase and decrease.

The above considerations can be illustrated by the following numerical calculations. Suppose that the specimen is heated instantaneously to a temperature T_0 and is then slowly cooled, so that the temperature varies in accordance with the equation

$$T = T_0/(1+\gamma t). \quad (28)$$

If the variation of temperature is governed by this law, Eqn.(26) and (27) can be solved by the method of quadratures, provided that the rate constants k_1 and k_2 vary with temperature in accordance with the Arrhenius law.

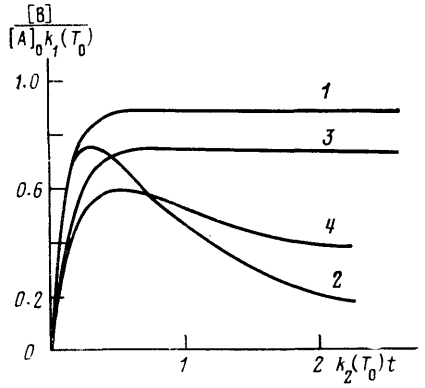


Figure 8. Kinetics of the variation of the concentration of B with temperature according to Eqn.(28) and subject to the kinetic mechanisms (21) (curves *1* and *3*) and (23) (curves *2* and *4*). Calculation performed for $k_2RT_0/E_2\gamma = 4$ (curves *1* and *2*) and 10 s^{-1} (curves *3* and *4*) and for $E_1 = E_2$ ($E' = 2E''$, $E_w = 2E_d$).

In this case, when the specimen is cooled fairly slowly, i.e. when

$$\gamma < \frac{k_2(T_0)RT_0}{E_2},$$

the kinetic curve for the variation of [B], described by Eqn.(27), passes through a maximum, which can be in no way expected when the final product B accumulates in accordance with mechanism (21). Fig.8 presents a numerical example of the calculation of the kinetic curves from Eqn.(26) and (27). Thus, for the extrapolation of the results of laboratory tests to variable operating conditions, the results of tests under constant conditions are insufficient and one must develop special programs whereby the kinetics of the ageing of the material under variable conditions can be described.

2. The Superposition Principle or the Principle of the Summation Defects

In the practical determination of the useful lifetime of the polymeric material one can frequently employ the so-called superposition principle or the principle of the summation of defects arising in the course of ageing[12,14]. This principle is based on the hypothesis that the breakdown of the material under any conditions takes place irreversibly and independently of the previous history of the specimen. Depending on the conditions, only the efficiency of the decomposition of the material changes. In conformity with

this principle, it is assumed[8] that for each material there should exist a single-valued function, the damage to the material ω, which increases monotonically in the course of ageing. Here the increment of ω is proportional to the efficiency of the ageing of the material under the given conditions and to the time during which the material has been exposed to these conditions:

$$\Delta\omega=\psi(\mathbf{X})\Delta t. \tag{29}$$

Accordingly, under variable conditions the quantity ω is obtained as a result of the summation of different influences $\mathbf{X}_i$:

$$\omega=\Sigma\psi(\mathbf{X}_i)\Delta t_i. \tag{30}$$

Since a change in the properties of the material represents the results of the independent action of different conditions, it is postulated that ageing proceeds with the same efficiency regardless of the sequences in which the material is acted upon by different influences.

Eqn.(30) can be formulated in a differential form for a continuous variation of operating conditions:

$$\frac{\mathrm{d}\omega}{\mathrm{d}t}=\psi(\mathbf{X}) \tag{31}$$

and can be extended to the case of multidimensional operating conditions for the materials:

$$\frac{\mathrm{d}\mathbf{Y}}{\mathrm{d}t}=\varphi(\mathbf{Y})\psi(\mathbf{X}). \tag{32}$$

The necessary feature for the applicability of the superposition principle follows from Eqn.(32), namely the presence of a single unambiguous trajectory along which the properties of the material vary under any operating conditions. Indeed it follows from Eqn.(32) that

$$\frac{\partial y_i}{\partial y_j}=\frac{\varphi_i(\mathbf{Y})}{\varphi_j(\mathbf{Y})}, \tag{33}$$

where subscripts i and j denote components of the vectors $\mathbf{Y}$ and $\phi(\mathbf{Y})$.

The material is finally damaged when the vector $\mathbf{Y}$ reaches a certain value $\mathbf{Y}_z$† i.e.

$$\int_{Y_0}^{Y_z}\frac{\mathrm{d}\mathbf{Y}}{\varphi(\mathbf{Y})}=\int_0^{\tau}\psi(\mathbf{X})\,\mathrm{d}t, \tag{34}$$

where the upper integration limit τ represents the useful lifetime of the material.

If the operating conditions are constant, then

$$\tau=\tau_0=\frac{1}{\psi(\mathbf{X})}\int_{Y_0}^{Y_z}\frac{\mathrm{d}\mathbf{Y}}{\varphi(\mathbf{Y})}; \tag{35}$$

We shall now express $\psi(\mathbf{X})$ in terms of τ_0 and shall substitute the resulting expression in Eqn.(24) assuming that the argument $\mathbf{X}$ varies with time. After cancelling out, we arrive at the familiar Bailey equation:

$$\int_0^{\tau}\frac{\mathrm{d}t}{\tau_0(\boldsymbol{X}(t))}=1. \tag{36}$$

Thus Bailey's equation can be used only in processes whose mechanism can also be described in the form of Eqn.(32). In particular, it follows from Eqn.(32) that the superposition principle is applicable to all processes whose kinetics are determined by a single elementary step. However, it ceases to be applicable even for the description of the kinetics of the accumulation of reaction products in a process consisting of two parallel reactions (21), since the partial derivative is a function of temperature; for example, it follows from Eqn.(21) that

$$\frac{\partial[\mathrm{B}]}{\partial[\mathrm{A}]}=\frac{k'}{k'+k''}.$$

The superposition principle is frequently applicable when one considers the ageing of materials used under critical conditions where a small change in the properties of the material lead to the breakdown of the latter. In this case there is a sharp diminution of the requirement for a single-valued trajectory along which the properties of the material vary. In fact, the current properties of the material in the equation describing the variation of its properties can be replaced by the initial values. The superposition principle can then be always employed when the rate of ageing is determined by the initial properties of the material.

Thus it is applicable to a process consisting of two parallel reactions. Indeed the rate of accumulation is determined solely by the initial concentration of substance A:

$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t}=k'[\mathrm{A}]_0.$$

Nevertheless one cannot describe with its aid the accumulation of the product of a consecutive reaction or any reaction which takes place in accordance with the autocatalytic law.

In particular, it is generally accepted[3,41] that the ageing of any polymeric materials is a chain process with degenerate branching. The kinetics of this process are clearly autocatalytic. The ratio of the rates of accumulation of the branching product, usually formed in the chain propagation reaction, and the products formed in the chain initiation steps—the effective chain length—usually depends strongly on the process conditions, which leads to failure of Eqn.(33) and hence to a non-single-valued trajectory for the variation of the properties of the material. Bailey's equation is therefore usually inapplicable to branched-chain processes.

In connection with the relatively wide use of prediction methods based on the superposition principle, the problem of discovering the features of the process mechanism and the characteristics of variable operating conditions, for which the application of this principle can lead to significant errors, has now become particularly acute. It is especially important to be able to observe these features in the course of accelerated tests on materials, the mechanism of the ageing of which is virtually unknown.

3. Optimisation of the Superposition Principle

The superposition principle is a special case of a more general procedure examined above (Section V, 1), which consists in the measurement of the rate of change of the properties of the material under different conditions. Eqn.(32) is a special case of Eqn.(16). However, as shown above, the formal application of even the general Eqn.(16) could not always permit the prediction of the variation of the properties of the material under variable conditions.

Nevertheless, it is evident that, when the instantaneous rates of change of all the properties of the material have been measured for all possible combination of these properties,

$$w(\mathbf{Y},\mathbf{X})=\left(\frac{\partial\boldsymbol{Y}}{\partial t}\right)_{\substack{\mathbf{Y}=\mathbf{Y}_0\\ t=0}}, \tag{37}$$

†In the general case $\mathbf{Y}_z$ represents a characteristic of the limit of the region of the operational suitability of the material and not a point.

then the kinetics of the variation of the properties of this material under any conditions can be described by solving the differential equation

$$\frac{d\mathbf{Y}}{dt} = w[\mathbf{Y}, \mathbf{X}(t)]. \quad (38)$$

In essence, Eqns.(16) and (38) have the same significance; the only different feature of Eqn.(38) is that the vector **Y**, which it includes, must characterise all the properties of the material determining the kinetics of the ageing process and not only some of them (for example, those important for practical purposes). On the other hand, in the derivation of Eqn.(16) the partial derivative was replaced by the total derivative without any justification. A rigorous application of Eqn.(16) or (38) implies that Eqn.(16) represents a system of differential equations taking into account not only the kinetics of the accumulation of B and Ω in the examples discussed above, but also the kinetics of the consumption of the initial substance and the kinetics of the variation of the concentration of the chain branching product.

As a result we obtain a system of equations identical to a system of chemical kinetic equations. Instead of Eqn.(17), we obtain from the kinetic scheme (21)

$$\frac{d[B]}{dt} = k_1 k_2 \frac{[A]}{[A_0]}, \quad \frac{d[A]}{dt} = -k_2[A], \quad (39)$$

and, instead of Eqn.(18), we have for the photochemical oxidation of polyolefins

$$\frac{d\Omega}{dt} = I[P], \quad \frac{d[P]}{dt} = \sqrt{kI[P]}, \quad (40)$$

where [P] is the concentration of the branching product.

In the general case the systems of equations obtained can differ in form from systems of chemical kinetic equations, but their structure must reflect, as it were, the logic of the process occurring and must take into account the variation of all the properties of the material which actually determine the process kinetics.

Unfortunately data on the variation of all the necessary properties of the material cannot always be obtained. For example, in a chain process it is sometimes difficult to follow the kinetics of the variation of the concentration of the branching product, since its nature may be unknown and, when it is known, its concentration may be below the sensitivity of the analysis.

At the present time there is no rigorous method whereby one can discover the properties whose variation is the primary cause of the variation of the remaining properties of the material. Nor is it clear whether it is at all possible to devise such a general method or whether the solution of this problem will remain for a long time in the hands of highly qualified specialists greatly experienced in the study of polymeric materials of a given class. The methods for the estimation of the significance of various factors employing factorial analysis[42] are as yet hardly applicable in this field, since they do not make it possible to elucidate the causal relation between different external factors and the properties of the material. On the other hand, the derivation of equations analogous to Eqn.(38), which take into account the variation of all the properties of the material and all the factors associated with the external conditions, is too laborious.

Thus the generalised superposition principle shows that there exists a possibility, in principle, of solving the problem of extrapolating the results of laboratory tests to any variable operating conditions. However, this principle shows how difficult it is to solve this problem without using information about the mechanism of the ageing of the material.

From the experimental point of view, it follows from the superposition principle that the measurement of the rate of change of the properties of material aged in different ways is most significant for prediction, and not the kinetics of the change of these properties under some conditions even if they do model fairly satisfactorily the operating conditions of the material from some particular point of view.

VI. INITIAL DATA FOR THE FORMULATION OF THE PROBLEM OF THE PREDICTION OF THE USEFUL LIFETIME

The accuracy of the determination of the useful lifetime of a material is usually not restricted solely by the difficulty of extrapolation of the results of tests to arbitrarily complex operating conditions. It is to a large extent determined by the accuracy with which the operating conditions of the material are known beforehand and how well the requirements which must be met by the material in a particular article have been formulated.

These at first sight simple tasks are in practice fairly complex, because one must understand which operating conditions in fact determine the kinetics of the ageing of the polymeric material and hence one can recognise how accurately these conditions are known beforehand only by having some idea about the factors which determine the variation of the properties of the material in the course of ageing. Only if it is known how the different properties of the material are inter-related can one formulate exactly the requirements which must be met by the stability of the article made of the given material.

Several examples illustrating this essential feature of the problem are discussed below.

1. Relation Between the Kinetics of the Variation of Practically Important Properties of a Polymeric Material and the Mechanism of the Ageing Process

Any polymeric material is characterised by a set of properties. From the practical point of view, the "external" properties of the material are important: its strength, lustre, permeability to moisture or gas, transparency, dielectric losses, combustibility, etc. These are not usually properties which determine the kinetics of the ageing of the material; their variation is a consequence of the physicochemical processes occurring in the material during its ageing. In order to record the kinetics of the ageing of the material and to elucidate the mechanism of this process, one usually measures quite different properties of the material: the variation of its composition, the formation and destruction of active species in it, the characteristics of the mobility of individual fragments of macromolecules, etc. Nevertheless, the useful lifetime of the material is determined by the kinetics of the variation of properties of practical importance. In this connection, the solution of the problem of the interrelation of different properties of the polymeric material is of primary importance in predicting its useful lifetime.

Relatively numerous studies have now been carried out in which the kinetics of the variation of properties of practical importance have been followed in the course of the ageing of many polymers[43]. The relation between certain properties of polymeric materials is known. For example, the dielectric losses are correlated with the number of polar groups in the polymer[44] and the elasticity of the polymer is related to the fraction and chemical structure of its amorphous phase[45].

However, unfortunately there have been virtually no studies on the quantitative relation between the kinetics of the variation of the properties of a polymeric material and the mechanism of its ageing. Such a relation has been established in a study[46] dealing with the kinetics of the variation of properties in the ageing of polyolefins. It has been shown that the variation of any physicomechanical characteristics of polyolefins is determined not only by the amount of light incident on the specimen but depends significantly also on the intensity of the photochemically active light. The higher the intensity of the light, the less effective (per quantum of light incident on the specimen) is the variation of the properties.

This result can be readily explained on the basis of data for the mechanism of the oxidation of the given polymer. The oxidation of polyolefins is a chain reaction with degenerate light-induced branching by the reaction products and with quadratic chain termination[45]. This process also proceeds more effectively at lower light intensities, since one of the principal branching products, the hydroperoxide, accumulates in the reaction which involves the propagation of a chain whose length, under conditions of quadratic chain termination, is known to be greater the lower the rate of initiation, i.e. the lower the intensity of the light.

An ambiguous quantitative relation has been established[46] between the kinetics of the variation of the mechanical properties of polypropylene and the total number of oxidation chain initiation steps occurring in the polymer throughout the process (the yield of radicals). This relation is purely empirical; neither its cause nor its characteristics are known exactly. Furthermore, it has actually been shown that the form of the relations between the mechanical characteristics and the yield of radicals is different for polymer specimens prepared in different ways. Nevertheless, the unambiguous nature of the relation already established made it possible to calculate the rate of change of mechanical properties under any conditions. The details of this study have been described by Slobodetskaya[36].

2. The Characteristics of Operating Conditions

The accuracy of the determination of the useful lifetime is governed to a large extent by the accuracy with which the operating conditions of a given material in the article have been specified. It is sometimes believed that the determination of the characteristics of the operating conditions is a simple task, attention being concentrated only on the difficulty of determination of internal stresses in the specimen or of the dynamics of the loads applied to it.

However, in practice there are too many factors acting on the polymer in the course of its use, so that even factorial design methods cannot always reveal which are the most significant. For example, only special studies revealed that the rate of atmospheric corrosion of metals is to a large extent determined by the concentration of sulphur compounds in the atmosphere[47].

Frequently only an understanding of the fundamental features of the mechanism of the ageing of the polymeric material makes it possible to discover the principal factors which determine its useful lifetime. It is then sometimes found that the determination of the characteristics of the operating conditions becomes an independent scientific task. For example, at the beginning of the 1970s the principal features of the mechanism of the ageing of polyolefins under atmospheric conditions became clear and all the necessary rate constants for the elementary reactions were found. However, even this could not lead to the solution of the problem of the determination of the useful lifetime of these polymers in different climatic zones. The point is that the ageing of polyolefins in open air takes place mainly as a result of the absorption of light by aliphatic hydroperoxides. On the other hand, aliphatic hydroperoxides absorb light only in the extreme ultraviolet region of the solar spectrum and the intensity of this component depends greatly on the angle of the sun above the horizon and on the latitude of the given site. Regular direct measurements of the ultraviolet component of the solar spectrum have not been made anywhere in the world except at the meteorological station of Moscow University. The problem of predicting the useful lifetime of polyolefins under real conditions therefore remained unsolved until a special study was carried out[48] showing how the average characteristics of the intensity and spectral composition of solar radiation in the ultraviolet can be calculated theoretically from data on the cloud cover and the geographical position of the given location. As a result, a special computer program was developed whereby it was possible to calculate the rate of change of the properties of olefins at any point on earth from data supplied by ordinary meteorological stations[49].

A completely different problem arose when prediction of the useful lifetime of polyolefins used to insulate pipes, already mentioned above, was considered[27]. The failure of the initial prediction is associated in this instance with the fact that no account was taken of the contact between the polymer and the environment.

An unusual characteristic of the operating conditions of a polymer may prove to be the size of the given article. Many polymeric materials are used in a plasticised state. The increase in the size of the articles made from such a material leads to two opposed phenomena. On the one hand, intense stresses arise in large articles which reduces the useful life of the latter. On the other hand, the plasticiser diffuses less from a large article and its initial properties are retained for a longer time.

The prediction of the useful lifetime of the material in such an article is a fairly difficult problem and the question arises of the extrapolation of the results of laboratory tests not only to the normal characteristics of the operating conditions (temperature, humidity, stress) but also to parameters of the size of the specimen.

The aim of this Section was not to consider comprehensively the problem of the formulation of initial data required for the determination of the useful lifetime of a polymeric material; this is an independent and fairly complex problem. The examples quoted merely illustrate the importance of this problem, to which inadequate attention is being devoted.

VII. KINETIC CLASSIFICATION OF AGEING MECHANISMS

The analysis described in previous sections shows that simplified approaches to prediction, which are suitable when the ageing of the polymeric material is determined by one elementary step, are usually inapplicable to the prediction of the variation of the properties of real materials, the mechanism of the ageing of which involves a complex set of different elementary processes.

Well-founded prediction must therefore be based, on the one hand, on the determination of the fundamental features of the possible mechanism of the ageing of the material, and, on the other hand, on the development of a series of type-specific methods of prediction suitable for the most common ageing mechanisms. Thus the prediction must be based on the classification of the possible mechanisms of the ageing of polymeric materials in terms of features essential for such prediction.

Unfortunately, at present it is impossible to point to any one study in which a sufficiently complete classification of the mechanisms of the ageing of polymeric materials has been given. Nevertheless, such a classification is being set up, albeit somewhat sporadically. Ageing processes are divided into classes based on different features: the chemical structure of the polymer, the ageing conditions, the physical and chemical nature of the processes predominating in the course of ageing, and the properties of the polymer which are of greatest practical importance. Examples of different processes associated with different methods of classification are presented in the Table.

Methods of classification of ageing processes.

Feature on which classification is based	Examples of processes
Chemical nature of material	Ageing of polyolefins Ageing of poly(vinyl chloride) Ageing of polyamides Ageing of natural rubbers and elastomers Ageing of polyurethanes Ageing of epoxy-compounds
Influences acting on materials	Oxidative degradation Photochemical oxidation Thermal degradation Photolysis Mechanical degradation Chemical degradation Radiation-induced degradation
Nature of physicochemical process	Radical transformations in polymer Photochemical transformations Structure formation in polymers Crystallisation Relaxation processes
Properties essential for practical purposes	Variation of mechanical properties Variation of dielectric properties Gas evolution Cracking

However, these are not the features which must underlie the classification of ageing processes necessary for the determination of the useful lifetime of the polymeric material. A kinetic classification of the mechanisms of the ageing processes is essential. The beginnings of such a classification already exist.

It is known that the ageing of a polymeric material is frequently not a simple irreversible reaction. In many instances there is a chain process and the prediction of the rate of change of the properties of the material decomposing via a chain mechanism requires, as we have seen in the previous Sections, a qualitatively different approach from that for a simple irreversible reaction. Furthermore the kinetics of the chain process in different polymeric materials and under different conditions can be also qualitatively different. Thus pure polyolefins and apparently many natural rubbers are oxidised via the mechanism involving a chain reaction with degenerate branching and quadratic termination[36,41].

The introduction of a thermal stabiliser into the olefin leads to the appearance in the kinetic process mechanism of what is in fact only one additional elementary reaction—the interaction of the thermal stabiliser and the peroxy-radical. However, the process kinetics do not change qualitatively, since chain termination becomes linear. The relatively slow change in the rate of accumulation of the hydroperoxide along a quadratic parabola in pure polyolefins is replaced in the thermally stabilised polyolefin by a characteristic relation with a so-called induction period. At the beginning of the process, during a prolonged time interval, the branching product (the hydroperoxide) hardly accumulates and then its concentration increases almost exponentially[50]. Despite the chemical similarity of both processes, they are very different kinetically.

An unbranched chain process has altogether different kinetic features. Under constant conditions, its rate is almost unaltered, but its dependence on temperature and the rate of initiation may be complex. The photochemical decomposition of many polymers occurring as a result of the absorption of light by the polymer molecule itself may serve as an example of processes of this kind.

Different kinds of photochemical processes can be treated in the same way. Together with processes proceeding as ordinary single-quantum reactions, two-quantum processes, which take place with the consecutive absorption of two light quanta, and even multiquantum chain processes, in which each chain propagation step requires the absorption of a new light quantum, are known. From the kinetic point of view, all these are qualitatively different.

Together with chemical changes, physical processes also take place in the course of ageing: crystallisation and recrystallisation as well as diffusion of different components of the polymeric material and the reaction products. Different kinds of stresses arise in the polymer and relax, and the polymer undergoes orientation or disorientation. The role of all these processes must be taken into account in classifying the possible kinetic features of ageing processes.

The ain of current studies on the ageing processes of polymeric materials is usually to demonstrate the existence and to determine the quantitative characteristics of individual elementary steps of the process; one may say that they are designed to discover sufficient evidence that the elementary steps do occur. On the other hand, for the prediction of the useful lifetime, it is necessary to have the characteristics of the ageing process of the polymeric material as a whole. Naturally these essential process characteristics consist of the characteristics of individual elementary steps. When the characteristics of all the elementary steps are known, the prediction of the useful lifetime of the material does not involve fundamental difficulties, as already stated. However, usually, particularly at the beginning of the study, such characteristics are not available and even the ageing mechanism is largely obscure. In this case on must solve the "converse" problem: it is necessary to discover the type of the mechanism of ageing from a set of certain features and then to seek on this basis the quantitative characteristics of the process necessary for the determination of the useful lifetime of the material.

We are thus faced, for example, with the problem of the features of experiments with the aid of which one can decide whether Bailey's equation for the determination of the useful lifetime of the material under variable conditions is applicable to the given material. Evidently the applicability or inapplicability of this equation is determined both by the mechanism of the ageing of the material and by the nature of the changes in its operating conditions. Under conditions which change little, the equation is always applicable, while in the case of an extensive variation of conditions it is not easy to decide whether the equation is applicable or not.

Thus the kinetic classification of ageing processes must be based not only on data for the mechanism of the ageing of the polymeric material but also on the basis of information concerning the operating conditions of the material in the given article. Unfortunately the solution of problems of this kind is only just beginning and the necessity for their solution

becomes apparent only when the use of traditional simplified methods leads to emergencies.

---o0o---

Summarising what has been said above, one can formulate the tasks for fundamental research on the performance of which depends the successful prediction of the useful lifetime of polymeric materials.

Firstly, it is necessary to discover, classify, and estimate the distribution of typical mechanisms for the variation of the properties of polymers under different conditions. The determination of the qualitative features of a particular mechanism is of greater importance than the detemrination of the rate constants for elementary processes. This makes it possible to discover on the basis of laboratory tests the type of the mechanism for the decomposition of the material and hence one can devise both a mathematical description of the ageing process of the material and a programme of accelerated tests directed to the determination of its useful lifetime.

Secondly, fundamental research should indicate the conditions governing the variation of the process mechanism. This will make it possible to establish the possible limits of the correct extrapolation of data obtained in accelerated tests or under conditions more severe than the operating conditions.

Thirdly, fundamental research should reveal the complete set of the properties of the polymeric material which determine the kinetics of the variation of its practically important characteristics in the course of its use. Only if the set of such properties and the way in which they can be characterised quantitatively are known will it be possible to compare two materials or to specify the variation of the properties of the material during its use.

Fourthly, fundamental research should indicate which factors in the operating conditions of the polymer induce changes in its properties and which can be characterised quantitatively.

Fifthly and finally, it is necessary to develop methods for the investigation of complex non-linear systems whereby one can predict their behaviour on the basis of preliminary studies and qualitative data on the relation between their properties.

On this basis, one must set up a method for the development of an optimum programme of preliminary studies on the material. The first four tasks refer to the field of chemical physics and that part of it where the kinetics and mechanisms of chemical processes are studied. The fifth task can be assigned to the field of applied mathematics, on the border between computational mathematics or mathematical statistics and experimental design.

A characteristic feature of the problem of prediction is the necessity for its daily solution. It is continually faced by various organisations occupied with problems of the application of polymeric materials. It arises when it is necessary to determine the guaranteed useful lifetime of articles produced by the new technology, when it is necessary to select the material for an article still only in the planning stage, and finally when one must devise a plan using a material already manufactured in various articles and in various branches of industry.

Errors in the solution of problems of this kind can cost the National Economy many millions of roubles and they can vitiate the efforts of many teams, directed towards the development of new articles and materials. Therefore the time available for the solution of the problem of prediction is usually dictated by practical considerations and the solution must be achieved regardless of the level, which, for example, studies on the mechanism for the variation of the properties of the given material have reached at the instant of the formulation of the given task.

REFERENCES

1. N.M.Emanuel', "Doklad na XVII Vsesoyuznoi Konferentsii po Vysokomolekulyarnym Soedineniyam" (Report at the XVIIth All-Union Conference on Macromolecular Compounds), Moscow, 1968.
2. N.M.Emanuel', "Zadachi Fundamental'nykh Issledovanii v Oblasti Stareniya i Stabilizatsii Polimerov, IV Polimernaya Shkola, Lektsiya I" (The Tasks of Fundamental Research into the Ageing and Stabilisation of Polymers. The IVth Polymer School. Lecture I), Tallin, 1970.
3. N.M.Emanuel', Uspekhi Khim., **48**, 2113 (1979)[Russ. Chem.Rev., No.12 (1979)].
4. D.K.Lloid [D.C.Lloyd?] and M.Lipov, "Nadezhnost', Organizatsiya Issledovaniya, Matematicheskii Apparat" (Reliability, Organisation of Research, and Mathematical Apparatus), Izd.Sovetskoe Radio, Moscow, 1964.
5. A.S.Prunnikov, "Nadezhnost' Mashin" (The Reliability of Machines), Izd.Mashinostroenie, Moscow, 1978.
6. B.D.Goikhman and A.N.Smekhunova, Uspekhi Khim., **49**, 1554 (1980)[Russ.Chem.Rev., No. (1980)].
7. A.N.Tikhonov and V.Ya.Arsenin, "Metody Resheniya Nekorrektnykh Zadach" (Methods for the Solution of Incorrectly Formulated Problems), Izd.Nauka, Moscow, 1974.
8. G.K.Krug, Yu.A.Sosulin, and V.A.Fatdeev, "Planirovanie Eksperimenta v Zadachakh Identifikatsii i Ekstrapolyatsii" (Experimental Design in Problems of Identification and Extrapolation), Izd.Nauka, Moscow, 1973.
9. M.A.Elizavetin, "Povyshenie Nadezhnosti Mashin" (Improvement of the Reliability of Machines), Izd. Mashinostroenie, Moscow, 1973.
10. GOST 9.035-75 "Reziny. Metod Uskorennogo Opredeleniya Garantiinogo Sroka Khraneniya Uplotnitel'nykh Detalei Nepodvizhnogo Soedineniya" [GOST (USSR Government Standard) 9.035-75 Rubbers. A Method for the Accelerated Determination of the Guaranteed Storage Time of The Sealing Components of a Stationary Junction].
11. GOST 9.045-75 ESZKS. "Pokrytiya Lkokrasochnye. Uskorennye Metody Opredeleniya Svetostoikosti" [GOST (USSR Government Standard) 9.045-75 ESZKS. Paint and Varnish Coatings. Accelerated Methods for the Determination of Resistance to Light].
12. A.V.Tobolsky, "The Structure and Properties of Polymers (Translated into Russian), Izd.Mir, Moscow, 1964.
13. Yu.S.Urzhumtsev and R.D.Maksimov, "Prognostika Deformiruemosti Polimernykh Materialov" (Prediction of the Deformability of Polymeric Materials), Izd. Zinatne, Riga, 1975.
14. P.M.Ogibalov, V.A.Lomakin, and B.P.Kishkin, "Mekhanika Polimerov" (The Mechanics of Polymers), Izd.Nauka, Moscow, 1975.
15. B.D.Goikhman, A.D.Moshenskii, and L.V.Selezneva, Kauchuk i Rezina, No.4, 49 (1968).
16. L.S.Fel'dshtein, V.G.Mukhadova, and L.G.Angert, Kauchuk i Rezina, No.6, 26 (1974).
17. GOST 9.034-74 ESZKS. "Reziny. Metody Opredeleniya Ravnodeistvuyushchei Temperatury" [GOST (USSR Government Standard) 9.034-74 ESZKS. Rubbers. Methods for the Determination of the Equivalent Temperature].

18. V.R.Regel', A.I.Slutsker, and E.E.Tomashevskii, "Kineticheskaya Priroda Prochnosti Tverdykh Tel" (The Kinetic Nature of the Strength of Solids), Izd. Khimiya, Moscow, 1974.
19. N.M.Emanuel', Vysokomol.Soed., **A21**, 2624 (1979).
20. V.R.Regel' and V.P.Tamuzh, Mekhanika Polimerov, No.3, 458 (1977).
21. B.Rosen (Editor), "Fracture Processes in Polymeric Solids: Phenomena and Theory" (Translated into Russian), Izd.Khimiya, Moscow, 1971.
22. E.V.Deyun, G.B.Manelis, and L.P.Smirnov, Dokl. Akad.Nauk SSSR, **237**, 859 (1977).
23. V.R.Regel and A.M.Leksovskii, Fiz.Tverd.Tela, 12, 3270 (1970).
24. E.V.Deyun, G.B.Manelis, E.V.Polianchik, and L.P.Smirnov, Uspekhi Khim., **49**, 1574 (1980)[Russ. Chem.Rev., No.8 (1980)].
25. N.M.Livanova, N.Ya.Rapoport, and V.B.Miller, Vysokomol.Soed., **A20**, 1893 (1978).
26. V.V.Panasyuk, "Predel'noe Ravnovesie Khrupkikh Tel s Treshchinami" (The Limiting Equilibria in Brittle Solids with Cracks), Izd.Nauka, Moscow, 1968.
27. V.A.Kargin and G.L.Slonimskii, "Kratkie Ocherki po Fiziko-Khimii Polimerov" (A Brief Outline of the Physical Chemistry of Polymers), Izd.Nauka, Moscow, 1967.
28. N.O.Karpukhin, T.V.Pokholok, and V.Ya.Shlyapintokh, Vysokomol.Soed., **A13**, 22 (1971).
29. E.V.Bystritskaya, O.N.Karpukhin, and T.S.Karpovich, Dokl.Akad.Nauk SSSR, **235**, 607 (1977).
30. A.A.Tager, "Fizikokhimiya Polimerov" (The Physical Chemistry of Polymers), Izd.Khimiya, Moscow, 1977.
31. E.V.Bystritskaya, O.N.Karpukhin, and T.S.Repina, Dokl.Akad.Nauk SSSR, **240**, 1380 (1978).
32. C.Tanford, "Physical Chemistry of Macromolecules" (Translated into Russian), Izd.Khimiya, Moscow, 1965.
33. G.Leibowitz [tentative spelling (Ed. of Translation)] (Editor), Symposium, "Breakdown" (Translated into Russian), Izd.Mir, Moscow, 1973–1976, Vols.1–7.
34. A.N.Melkumov, V.P.Prutkin, V.E.Branovitskii, and L.I.Tavshchunskaya, Mekhanika Polimerov, No.2, 353 (1975).
35. N.Ya.Rapoport, S.I.Berulova, A.L.Kovarskii, I.N.Musoelyan, Yu.A.Ershov, and V.B.Miller, Vysokomol.Soed., **A17**, 2521 (1975).
36. E.M.Slobodetskaya, Uspekhi Khim., **49**, 1594 (1980) [Russ.Chem.Rev., No.8 (1980)].
37. V.M.Anisimov and O.N.Karpukhin, Izv.Akad.Nauk SSSR, Ser.Khim., 1914 (1973).
38. V.M.Anisomov, O.N.Karpukhin, and A.M.Mattucci, Dokl.Akad.Nauk SSSR, **214**, 828 (1974).
39. V.M.Anisimov, M.E.Dzhanashvili, O.N.Karpukhin, and G.E.Krichevskii, "Tezisy I Vsesoyuznoi Konferentsii po Svetostabilizatsii Okrashennykh Volokon i Plenok" (Abstracts of Reports of the Ist All-Union Conference on the Stabilisation of Dyed Fibres and Films with Respect to the Action of Light), Moskovskii Tekstil'nyi Institut, Moscow, 1979, p.8.
40. E.N.Savinov, V.M.Anisimov, and O.N.Karpukhin, Dokl.Akad.Nauk SSSR, **253**, 164 (1977).
41. A.S.Kuz'minskii, Vysokomol.Soed., **A19**, 1091 (1977).
42. V.V.Nalimov and N.A.Chernova, "Statisticheskie Metody Planirovaniya Eksperimenta" (Statistical Methods for Experimental Design), Izd.Nauka, Moscow, 1965.
43. "Mezhdunarodnyi Simpozium po Makromolekulyarnoi Khimii, Tezisy Dokladov" (International Symposium on Macromolecular Chemistry. Abstracts of Reports), Tashkent, 1978, Vol.4.
44. B.I.Sazhin (Editor), "Elektricheskie Svoistva Polimerov" (Electrical Properties of Polymers), Izd. Khimiya, 1970.
45. O.N.Karpukhin and E.M.Slobodetskaya, Uspekhi Khim., **42**, 391 (1973)[Russ.Chem.Rev., No.3 (1973)].
46. O.N.Karpukhin and E.M.Slobodetskaya, Vysokomol. Soed., **18A**, 2700 (1976).
47. "Tezisy Dokladov Konferentsii Stran SEV po Probleme Atmosferostoikosti Materialov, Kutaisi, 1978" (Abstracts of Reports at the Conference of the Socialist Economic Community (SEV)[COMECON?] Countries on the Problem of the Resistance of Materials to the Action of the Atmosphere, Kutaisi, 1978).
48. V.A.Belinskii, M.B.Garadzha, E.I.Nezval', and L.M.Mezhennaya, "Ul'trafioletovaya Radiatsiya Solntsa i Neba" (The Ultraviolet Radiation from the Sun and Sky), Izd.Moskov.Gos.Univ., Moscow, 1968.
49. E.M.Mostovaya, E.M.Slobodetskaya, O.N.Karpukhin, and B.V.Novozhilov, Plast.Massy (in the Press).
50. Yu.A.Shlyapnikov, V.B.Miller, M.B.Neiman, E.S.Torsueva, and B.A.Gromov, Vysokomol.Soed., 2, 1409 (1960).

Institute of Chemical Physics,
USSR Academy of Sciences,
Moscow

Translated from *Uspekhi Khimii*, **49**, 1554-1573 (1980) U.D.C. 541.64:539.3

Prediction of the Variation of the Properties of Polymeric Materials after Prolonged Storage and Use

B.D.Goikhman and T.P.Smekhunova

The fundamental problems of the prediction of the changes in the properties of polymeric materials (in consequence of ageing, mass transfer, and the application of stresses) after prolonged storage and use are examined. The experimental conditions and the methods of interpretation of experimental data as well as characteristics of the method of accelerated tests on articles made from polymeric materials are discussed.
The bibliography includes 66 references.

CONTENTS

I. Introduction 748
II. The equivalent temperature as a characteristic of natural climatic conditions under which articles are stored and used 749
III. Changes in the properties of polymeric materials on ageing 750
IV. Changes in the properties of materials due to mass transfer processes 753
V. Prediction of the lifetimes of materials 754
VI. Accelerated tests on articles made from polymeric materials 755

I. INTRODUCTION

The increasing application of polymeric materials (PM) in various branches of the National Economy and the necessity to optimise their properties have given rise to the problem of improving the accuracy in predicting the duration of the technical suitability of the relevant articles.

On storage and during use, articles made of polymeric materials are acted upon by various factors: temperature, moisture, oxygen, ozone, light, radiation, corrosive media, biological factors, and applied forces. Depending on the duration and intensity of the influence, these factors lead to reversible and irreversible physicochemical processes, which include the following:

(a) thermal, radiation-induced, and light-induced ageing (chemical degradation and structure formation reactions, structural rearrangements at a supermolecular level), leading to irreversible changes in the properties of the polymeric material.

(b) Phase transformations in the polymeric material, which give rise to reversible changes in its properties.

(c) Mass transfer (relative migration of plasticisers in various elements of the articles, the removal of volatile components, the diffusion of moisture, etc.), causing changes in various properties of the articles.

(d) The accumulation of defects in the articles (constructions) owing to stresses active during storage and use, which lead to an alteration of the properties of the polymeric material, a change in its geometry, and the breakdown of the integrity of the constructions.

The influence of the above environmental factors on the polymeric material must be considered in terms of interrelations between them. For example, the simultaneous influence of heat, oxygen, and moisture gives rise to thermo-oxidative degradation (structure formation) in the material and hydrolytic degradation via different types of bonds, which is the reason for the complex variation of the properties of the polymeric material. The reversible and irreversible processes occurring in the polymeric material under the influence of the environment can be greatly accelerated if the articles are in a strained-deformed state.

In the problem of the estimation of the capacity for retention of the operational characteristics of the given articles the direct and converse tasks are distinguished. The direct task consists in estimating the storage times of the articles in terms of the permissible changes in their operational characteristics. The converse task consists in determining the required level of operational characteristics of the given articles to ensure their usability during a specified time. Formally, both problems are solved on the basis of the following condition:

$$Y_j(0)\rho_j(t) \geqslant [Y_j], \qquad (1)$$

where $[Y_j]$ and $Y_j(0)$ are respectively the maximum permissible and the initial characteristics of the article and $\rho_j(t)$ is the coefficient of the change in the characteristic Y_j with time (relative to the initial value).

The index of reliability, taking into account the sum total of the operational characteristics of the articles, is a generalised characteristic of the usability of the given articles. In view of the variation in the characteristics of the materials with time and the accumulation of defects in the articles under the influence of external conditions, the reliability index is a function of the storage time or the time during which the given articles are used. If this function has been determined quantitatively, the storage time can be found as the time required to attain the limiting permissible level of reliability; on the other hand, if the storage time has been specified, then the level of change in reliability can be determined from the above relation. In other words, in this case the problem also reduces to the solution of Eqn.(1), in which Y_j is the reliability index and $\rho_j(t)$ is the coefficient of its time variation. Here one should note that a certain excess reliability of the article at the beginning of the storage time is an inevitable "advance contribution" necessary to ensure the usability of the article within the limits of the specified time.

The correct solution of the kinetic problem of reliability involves considerable difficulties in most cases. For this reason, the following approach has come to be widely used in engineering practise. Eqn.(1) is solved for each of the characteristics which determine the usability of the article. To ensure the specified useful lifetime, the standardised requirements to be met by the characteristics are specified taking into account their time variation.

A characteristic feature of the problem of predicting the changes in the properties of a polymeric material is the short duration of laboratory tests at the stage involving

the development of the articles, i.e. under conditions where no direct experience in the use of the article can be gained. The problem can only be solved on the basis of the laws of chemical and physical kinetics and thermodynamics.

The majority of studies devoted to the prediction of changes in the operational properties of polymeric materials are characterised by an endeavour to simplify to the maximum possible extent the methods of interpretation of the kinetic $Y_j(t)$ curves. This frequently leads to the unjustified exclusion from consideration of a number of processes and hence to errors in prediction. This review deals with a series of practically most important aspects of the problem of prediction of the changes in the properties of polymeric materials on prolonged storage and use.

II. THE EQUIVALENT TEMPERATURE AS A CHARACTERISTIC OF NATURAL CLIMATIC CONDITIONS UNDER WHICH ARTICLES ARE STORED AND USED

In terms of thermal and other natural influences, the territory of the USSR can be divided into zones of cold, temperate, and hot climates. The climatic regions of the USSR differ considerably in terms of temperature, relative humidity, intensity of solar radiation, and other factors[1]. For example, the average diurnal temperature varies in the range from −50° to +40 °C, the hourly temperatures range from −60° to +45 °C, the maximum daily temperature amplitudes range from 20° to 30 °C, the average annual relative humidity is between 40 and 75%, the overall solar radiation intensity is between 87.7 and 158.5 kcal cm^{-2}, and the annual atmospheric precipitation ranges from 202 to 2788 mm.

The temperatures at which articles are stored, which in many respects determine the intensity of physicochemical processes, are particularly important. Furthermore, in many instances a change in the temperature of ambient air leads to the appearance and stresses in the articles (for example, diurnal variations in temperature induce non-stationary temperature stresses, while seasonal variations give rise to stationary stresses when there is a difference between the coefficients of thermal expansion of the constructional elements).

Variation of the temperature of ambient air during the storage of the articles within wide limits (up to 100 °C) makes it necessary to take into account the non-isothermal conditions in predicting the properties of the materials. The solution of kinetic equations under the conditions of a non-stationary temperature field may be carried out on a computer using the known laws governing the variation of temperature with time[2].

One of the ways in which non-stationary temperature conditions can be taken into account involves the introduction of the so-called equivalent temperature[3,4]. This term is understood as a conventional constant temperature at which the same changes take place in the given material during the time under consideration as under non-stationary temperature conditions. For chemical reactions described by the relation

$$\frac{dc}{dt} = -A_0 \exp\left(-\frac{U}{RT}\right) f(c) , \qquad (2)$$

where c is the concentration of the reactant, U the apparent process activation energy (in the general case the temperature coefficient of the rate of the process), A_0 the pre-exponential factor, R the gas constant, and $f(c)$ a function independent of temperature, the present authors[4] found an

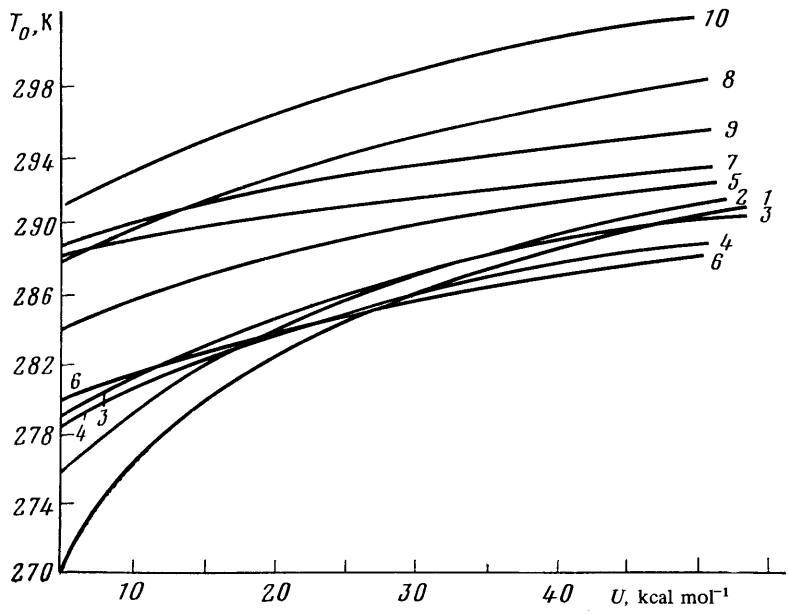


Figure 1. The $T_0(U)$ relation for representative points according to the results of observations carried out at specified times in different climatic regions: 1) very cold; 2) cold; 3) moderately cold; 4) moderately cold and moist; 5) moderately warm; 6) moderately warm and moist; 8) hot and dry; 9) moderately hot and moist; 10) very hot and dry.

expression describing the equivalent temperature:

$$T_0 = -\frac{U}{R}\left\{\ln\left[\frac{1}{t_0}\sum_{j=1}^{n}\Delta t_j \exp\left(-\frac{U}{RT_j}\right)\right]\right\}^{-1}, \qquad (3)$$

where n is the number of intervals Δt_j with an average temperature T_j during the time interval t_0 under consideration.

This expression for the equivalent temperature was obtained for decomposition processes, creep, the relaxation of stresses, etc.[4] The identity of the expressions for the equivalent temperature is due to the fact that the temperature dependence of the rates of different chemical and physical processes is described by analogous relations of the Arrhenius type.

It follows from Eqn.(3) that the equivalent temperature is a function of the apparent process activation energy and of the distribution of temperatures. For a known distribution of temperatures, the dependence of T_0 on U can be calculated beforehand. Fig.1 presents plots of T_0 against U calculated by Eqn.(3) for different climatic zones in the USSR using data from Ref.1†.

One should note that the equivalent average temperatures are not the same and in many cases there is not even a qualitative correlation between them. For example, the average annual temperature in the zone of the temperate, warm, and moist climate is 6.0 °C, while in the zone of the very cold climate it is −12.5 °C.[1] For the same climatic zones, the equivalent temperatures for $U = 35$ kcal mol^{-1} are respectively 13.3° and 14.3 °C (Fig.1), i.e. a higher equivalent temperature corresponds to a lower average annual temperature. Therefore treatment based on average annual temperatures can lead to significant errors in calculations in view of the considerable dependence of the rates of the processes on temperature.

The equivalent temperature found from Eqn.(3) can be regarded not only as the extrapolation temperature in predicting the changes in the properties of materials but also as a generalised characteristic of the temperature conditions in the storage and use of materials. It follows from the $T_0(U)$ relations in Fig.1 that the values of T_0 for different climatic zones are significantly different (up to 20 °C). In view of the significant dependence of the rates of processes on temperature, a difference of 3–4 °C in the equivalent temperature leads to a considerable difference in the rates of processes and the storage time.

The Table presents the values of T_0 and the relative rates (w/w_{cold}) of physicochemical processes in different climatic zones of the USSR. The rate of processes in the zone of the cold climate (w_{cold}) has been adopted arbitrarily as unity. Evidently the rates of physicochemical processes in different climatic regions can differ severalfold. Nevertheless the specified storage and utilisation times for articles are as a rule stated to be the same for the entire territory of the USSR (they are calculated for the most severe conditions). After this time has elapsed, the stock of given articles can differ severalfold depending on the storage conditions.

Bearing in mind that the zone of the dry, hot climate constitutes only ~10% of the territory of the USSR (the zones of the cold and temperate climates constitute 67 and 23% of the territory of the USSR respectively)[1], the desirability and economic efficiency of differentiating the storage times as a function of temperate conditions, at least for large and expensive articles used under the conditions of a single climatic region, becomes evident.

The relative rates of processes in different climatic regions of the USSR.

Climatic region	$U = 15$ kcal mol^{-1}		$U = 25$ kcal mol^{-1}		$U = 35$ kcal mol^{-1}	
	T_0, K	w/w_{cold}	T_0, K	w/w_{cold}	T_0, K	w/w_{cold}
Cold	281.9	1.0	285.6	1.0	288.3	1.0
Moderately warm	287.0	1.58	289.0	1.65	290.6	1.7
Dry and hot	291.2	2.46	294.0	3.5	296.0	4.8

III. CHANGES IN THE PROPERTIES OF POLYMERIC MATERIALS ON AGEING

The experimental methods for the prediction of the changes in the properties of polymeric materials during ageing are based on accelerated tests under conditions of increased temperature, moisture concentration, oxygen, radiation intensity, stresses, etc.

A survey of studies[6–16] during recent years in the Soviet literature shows that the curves describing the variation of the characteristics of materials during ageing under forced conditions are complex. Nevertheless, the authors of these studies used simplified methods for the interpretation of experimental kinetic curves in calculating the expected changes in the properties of materials or their storage times. This approach can lead to contradictory estimates of the expected changes[10] and also, as will be shown below, to not only quantitative but also qualitative errors. This leads in its turn to errors in the determination of the times of technical suitability of articles or unjustifiably high specifications which must be met by the operational characteristics.

In the general case the characteristic of a material investigated can be expressed in the form

$$Y_j = f_i(c_1, c_2, \ldots, c_n), \qquad (4)$$

where Y_j is the characteristic of the material under consideration and c_i the concentration of bonds of the ith type (chemical, physical) which determine the level of Y_j.

The time variation of the characteristic Y_j is evidently determined by the law governing the variation of concentration:

$$c_i = c_i(t, T, \xi), \; i = 1, 2 \ldots n \qquad (5)$$

(here t is the time, T the temperature, ξ the stress, radiation dose, the concentration of oxygen, etc.).

When the mechanism of ageing, which determines the form of function (5), and the law governing the establishment of properties (4) are known, the relation $Y_j = f(t, T, \xi)$ is unambiguously defined and the problem of prediction reduces to the corresponding analytical calculations at the storage and operating temperatures of the material. This in turn indicates the need to investigate and determine the quantitative relations between the rate of ageing and different factors. The determination of the mechanism of ageing and the

† In the absence of data on the distribution of temperature in the given climatic region, the equivalent temperature can be estimated from average minimum and maximum monthly temperatures[5]. The distribution of temperature on the surface and in the bulk of the articles differ somewhat from the distribution of temperature in the ambient air. In the absence of the effect of solar radiation, the corresponding values of T_0 will be lower than those in Fig.1.

law governing the establishment of properties would be the best guarantee of a reliable prediction.

However, in most cases the investigator does not have the necessary information concerning the structure of Eqns.(4) and (5) and the corresponding kintic constants. The generally accepted approach therefore consists in the study of the kinetics of the variation of the characteristics of the material under investigation $Y_j(t, T)$ with subsequent extrapolation of the results to the real temperature conditions.

We shall analyse the possible features of the variation of the characteristic $Y_j(t)$ (for example, in thermal ageing). We shall assume that relation (4) can be represented by the fairly general expression

$$Y_j = \sum_{i=1}^{n} \alpha_{ji} c_i^{m_{ji}}, \qquad (6)$$

where α_{ij} and m_{ji} are coefficients.

It follows from Eqns.(5) and (6) that, even under the conditions of simple kinetic laws governing the variation of the concentrations of bonds, the Y_j characteristic varies with time in a complex manner. The identity of the kinetic laws governing the variation of Y_j and c_i in terms of relative units obtains only for $n = 1$ and $m_{ji} = 1$ (in this case the kinetic parameters of the changes in the above quantities are identical). For $n = 1$ and $m_{ji} \neq 1$, the kinetic parameters of the variation of the bond concentration and of the characteristic are not identical even in the simple case where the bond concentration varies in accordance with the first-order law. For $n = 2$ and $m_{ji} = 1$, the above kinetic parameters also differ.

The different operating characteristics of the material are different functions of the concentration of the same bonds. In other words, the coefficients of Eqn.(6) for different characteristics of the material can be different. Therefore the same chemical and physical transformations in the material can lead to different changes in particular operating characteristics. The kinetic parameters of the variation of different characteristics can therefore also differ. In particular, the apparent activation energy U—the temperature coefficient of the rate of change of the characteristics—may not be the same as the true activation energy for the physicochemical process. The presence of stable bonds and the occurrence of recombination processes lead to a limiting value of the characteristic Y_j^{∞}.

For parallel competing first-order processes (structure formation and degradation) with $n = 2$ and $m_{ji} = 1$, we have

$$c_1 = c_1^0 \exp(-k_1 t); \quad c_2 = c_2^{\infty} - (c_2^{\infty} - c_2^0)\exp(-k_2 t) \qquad (7)$$

and

$$Y_j = \gamma_1 \exp(-k_1 t) - \gamma_2 \exp(-k_2 t) + Y_j^{\infty}, \qquad (8)$$

where k_1 and k_2 are rate constants, c_1^0 and c_2^0 are the concentrations at time $t = 0$, c_2^{∞} is the limiting concentration of bonds, and γ_1 and γ_2 are coefficients which are functions of c_1^0, c_2^0, and c_2^{∞}.

The plot of function (8) has an extremum and the corresponding asymptotic section. Thus for relatively simple hypotheses, the curves describing the variation of the characteristics of materials during ageing have a complex form. Nevertheless, in practical predictions of the changes in operating characteristics during thermal ageing, one normally employs elementary kinetic equations (of zero, first, and second orders), the treatment being limited in the case of complex $Y_j(t)$ curves to the description of their initial sections only[9-11,15]. There is a similar possibility of qualitative errors. This can be readily shown in relation to Eqn.(8). We shall assume that in the range of the temperatures of forced tests $k_1 > k_2$; the $Y_j(t)$ curves are then characterised by a minimum. The prediction based on the initial sections of these curves indicates a decrease of Y_j under real conditions. However, in consequence of the difference between the activation energies, there is also a possibility of a change in the ratio of the rates in the temperature range where the materials are used ($k_2 > k_1$). In this case there is a change also in the nature of the $Y_j(t)$ curve under real conditions (a maximum appears).

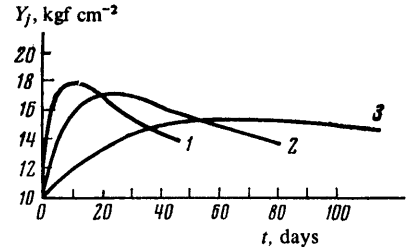


Figure 2. Calculated $Y_j(t)$ curves at different temperatures (°C): 1) 90; 2) 80; 3) 70.

We shall illustrate this by the following example. Suppose that the variation of the characteristic Y_j (for example, the short-term strength) is described by Eqn.(8) with $\gamma_1 = 13.8$, $\gamma_2 = 9.8$, $Y_j^{\infty} = 6$ kgf cm^{-2}, $k_1 = 7.4 \times 10^{-6} \exp(-14\,700/RT)$ days^{-1}, and $k_2 = 3.2 \times 10^{17} \exp(-30\,000/RT)$ days^{-1}. The calculated $Y_j(t)$ curves at 90°, 80°, and 70 °C have the form shown in Fig.2. The prediction based on the initial sections of these curves (up to the $Y_j = 12$ kgf cm^{-2} level), fitted by a first-order equation, indicates an increase of Y_j to 11.1 kgf cm^{-2} after ten years at 20 °C. On the other hand, calculation of the predicted $Y_j(t)$ curve by the initial Eqn.(8) indicates a decrease of the characteristic from 10.0 kgf cm^{-2} to 6.6 kgf cm^{-2} (Fig.3).

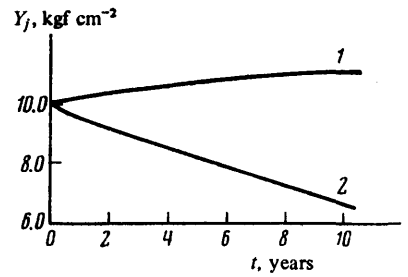


Figure 3. Predicted $Y_j(t)$ curves at 20 °C: 1) calculated from the initial sections of the curves in Fig.2; 2) calculated from the Eqn.(8).

Another common method of predicting the change in the properties of a polymeric material on thermal ageing is the so-called graphoanalytical method[10-14,21,22]. The essence of the method consists in the determination of the time t_{Y_j} for the attainment of identical values of Y_j from experimental

$Y_j(t)$ curves at different temperatures. The results are used to plot $\ln t_{Y_j} = f(1/T)$ and to find the time at the operating temperature by a linear extrapolation. The predicted $Y_j(t)$ curve at the operating temperature can be constructed on the basis of the complete set of values obtained.

It is easy to show that the linear relation between $\ln t_{Y_j}$ and $1/T$ is possible only in the case where the change in the characteristics is described by the kinetic equation

$$\frac{dY_j}{dt} = -A_0 \exp\left(-\frac{U}{RT}\right) f(Y_j). \qquad (9)$$

This postulates in its turn that the parameter U is independent of Y_j, i.e. that the $\ln t_{Y_j} = f(1/T)$ linear plots are parallel for different Y_j. This limits the region of applicability of the combined graphical and analytical method. The same limitation applies also to the familiar method of transformation coefficients[23]. In the case of curves with extrema, the application of these methods can also lead to qualitative errors in predicting the changes in the properties of materials.

It follows from the foregoing that, when the mechanism of ageing is unknown, in order to increase the reliability of the prediction of the changes in the properties of a polymeric material one must endeavour to discover the principal components of the process involving a change in Y_j and to obtain an analytical description of the latter. For this purpose, one can use the procedures of formal kinetics[23,24]. Frequently the form of the $Y_j(t)$ curves can be suggested by a version of the analytical curve fitting method. For example, in the case of S-shaped curves one can use formally the autocatalytic[23,24] or Kolmogorov–Erofeev[25,27] equation; experimental curves with asymptotic sections can be described by Eqn.(8). In the latter case, in particular, the parameters of the equation can be found by graphical or analytical methods[28,29] and Y_j^∞ is obtained by extrapolating the linearised relation $dY_j/dt = f(Y_j)$, corresponding to the last section of the $Y_j(t)$ curve, to the zero value of dY_j/dt or by the method# quoted by Shenk[30].

Naturally, mathematical modelling methods can be used for prediction on the basis of $Y_j(t)$ curves when the ageing mechanism is unknown[31].

We shall indicate yet another method whereby experimental $Y_j(t)$ curves can be fitted. Applying the methods for the expansion of functions, it is easy to show that Eqn.(6), corresponding to different varieties of relation (5), leads to a possible representation of the function $Y_j(t)$ by the experimental series

$$Y_j = Y_j^\infty + \sum_{i=1}^{n} \gamma_i \exp(-k_i t), \qquad (10)$$

where γ_i can be both positive and negative. The coefficients of Eqn.(10) naturally cannot always have a clear-cut physical significance, but, by fitting this equation to experimental data, one increases significantly the accuracy of the prediction and the determination of the principal components of the process involving the variation of $Y_j(t)$ is to some extent guaranteed. The coefficients of Eqn.(10) can be determined by the above procedure for Eqn.(8). Here the procedure used to search for the coefficients of the equation can reveal the fundamental stages (components) of the process involving the variation of $Y_j(t)$.

The method is based on the solution of the $Y_j = f(t)$ relation linearised with respect to t.

As an example, we shall consider the ageing of rubber based on SKMS-10 raw rubber. Fig.4 presents data for the accumulation of the residual deformation (ε_{res}) of the rubber under natural conditions. Analysis shows that the experimental data for the ageing of this rubber at 50–90 °C[32] are described satisfactorily by the equation

$$\varepsilon_{res} = \varepsilon_{res}^\infty - \gamma_1 \exp(-k_1 t) - \gamma_2 \exp(-k_2 t), \qquad (11)$$

where $\varepsilon_{res}^\infty = 97.5\%$, $\gamma_1 = 68.5\%$, $\gamma_2 = 29.0\%$, $k_1 = 3.2 \times 10^8 \exp(-16\,300/RT)$ days^{-1}, and $k_2 = 2.5 \times 10^{10} \exp(-17\,400/RT)$ days^{-1}. The $\varepsilon_{res}(t)$ for the regions of Central Asia and Transbaikal were calculated from the relations obtained. Fig.4 shows that the prediction is confirmed satisfactorily by observations carried out over many years.

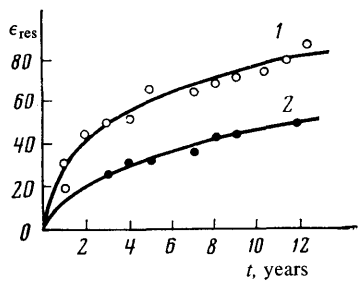


Figure 4. Kinetics of the accumulation of the residual deformation in rubber on storage in the regions of Central Asia (curve *1*) and Transbaikal (curve *2*) [the calculated curves were plotted on the basis of Eqn.(11) for $T_0 = 295.5$ K (curve *1*) and 283 K (curve *2*); the experimental points are based on the data of Dobrosklonskaya et al.[32]].

Mechanical stresses can have a significant influence on the rates of chemical reactions[33]. Under the influence of mechanical loads, chemical bonds are ruptured in polymers and free radicals are formed, giving rise to a chain of subsequent reactions[34]. The accelerating effect of mechanical stresses on thermal degradation processes in low-pressure polyethylene has been studied experimentally[35]. It has been shown[36] that mechanical stresses influence the apparent activation energy and the pre-exponential factor for the ageing of rubbers. According to the theory of absolute reaction rates[33], this implies that the stresses influence not only the energy barrier for the reactions but also the entropy of activation, which reflects the necessity for a specific orientation of the macromolecules.

Since the activation energy depends on the extent of the stresses, it is useful to study the ageing of materials in the stressed state at different temperatures under the conditions of constant stresses. The rates of processes then obey the Arrhenius equation, which can be used for extrapolation in the prediction. Tests under conditions of constant deformation complicate the task involved in the prediction owing to the temperature dependence of the rate of relaxation of stresses. Because of this, the level of stresses is different at different temperatures and hence there is a change in the apparent activation energy for the process. The use of the simple Arrhenius equation for prediction is in this case illegitimate.

The establishment of exact quantitative relations between the rate of ageing, on the one hand, and temperature and the extent of the stress on the other, makes it possible to calculate by numerical integration methods the predicted changes in the characteristics of materials under conditions of non-stationary stresses and temperatures[36].

IV. CHANGES IN THE PROPERTIES OF MATERIALS DUE TO MASS TRANSFER PROCESSES

Mass transfer phenomena are due to contact between the polymeric material and the surrounding medium and with other elements of the given articles. There is then a possibility of both physical and chemical transformations. Physical transformations are due to plasticisation, swelling, the formation of pores, etc.; chemical transformations are caused by the interaction of the diffusing substance with different functional groups of the polymer.

In the study of the interaction of a given article with the environment one usually investigates the changes of characteristics as a function of the duration of the influence of the medium (for example, increase in moisture content)[16-18]. The results of such tests indicate a sensitivity of articles to particular influences, but they are insufficient for the solution of the problems of prediction, since they refer to a specific geometry of the specimen, degree of penetration, etc.

For predictions of the changes due to physical transformations, it is necessary to establish the law governing the variation of the concentration of the diffusing substance with time at any point within the article:

$$a_i = a_i(r, t) \tag{12}$$

(here a_i is the concentration and r the flux coordinate) and the dependence of the characteristic of the material on concentration:

$$Y_j = Y_j(a_i). \tag{13}$$

By solving the mass transfer equation[29]

$$\frac{\partial \mu}{\partial t} = D\nabla^2\mu, \tag{14}$$

where μ is the chemical potential and D the diffusion coefficient, one determines the law governing the variation of concentration $a_i(r, t)$. The dependence of the characteristics of the material on the concentration $Y_j(a_i)$ is established experimentally. Simultaneous solution of Eqns.(12) and (13) yield the relation

$$Y_j = f(r, t). \tag{15}$$

If the diffusing substance participates in the chemical reactions responsible for the changes in the properties of the material) for example, water in hydrolytic degradation reactions[37-41]), then in the prediction one must solve the non-stationary kinetic problem taking into account the diffusion of the reactants:

$$\frac{\partial \mu}{\partial t} = D\nabla^2\mu - g(\mu), \tag{16}$$

where $g(\mu)$ is the rate of loss of the diffusing reactant (in units of chemical potential) owing to the chemical reaction. An evident condition for the solution of the problem is the determination of the mechanism and kinetics of the chemical reaction involving the diffusing reactant, which determine the $g(\mu)$ relation and the $Y_j = f(c_1, c_2, \ldots, c_n, a_i)$ relations.

The problem of the influence of atmospheric moisture is particularly important. It is known that, for many constructional polymeric materials, a change in humidity by several hundredths per cent leads to significant changes in operating properties. The endeavour to take into account the influence of moisture in accelerated tests for ageing (the so-called thermal-humidity ageing) is frequently expressed by the fact that tests at elevated temperatures are carried out at the level of the real relative humidity[42-44] (for example, 80 °C and a humidity of 80%). While the humidity under storage conditions is apparently reproduced, such tests can lead to considerable errors since the limiting (equilibrium) moisture content of the material changes significantly as the temperature is altered. This leads to non-equivalent changes in the properties of the material for purely physical reasons.

In order to separate chemical and physical transformations in thermal-humidity ageing, one can employ the method of conditioning the specimens, which consists in the fact that before and during thermal-humidity tests the specimens are maintained at the same relative humidity and temperature until the attainment of a state of equilibrium before measuring the characteristics. The conditioning method is based on the reversibility of the changes in the properties of the material due to physical transformations. The changes in properties detected in the course of tests on the material are due solely to chemical transformations.

The tests involved in estimating the changes in the properties of materials due to physical transformations are carried out by maintaining the specimens at different humidities at a low temperature (20–25 °C). Under these conditions, chemical transformations are hardly manifested during the experiment. The experiments are used to determine the sorption isotherms, the diffusion coefficients, and the $Y_j(a_i)$ relation.

We shall consider the changes in the operating properties of polymeric materials due to chemical transformations in thermal-humidity ageing. The simplest example is the case where the characteristic of the material Y_j investigated is determined by a single type of bond subject to hydrolytic degradation. Assuming that

$$Y_j = \alpha c^n, \quad \frac{dc}{dt} = -k_1 cW, \quad \frac{dW}{dt} = -k_1 cW + k_2(W_e - W), \tag{17}$$

where W and W_e are the current and limiting (equilibrium) moisture contents of the material and k_2 is the mass exchange rate constant, we obtain for the quasi-stationary state ($dW/dt \cong 0$) [45]

$$W = \frac{k_2 W_e}{k_1 c + k_2}, \quad \frac{dc}{dt} = -\frac{k_1 c k_2 W_e}{k_1 c + k_2}. \tag{18}$$

When the process takes place in the kinetic region (for example, in the case of film materials), we have

$$k_2 \gg k_1 c, \quad \frac{dc}{dt} = -k_1 W_e c; \quad \frac{dY_j}{dt} = -\tilde{k}_1 Y_j; \quad \tilde{k}_1 = nk_1 W_e. \tag{19}$$

In the diffusion region

$$k_2 \ll k_1 c, \quad \frac{dc}{dt} = -k_2 W_e; \quad \frac{dY_j}{dt} = -\tilde{k}_2 Y_j^{1-1/n}, \quad \tilde{k}_2 = n\alpha^{1/n} k_2 W_e. \tag{20}$$

Using the equation of the Freundlich isotherm

$$W_e = \chi p^{1/\nu}, \tag{21}$$

the Clausius–Clapeyron equation for equilibrium systems

$$\frac{d \ln p}{d(1/T)} = -\frac{Q}{R} \tag{22}$$

(p is the water vapour pressure, Q the heat of sorption, and χ and ν are coefficients), and the equation for the temperature dependence of the constants k_1 and k_2, it is easy to show that

$$\tilde{k}_1 = a_1 p^{1/\nu} \exp\left(-\frac{U - Q/\nu}{RT}\right); \quad \tilde{k}_2 = a_2 p^{1/\nu} \exp\left(-\frac{E - Q/\nu}{RT}\right), \tag{23}$$

where U and E are respectively the apparent activation energy for the reaction and diffusion and a_1 and a_2 are coefficients.

Eqns.(23) determine the temperature dependence of the effective rate constants $\tilde{k}_1$ and $\tilde{k}_2$ for the variation of the characteristic Y_j. If tests at different temperatures are carried out at $p = \text{const}$., then it follows from Eqn.(23) that the dependences of $\ln \tilde{k}_1$ and $\ln \tilde{k}_2$ on $1/T$ are linear, which makes it possible to employ them for the prediction of the rate of change of Y_j when the material is stored under real conditions. The apparent activation energy is then determined by the differences $U - Q/\nu$ and $E - Q/\nu$ respectively.

If the materials are tested at a constant relative humidity of air ϕ, then, bearing in mind that

$$p = p_{sat} \cdot \varphi; \quad p_{sat} = \lambda \exp(-L/RT) \tag{24}$$

(p_{sat} is the water vapour pressure, L the heat of vaporisation, and λ a coefficient), we obtain

$$\tilde{k}_1 = b_1 \varphi^{1/\nu} \exp\left(-\frac{U - Q/\nu + L/\nu}{RT}\right); \quad \tilde{k}_2 = b_2 \varphi^{1/\nu} \exp\left(-\frac{E - Q/\nu + L/\nu}{RT}\right), \tag{25}$$

where b_1 and b_2 are coefficients. Eqns.(25) also make it possible to use for prediction the linear dependences of $\ln \tilde{k}_1$ and $\ln \tilde{k}_2$ on $1/T$, but naturally with coefficients different to those in Eqn.(23).

The above relations (17)–(25) describe the changes in characteristics occurring in consequence of chemical transformations under the influence of water. The corresponding coefficients can be found from experimental $Y_j(t)$ curves obtained by the method of conditioning the specimens. The overall change in the properties of the material is determined as the sum of the changes due to chemical and physical transformations.

One must note that Eqns.(17)–(25) refer to certain limiting situations. In the general case a correct prediction of the changes in the properties of the material is possible on the basis of the diffusion-kinetic model defined by Eqn.(16).

V. PREDICTION OF THE LIFETIMES OF MATERIALS

Ideas concerning the breakdown of materials as a process occurring in time have come to be generally accepted[47–53]. The breakdown of bodies under the influence of stresses can be regarded as a chemical degradation reaction activated by the stress. Different types of reactions have been analysed in a number of studies[54–58] and in the review of Deyun et al.§

The time before the breakdown of the material under the influence of a constant stress σ under the conditions of a constant temperature is referred to as the lifetime of the material τ. Experimental $\tau(\sigma)$ relations constitute the basis for the prediction of the lifetime. The empirical relations (at $T = \text{const}$.)

$$\tau = A \exp(-\alpha\sigma), \tag{26}$$

$$\tau = B\sigma^{-m}, \tag{27}$$

where α, m, A, and B are coefficients, have come to be most widely used.

Eqn.(26) usually holds for rigid polymeric materials, while Eqn.(27) is valid for elastomers. It has been shown[55,60] that Eqns.(26) and (27) constitute limiting cases of more general $\tau(\sigma)$ relations; the region of their applicability is determined by the extent of the stresses. Eqn.(27) holds as a rule in the region of low stresses and Eqn.(26) in the region of higher stresses. Since in experiments involving the determination of the $\tau(\sigma)$ relation one measures the time before the breakdown of the specimen under the influence of the stress, τ is frequently referred to as the mechanical lifetime.

During storage and use, articles made from polymeric materials are subjected to stresses and temperatures which vary with time. Under these conditions, the lifetime can be calculated on the basis of particular models of the process (physical, chemical, and mechanical)[48,49,55–58,60,61].

The breakdown of the material is characterised by the degree of accumulation of defects. From the standpoint of chemical kinetics, the degree of accumulation of defects in the material is measured by the ratio of the amount of ruptured bonds to the total number of bonds per unit cross-sectional area of the specimen. In the mechanics of continuous media, the ratio of the time of application of the load to the lifetime or ratio of the acting stress to the breaking stress as well as other criteria serve as measures of the extent of damage at a constant acting stress, while under non-stationary conditions the corresponding integral functions serve as the relevant measures. The limiting degree of accumulation of defects, usually set equal to unity, serves as a criterion of the breakdown.

The criteria of Bailey[48,49]

$$\int_0^{t_b} \frac{dt}{\tau(\sigma, T)} = 1, \tag{28}$$

Il'yushin[60]

$$\int_0^{t_b} \frac{d\sigma}{S(t_b - t)} = 1 \tag{29}$$

and others[61,62] have come to be most widely used in engineering practice [in these relations t is the time of application of the load, t_b the time before breakdown, and S the breaking (constant) stress]. Being of phenomenological origin, these criteria have a physical basis in many instances. For example, the applicability of Bailey's criterion has been examined from the standpoint of the kinetics of the development of cracks[63].

Much experience has been gained in engineering practice as regards these criteria and the limitis of their applicability have been established. Bailey's criterion, defined by Eqn. (28), which expresses the principle of the summation of defects but does not take into account the history of the applied load, is the simplest.

In contrast to Bailey's criterion, Il'yushin's criterion, defined by Eqn.(29), reflects the history of the applied load, while non-linear criteria examined in a number of studies[60–62] make it possible to take into account more accurately the complex laws governing the effect of the load and the mechanical behaviour of bodies in terms of empirical coefficients.

As already stated, the breakdown criteria are used to estimate the lifetime of the material (article) under the conditions of a non-stationary stress. The properties of the material are then assumed to be unchanged. Under real storage and operating conditions, the properties of the polymeric material vary owing to ageing, mass transfer, etc. processes. The real lifetime of the material can then differ significantly from the lifetime predicted on the basis of the results of mechanical tests in which the effect of factors other than stresses is usually excluded[63].

§ See E.V.Deyun, G.B.Manelis, E.V.Polianchuk, and L.P.Smirnov, Uspekhi Khim., **49**, 1574 (1980) [Russ.Chem. Rev., No.8 (1980)].

The criteria of long-term strength, extended to the case of physicochemical transformations, will be used to predict the real lifetime. As a simple example, we shall examine Bailey's criterion, which can be formulated as follows in this instance:

$$\int_0^{t_b} \frac{dt}{\tau(\sigma, T, \eta)} = 1, \qquad (30)$$

where η is the extent of the change in the properties of the material owing to physicochemical transformations. Assuming, in accordance with Eqn.(27), that

$$\tau = B(\eta)\sigma^{-m(\eta)} \qquad (31)$$

and taking into account the fact that $\eta = \eta(t)$, we obtain from Eqn.(30) for σ, $T = \text{const.}$,

$$\int_0^{\tau_s} B^{-1}(t)\,\sigma^{m(t)}\,dt = 1, \qquad (32)$$

where τ_s is the time before the breakdown of the material for constant stresses and at a constant temperature (the lifetime). Having established the characteristics of the variation of $B(t)$ and $m(t)$ during ageing, mass exchange, and other transformations, it is possible to calculate the lifetime from Eqn.(32). In the general case calculations by Eqn.(30) or (32) are performed by numerical integration.

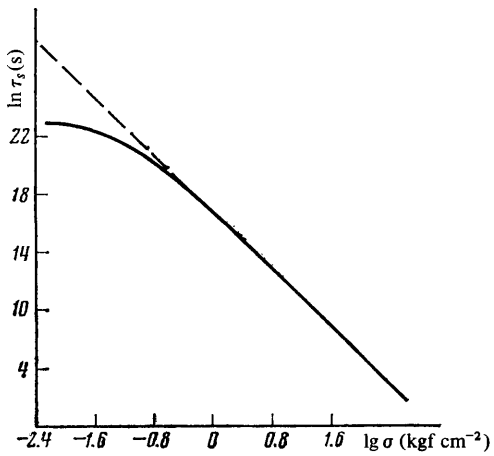


Figure 5. Dependence of $\ln \tau_s$ on $\ln \sigma$ for $B_0 = 10^7$ s, $m = 5$, and $k = 5.7 \times 10^{-9}$ s^{-1} (the curve in the absence of transformations is shown dashed)[64].

In order to elucidate the fundamental characteristics of the $\tau_s(t)$ relation, we shall consider the following example. It is known that, in the ageing of many polymeric materials up to a degree of conversion of 25–50%, the exponent m in Eqn.(27) hardly changes; the variation of the lifetime is due to the variation of the coefficient B. Assuming that the coefficient B changes as a result of ageing in accordance with the first-order equation

$$B = B_0 \exp(-kt), \qquad (33)$$

where k is the rate constant for the ageing process, we obtain, after integrating Eqn.(32),

$$\tau_s = k^{-1} \cdot \ln(1 + kB_0\sigma^{-m}) = k^{-1} \ln(1 + k\tau_0), \qquad (34)$$

where $\tau_0 = B_0\sigma^{-m}$ is the lifetime determined by the action of mechanical stresses. For $k\tau_0(\sigma) \ll 1$, we have

$$\ln(1 + k\tau_0) \simeq k\tau_0; \quad \tau_s \simeq \tau_0. \qquad (35)$$

This condition limits the region where Eqns.(26) and (27) can be used to predict the strength and lifetime of the materials. When $k\tau_0 \gg 1$, we have $\tau_s < \tau_0$, i.e. the real lifetime is shorter than the mechanical lifetime.

Evidently, when $\sigma \gg (kB_0)^{1/m}$, we have

$$\ln \tau_s = \ln B_0 - m \ln \sigma, \qquad (36)$$

and, when $\sigma \ll (kB_0)^{1/m}$, we have

$$\tau_s = k^{-1} \ln(kB_0) - mk^{-1} \ln \sigma\,. \qquad (37)$$

Thus the linear relation $\ln \tau_s = f(\ln \sigma)$ is converted into the linear relation $\tau_s = f(\ln \sigma)$. The lifetime curve constructed by plotting $\ln \tau_s$ against $\ln \sigma$ shows a characteristic inflection (Fig.5). Fig.5 shows that the difference between the lifetimes τ_s and τ_0 for low stresses can reach two decadic orders of magnitude.

This approach to the prediction of the lifetime of a polymeric material under the conditions of physicochemical transformations can be used virtually whatever the law governing the variation of the parameters of the mechanical lifetime and whatever other criteria of long-term strength are employed. A necessary condition for this purpose is the study of the kinetics of the physicochemical transformations and the determination of the relation between the parameters of the mechanical lifetime and the degree of transformation.

VI. ACCELERATED TESTS ON ARTICLES MADE FROM POLYMERIC MATERIALS

Articles made from polymeric materials differ from specimens of the materials in the first place by the presence of stresses due to the geometry and size of the articles and also the external influences to which they are subjected. In order to estimate the lifetime of articles made from polymeric materials, accelerated tests are frequently resorted to, i.e. tests are made on the whole article or on its individual components for the influence of various operating factors (temperature and humidity of the surrounding air, temperature differences, radiation, and applied loads).

Accelerated tests on an article without a detailed elucidation of the characteristic features of the variation of the properties of the relevant materials are frequently regarded as the only method of predicting their lifetime. The task to be performed in selecting the conditions for such tests is believed to involve the modelling of the operating conditions[65]. This approach can hardly be regarded as useful, since a well-founded choice of conditions for the tests is impossible without knowing the characteristics of the variation of the properties of the materials. Furthermore, there is a possibility of the case where the predicted changes in the characteristics of the article under storage and operating conditions can amount to a fraction per cent and complex and expensive tests are then pointless.

We believe that the task of accelerated tests is not the modelling of external factors but the reproduction of the changes in the characteristics of the articles which are to be expected during storage and use. These tests are carried out in order to confirm the predicted changes in the characteristics of the articles under the influence of various factors only in those cases where the predicted changes are significant and have a negative influence on the suitability of the material for its purpose and when allowance for the changes in all the characteristics of the article is difficult. The conditions of accelerated tests on articles can be chosen only on

the basis of the study of the kinetics of the variation of the characteristics of the materials. The parameters of the tests are selected on the basis of the condition that identical changes in the operating properties of the polymeric material under operating conditions are reproduced in the accelerated tests:

$$\Delta Y_j(t_0, \chi_0) = \Delta Y_j(t_a, \chi_a). \quad (38)$$

where t_0 and t_a are the storage time and the duration of accelerated tests and χ_0 and χ_a are the parameters of the storage conditions and the conditions of the accelerated tests (temperature, stress, relative humidity, radiation dose, etc.). Tests designed to reproduce the changes in the properties of the material during ageing, mass transfer, and under the influence of stresses are special cases.

Tests for thermal ageing are carried out by maintaining the article at a specified constant temperature T_a during the so-called equivalent time t_a. In simple cases where the change in Y_j is described by Eqn.(9), the time t_a can be calculated from the relation[65,66]

$$t_a = t_0 \exp\left[\frac{U}{R}\left(\frac{1}{T_a} - \frac{1}{T_0}\right)\right]. \quad (39)$$

Calculation of the equivalent time t_a by Eqn.(39) without taking into account the specific kinetic features of $Y_j(t)$ can lead to significant errors. The most general method for the determination of t_a therefore consists of the following steps. On the basis of the known kinetics of the variation of the characteristic of the material during ageing, one plots the predicted curve $Y_j(t)$ for specified storage conditions ($T = T_0$) and the curve $Y_j(t)$ under forced conditions ($T = T_a$). The greatest changes in Y_j are determined from the predicted curve and the time t_a corresponding to the attainment of these changes at $T = T_a$ is found (Fig.6). One must then bear in mind that in the case of complex processes the maximum changes in properties cannot always be reproduced in accelerated tests. Thus, for processes described by Eqn.(8), there exists a temperature T_* above which no changes occurring under real storage conditions can be reproduced owing to the inversion of the curves $Y_j(t)$. This is in no way caused by a change in the mechanism of the processes but is due to a change in the ratio of their rate constants. The quantity T_* is defined by the expression

$$T_* = \frac{U_1 - U_2}{R \ln (A_1/A_2)}, \quad (40)$$

where U_1 and U_2 are apparent activation energies and A_1 and A_2 are the pre-exponential factors associated with the corresponding rate constants. One should bear in mind that, when $T < T_*$, it is possible to reproduce only those changes which do not exceed the level corresponding to T_a.

In accelerated tests on articles made from different polymeric materials the problem of the simulation of several processes arises. The choice of the equivalent times t_a on the basis of the apparent activation energy for a certain process in any given material can lead to unduly extensive or, conversely, insufficient transformations in other materials. Analysis shows that the problem of the reproduction of the real changes in Y_j in a multielement article can be solved rigorously only in a few instances. These include cases where Eqn.(9) holds for each element (material) and there is a definite relation between the kinetic parameters[66].

The parameters of the conditions of accelerated tests for the influence of mass transfer processes can also be chosen from the condition for the attainment of identical changes in properties during storage and accelerated tests. For this purpose, one calculates from the solution of mass transfer equations the change in the concentration of the diffusing substance under storage conditions and in accelerated tests: $a_i = f(t, r)$. Using the relation $Y_j = f(a_i)$, one plots on the basis of the data obtained the curves $Y_j = f(t, r)$ from which one determines the duration of the tests in accordance with the scheme illustrated in Fig.6. In this case accelerated tests are carried out at an elevated temperature and concentration of the diffusing substance (for example, atmospheric moisture). These tests can be combined with tests of the reproducibility of the changes in the properties of the material during ageing.

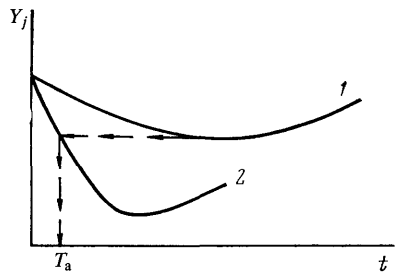


Figure 6. Selection of the duration of tests: 1) predicted $Y_j(t)$ curve describing the variation of the characteristics of the material under the conditions of storage or use at $T = T_0$; 2) the curve describing the variation of the characteristics of the material under the conditions of accelerated tests at $T = T_a$.

Under the storage conditions, articles made from polymeric materials are subjected to prolonged stresses. These include stresses due to gravitational forces, stationary and non-stationary temperature stresses induced by seasonal and diurnal changes in temperature, etc. Well-founded conditions for accelerated tests, designed to check the influence of various forces (the level of stresses, amplitude, temperature, duration), are selected on the basis of identity conditions in the accumulation of defects during storage and accelerated tests[66]:

$$\pi(T_0, \sigma_0^e, \eta_0, t_0) = \pi(T_a, \sigma_a^e, \eta_a, t_a), \quad (41)$$

where π is the level of accumulated defects and σ^e are equivalent stresses in the article. When Bailey's integral is used as a measure of the accumulation of defects (π), the above condition is formulated as follows:

$$\int_0^{t_0} \frac{dt}{\tau(\sigma_0^e, T_0, \eta_0)} = \int_0^{t_a} \frac{dt}{\tau(\sigma_a^e, T_a, \eta_a)}. \quad (42)$$

Consider the following example. We assume that the article made from a polymeric material is stored at a temperature T_0 and is subjected to a stress σ_0^e during a period t_0. The corresponding quantities σ_a^e and T_a are chosen for the accelerated tests. Assuming for simplicity that $\eta_0 = \eta_a = 0$, we obtain from Eqn.(42)

$$t_a = t_0 \frac{\tau(\sigma_a^e, T_a)}{\tau(\sigma_0^e, T_0)}. \quad (43)$$

In this case, when the relation $\tau(\sigma)$ is determined by Eqn. (27), we have, for $T_a = T_0$,

$$t_a = t_0 \left(\frac{\sigma_0^e}{\sigma_a^e}\right)^m. \quad (44)$$

Since for a polymeric material we usually have $m > 6$, the increase of stresses under the conditions of accelerated tests makes it possible to reduce greatly their duration. For example, for $\sigma_a^e = 2\sigma_0^e$ and $m = 7$, we obtain $t_a < 0.01 t_0$ when $T_a = T_0$.

For an exponential relation between the lifetime and σ [Eqn. (26)], it follows from Eqn.(43) that

$$t_a = t_0 \exp [\alpha (\sigma_0^e - \sigma_a^e)]. \quad (45)$$

When $\sigma = \text{const.}$, the following relation usually holds[48,49]:

$$\tau = p \exp (U_b/RT) \quad (46)$$

where U_b is the apparent activation energy for the breakdown and p a coefficient. It follows from Eqns.(43) and (46) that, when $\sigma_a^e = \sigma_0^e$,

$$t_a = t_0 \exp \left[\frac{U_b}{R} \left(\frac{1}{T_a} - \frac{1}{T_0} \right) \right]. \quad (47)$$

The above relations indicate the possibility of intensifying accelerated tests on articles by the application of forces and elevated temperatures.

This approach can be used also in tests for cyclic influences of forces[66]. From Eqn.(41), one can calculate the time during which articles must be thermostatted at negative temperatures and the number of cycles simulating the influence of diurnal oscillations in temperature.

---o0o---

It follows from the foregoing that the endeavour to simplify unduly the methods for the interpretation of kinetic curves and the determination of the parameters of accelerated tests can lead to gross errors, including qualitative errors.

A correct prediction is based on the study of the kinetics of the variation of the properties of materials under the influence of various factors and the mechanisms of the processes taking place.

REFERENCES

1. GOST 16 350-70. Klimat SSSR. Raionirovanie i Kharakteristiki Klimaticheskikh Parametrov dlya Promyshlennykh Izdelii" [GOST (USSR Government Standard) 16 350-70. The Climate of the USSR. Regional Variation and Characteristics of the Climatic Parameters for Industrial Articles].
2. V.E.Zotkin and V.N.Vorob'ev, Standarty i Kachestvo, No.8, 52 (1978).
3. V.D.Goikhman, A.D.Moshchenskii, and L.V.Selezneva, Kauchuk i Rezina, No.4, 49 (1968).
4. B.D.Goikhman and T.P.Smekhunova, Fiziko-Khimicheskaya Mekhanika Materialov, No.1, 92 (1977).
5. L.S.Fel'dshtein, M.G.Muradova, and L.G.Angert, Kauchuk i Rezina, No.6, 26 (1974).
6. A.G.Dement'ev, O.G.Tarakanov, P.I.Seliverstov, and E.V.Belova, Plast.Massy, No.5, 47 (1974).
7. A.K.Zhitinkina, A.G.Dement'ev, N.A.Tolstykh, and O.G.Tarakanov, Plast.Massy, No.5, 50 (1974).
8. A.G.Dement'ev, O.G.Tarakanov, P.I.Seliverstov, and E.V.Belova, Plast.Massy, No.5, 52 (1974).
9. I.F.Legrei and M.N.Bokshitskii, Plast.Massy, No.2, 54 (1974).
10. E.I.Kirillova, Plast.Massy, No.3, 49 (1973).
11. N.P.Lazareva, S.S.Khin'kis, M.F.Utyugov, M.S.Borodulina, T.S.Sokolova, and E.P.Matveeva, Plast.Massy, No.7, 75 (1973).
12. N.N.Pavlov, V.A.Sade, and G.A.Kudryavtseva, Plast. Massy, No.3, 52 (1974).
13. E.L.Vinogradov, L.I.Godunova, A.M.Lobanov, N.V.Lysenko, L.M.Terent'ev, and S.S.Khin'kis, Plast. Massy, No.4, 44 (1976).
14. A.G.Dement'ev, L.N.Malinin, V.V.Strakhov, and V.K.Anan'ev, Plast.Massy, No.1, 52 (1977).
15. E.L.Vinogradova, M.G.Bruk, and A.L.Vdovina, Plast. Massy, No.5, 51 (1977).
16. M.E.Sarkisyan, V.L.Kravchenok, and V.S.Petrov, Mekhanika Kompozitnykh Materialov, 1, 163 (1979).
17. V.M.Shcherbakov, S.V.Mazur, Kh.V.Solomon, and V.M.Gal'perina, Plast.Massy, No.10, 37 (1962).
18. G.O.Tatevos'yan and I.G.Kuznetsova, Plast.Massy, No.2, 52 (1963).
19. A.V.Tobolsky, "Properties and Structures of Polymers" (Translated into Russian), Izd.Khimiya, Moscow, 1964.
20. B.A.Dogadkin, B.K.Karmin, and I.I.Gol'berg, Dokl. Akad.Nauk SSSR, **53**, 331 (1946).
21. GOST 9033-74. Reziny. Metod Prognozirovaniya Izmeneniya Svoistv pri Termicheskom Starenii" [GOST (USSR Government Standard) 9033-74. Rubbers. Methods for the Prediction of the Changes in Properties on Thermal Ageing].
22. GOST 9035-74. Reziny. Metod Uskorennogo Opredeleniya Garantiinogo Sroka Khraneniya Uplotnitel'nykh Detalei Nepodvizhnykh Soedinenii [GOST (USSR Goverment Standard) 9035-74. Rubbers. Method for the Rapid Determination of the Guaranteed Storage Time of the Sealing Components of Fixed Junctions].
23. N.M.Emanuel' and D.G.Knorre, "Kurs Khimicheskoi Kinetiki" (A Course of Chemical Kinetics), Izd. Vysshaya Shkola, Moscow, 1969.
24. S.W.Benson, "The Foundations of Chemical Kinetics" (Translated into Russian), Izd.Mir, Moscow, 1964.
25. A.N.Kolmogorov, Izv.Akad.Nauk SSSR, Ser.Mat., 3, 355 (1937).
26. B.V.Erofeev, Dokl.Akad.Nauk SSSR, **52**, 515 (1946).
27. D.A.Young, "Decomposition of Solids" (Translated into Russian), Izd.Mir, Moscow, 1969.
28. A.A.Tatarnikov, Kauchuk i Rezina, No.3, 34 (1976).
29. A.V.Lykov, "Teoriya Teploprovodnosti" (Theory of Thermal Conductivity), Izd.Vysshaya Shkola, Moscow, 1967.
30. N.E.Shenk, Int.J.Chem.Kinet., **6**, 577 (1973).
31. L.S.Polak (Editor), "Primenenie Vychislitel'noi Matematiki v Khimicheskoi i Fizicheskoi Kinetike" (Application of Computational Mathematics to Chemical and Physical Kinetics), Izd.Nauka, Moscow, 1969.
32. M.S.Dobrosklonskaya, V.G.Rebizova, and A.S.Kosenkova, Kauchuk i Rezina, No.4, 9 (1968).
33. S.Glasstone, K.J.Laidler, and H.Eyring, "Theory of Rate Processes" (Translated into Russian), Inostr. Lit., Moscow, 1948.
34. S.E.Bresler, S.N.Zhurkov, E.N.Kazbekov, E.M.Sominskii, and E.E.Tomashevskii, Zhur.Tekh.Fiz., **29**, 358 (1959).
35. V.E.Korsukov, V.I.Vettegren', I.I.Novak, and L.P.Zaitseva, Vysokomol.Soed., **16**, 1538 (1974).
36. G.I.Sarser, B.D.Goikhman, N.G.Kalinin, and A.N.Tynnyi, Fiziko-Khimicheskaya Mekhanika Materialov, No.1, 89 (1975).
37. N.Grassie, "Chemistry of High Polymer Degradation Processes" (Translated into Russian), Inostr.Lit., Moscow, 1959.
38. G.E.Zaikov and Yu.V.Moiseev, Plast.Massy, No.11, 43 (1972).
39. L.V.Ivanov, Yu.V.Moiseev, and G.E.Zaikov, Vysokomol.Soed., **14A**, 1057 (1972).

40. L.V.Ivanov, Yu.V.Moiseev, and G.E.Zaikov, Izv.Akad. Nauk SSSR, Ser.Khim., 2501 (1970).
41. G.E.Zaikov, Uspekhi Khim., **44**, 1805 (1975) [Russ. Chem.Rev., No.10 (1975)].
42. GOST 21 126-75. Izdeliya Elektrotekhnicheskie. Materialy, Pokrytiya, Uzly i Detali. Metody Uskorennykh Ispytanii na Dolgovechnost' i Sokhranyaemost' v Agressivnykh Sredakh. Obshchie Polozheniya [GOST (USSR Government Standard) 21 126-75. Electrotechnical Articles. Materials, Coatings, Junctions, and Components. Methods for Accelerated Tests for the Lifetime and Capacity for Storage in Corrosive Media. General Postulates].
43. GOST 9044-75. Pokrytiya Lakokrasochnye. Uskorennye Metody Opredeleniya Svetostoikosti [GOST (USSR Government Standard) 9044-75. Paint and Varnish Coatings. Accelerated Methods for the Determination of Resistance to Light].
44. GOST 17 171-71. Plastmassy. Metody Ispytaniya na Starenie pod Vozdeistviem Iskusstvennykh Klimaticheskikh Faktorov [GOST (USSR Government Standard) 17 171-71. Plastics. Methods for Tests for Ageing under the Influence of Artificial Climatic Factors].
45. D.A.Frank-Kamenetskii, "Diffuziya i Teploperedacha v Khimicheskoi Kinetike" (Diffusion and Heat Transfer in Chemical Kinetics), Izd.Nauka, Moscow, 1967.
46. S.Brunauer, "The Adsorption of Gases and Vapours" (Translated into Russian), Inostr.Lit., Moscow, 1948, Vol.1.
47. S.N.Zhurkov, Izv.Akad.Nauk SSSR, Neorg.Materialy, 3, 1767 (1967).
48. V.R.Regel', A.I.Slutsker, and E.E.Tomashevskii, "Kineticheskaya Priroda Prochnosti Tverdykh Tel" (The Kinetic Nature of the Strength of Solids), Izd. Nauka, Moscow, 1974.
49. G.M.Bartenev and Yu.S.Zuev, "Prochnost' i Razrushenie Vysokoplastichnykh Materialov" (The Strength and Breakdown of Highly Plastic Materials), Izd.Khimiya, Moscow–Leningrad, 1964.
50. V.E.Gul', "Prochnost' Polimerov" (The Strength of Polymers), Izd.Khimiya, Moscow–Leningrad, 1964.
51. W.G.Knauss, Mekhanika (Periodicheskii Sbornik Perevodov Inostrannykh Statei), No.2, 116 (1974).
52. C.B.Henderson, P.H.Graham, and C.N.Robinson, Inst.Journ.of Fract.Mechan., **6**, 33 (1970).
53. A.S.Krausz and H.Eyring, "Deformation Kinetics", Wiley, Interscience, New York, 1975.
54. A.Tobolsky and H.Eyring, J.Chem.Phys., 11, 125 (1943).
55. G.B.Manelis, L.P.Smirnov, and E.V.Polianchik, Dokl. Akad.Nauk SSSR, **215**, 1157 (1974).
56. G.B.Manelis, L.P.Smirnov, E.V.Polianchik, and S.N.Bloshenko, Vysokomol.Soed., A19, 86 (1977).
57. G.B.Manelis and E.V.Polianchik, Vysokomol.Soed., A20, 125 (1978).
58. G.B.Manelis, L.P.Smirnov, and E.V.Polianchik, Dokl. Akad.Nauk SSSR, 217, 139 (1974).
59. B.D.Goikhman, Problemy Prochnosti, No.8, 18 (1972).
60. A.A.Il'yushin, Mekhanika Tverdogo Tela, No.3, 21.
61. V.V.Moskvitin, "Soprotivlenie Vyazkouprugikh Materialov" (The Resistance of Viscoelastic Materials), Izd.Nauka, Moscow, 1972.
62. Yu.Ya.Bart, V.P.Trifonov, A.B.Kozachenko, and N.I.Malinin, Mekhanika Polimerov, 5, 791 (1975).
63. I.G.Barenblatt, V.M.Entov, and R.A.Salganik, Mekhanika Tverdogo Tela, No.2, 148 (1967).
64. B.D.Goikhman, Fiz.-Khim.Mekhanika Materialov, No.3, 65 (1975).
65. V.E.Zotkin, Standarty i Kachestvo, No.9, 62 (1977).
66. B.D.Goikhman, Plast.Massy, No.2, 56 (1971).

Translated from *Uspekhi Khimii*, 49, 1574-1593 (1980) U.D.C. 541.64:539.3

Kinetic Models for the Prediction of the Lifetime of Polymeric Materials

E.V.Deyun, G.B.Manelis, E.B.Polianchik, and L.P.Smirnov

Theoretical and experimental data for the degradation of polymers under the influence of mechanical stresses are surveyed from the standpoints of chemical physics. Kinetic models for the bulk-phase breakdown of polymers are examined and an approach is formulated to the prediction of the lifetime of articles made from polymeric materials.
The bibliography includes 123 references.

CONTENTS

I. Introduction 759
II. Theory of the breakdown of solids 759
III. Kinetic models of the bulk-phase breakdown of polymers 760
IV. The role of the mechanical model in the kinetic theory of strength 766

I. INTRODUCTION

One of the principal problems which the theory and practical applications of polymeric materials face as a result of progress in science and engineering is a quantitative prediction of the useful lifetime of polymeric materials and control of their stability[1]. The urgency of these problems is due to the expansion of the fields in which polymeric materials are applied, the wide variety of types of polymeric articles, the regimes and conditions under which they are employed, and the increase in the number of classes of polymers used; it is also associated with the need to solve problems involving ways of insuring the reliability of polymeric articles, the choice of the optimum polymeric material for a particular article, the design of a polymeric material, etc.

In technology, medicine, and other fields polymers are used mainly as constructional materials. The stability (lifetime) of a particular construction comprising a given polymer under specified conditions and operating regimes can be characterised by the time during which the article either breaks down or undergoes significant changes in its shape and dimensions, as a result of which the construction loses its suitability for the prescribed purpose. Problems of the stability of polymeric articles are considered below from the standpoint of their breakdown under the influence of mechanical forces.

The review does not deal with the characteristics of the breakdown of composite polymeric materials. Experimental and theoretical studies devoted to this problem are being published with an increasing frequency and their analysis requires a special survey.

II. THEORY OF THE BREAKDOWN OF SOLIDS

There is at present no unanimous view on the breakdown of solids, particularly polymers; there is therefore no generally accepted mathematical procedure whereby one could estimate quantitatively the strength characteristics, predict their changes during use, and determine the conditions under which breakdown occurs. It is possible to distinguish two main and to a large extent conflicting views on the breakdown process—static and kinetic[2-4].

The traditional view on the breakdown process is that breakdown is a critical event. In the mechanics of continuous media and in physical theories taking into account the atomic-molecular structure of bodies the static approach to the problem of strength involves the introduction of concepts of limiting states and ultimate strengths[3,5]. There is a whole series of theories of the limiting state, each of which is based on specific hypotheses concerning the breakdown condition. A common feature of all these theories is the claim that the breakdown of any body occurs when a certain function of the components of the stresses and deformation tensors or the deformation energy exceeds a specific quantity $C_{\lim}$, which is believed to be a fundamental physical constant of the given body[2,3,6]. In practice it is very often assumed that breakdown occurs if one of the principal stresses reaches its limiting value $\sigma_{\lim}$, which can be determined experimentally by testing a material for rupture on extension and under so-called standard conditions (at a specified constant temperature, pressure, and rate of deformation).[3,7] Together with $\sigma_{\lim}$, $\varepsilon_{\lim}$—the maximum deformation determined under standard conditions—is used as the ultimate strength[3,8].

The experimental studies of the breakdown of many materials established a series of facts indicating the kinetic nature of the process: it has been shown that the limiting characteristics ($\sigma_{\lim}$, $\varepsilon_{\lim}$) depend on the regime and conditions under which the tests are carried out (preliminary load, rate of deformation, and temperature)[7-10]; it has been established that the breakdown of a body occurs also following the application of stresses weaker than the ultimate strength $\sigma_{\lim}$; under these conditions, the weaker the stress the longer the lifetime of the specimen under load, until the instant of rupture t_r.[4,11-13] Systematic studies on hundreds of objects (inorganic salts, metals, alloys, polymers, and composite materials) established that the dependence of t_r on the temperature T and on the stress σ for materials of different chemical types is the same and can be described by the equation

$$t_r = t_0 \exp \frac{U_0 - \gamma\sigma}{RT}, \qquad (1)$$

where t_0, U_0, and γ are constants of the material.

Attempts to explain the conflict between the assumption of the critical nature of breakdown and the time dependence of strength and hence to develop a mathematical procedure which could take into account the fact that the breakdown is a function of time, whilst retaining the static approach, have been frequently made[14-18].

Thus the kinetic nature of the breakdown of polymers is frequently related to the characteristic features of the behaviour of polymeric materials, consisting in a significant alteration of their limiting characteristics as a function of time under the influence of heat, moisture, and many other factors[7,19-21]. The decrease of the limiting characteristics $C_{\lim}$ is usually defined as the ageing of the material and its increase is believed to be due to structure formation processes (crystallisation, orientation of macromolecules, etc). In the

prediction of the time corresponding to the breakdown of the polymeric structure within the framework of the static approach to breakdown, but with allowance for thermal ageing, the kinetic parameters describing the time variation of C_{lim} are usually determined experimentally by accelerated tests[7,22]. The method consists in maintaining specimens at elevated temperatures for specified periods without the application of mechanical stresses, this being followed by the determination of the limiting characteristics under standard conditions and by the calculation from the $C_{lim}(t)$ kinetic curves obtained, of the activation energy and the pre-exponential factor and the determination of the kinetic law of the reaction. When the results are extrapolated to the temperature range in which the given polymeric material is actually used, it is assumed that the characteristics of the variation of C_{lim} determined in the tests are maintained.

In order to describe the kinetics of the ageing and structure formation process, the combined graphical and analytical method[23,24] is used together with the mathematical procedure employed in describing the kinetics of chemical reactions[22,25], which, incidentally, is not justified from the theoretical point of view, because the relation between the limiting properties and the concentration of the chemical groups and bonds has not been established. The time of the breakdown of the object is determined in this approach as the time of attainment at any point in the construction of equality between C_{lim}, calculated for the operating conditions and regime for the given construction, and the value of this characteristic calculated in the analysis of the strained-deformed state of the construction under the given conditions (Fig.1). We emphasise that here one assumes in essence that the kinetics of the variation of the limiting characteristic $C_{lim}(t)$ are determined solely by the law governing the variation of the temperature $T(t)$ and are independent of the stress $\sigma(t)$.

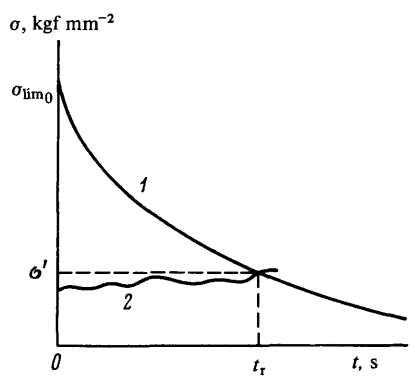


Figure 1. Scheme for the prediction of the breakdown time of a polymeric object taking into account the thermal ageing of the polymer: *1*) kinetic $\sigma_{lim}(t)$ curve for the given polymeric material under the operating conditions and regime of a specific construction; *2*) law governing the variation of the stress $\sigma(t)$ at a characteristic point for the given object under specified operating conditions and regime.

It can be shown that in this approach the activation energy for the breakdown process is equal to the activation energy for the ageing process E_{age} and is independent of σ, while the $t_r(\sigma)$ relation is much less pronounced than the relation described by Eqn.(1). Indeed, it is evident, for example, in the case of the variation of σ_{lim} during ageing in accordance with the first-order equation $\sigma_{lim} = \sigma_{lim_0}\exp(-kt)$, where $k = k_0\exp(-E_{age}/RT)$, that the relation $t_r(T, \sigma)$ should be described by the equation

$$t_r = \frac{\ln \lim 0/\sigma'}{k_0} \exp \frac{E_{age}}{RT}, \qquad (2)$$

where σ' is the stress at the instant of breakdown and σ_{lim0} is the ultimate strength of the initial "non-aged" material. Thus allowance for the thermal ageing of polymeric materials does not explain satisfactorily the inconsistency between the concept of breakdown as a critical, limiting event and the experimental time variation of strength described by Eqn.(1).

It has been suggested that the kinetic nature of breakdown be taken into account by introducing into Griffith's formula[26] for the ultimate strength of a solid with a crack of length l_{cr}, i.e.

$$\sigma_{lim} = [2wE/\pi(1-\nu^2)l_{cr}]^{0,5} \qquad (3)$$

the relation between Young's modulus E and the rate of deformation[14] or by replacing Young's modulus by the relaxation modulus $E(t)$ and taking into account the time variation of the cohesive energy of breakdown w.[15]

Detailed analysis of the time variation of the strength of solids and direct studies of the elementary reactions occurring in polymers subjected to a mechanical load led to the conclusion[4] that the time variation is not determined by the accompanying processes (such as the sorption of moisture[16], the redistribution of stresses in heterogeneous materials[17], etc.) but is inherent in the very mechanism of the breakdown. Experimental study of the $t_r(T, \sigma)$ relation together with theoretical ideas concerning the decrease of the energy barrier in the force field served as a basis for the creation of a kinetic theory of the strength of solids, which constitutes the second of the possible approaches to the breakdown process. According to this theory[4], the external mechanical force does not as a rule itself lead to the rupture of interatomic bonds; by deforming these bonds, it merely accelerates the breakdown process, reducing the activation barrier. The rupture of strained interatomic bonds takes place as a function of time under the influence of the thermal movement of atoms (thermal fluctuations).

III. KINETIC MODELS OF THE BULK PHASE BREAKDOWN OF POLYMERS

In a number of studies the kinetics of the bulk-phase breakdown of solids are described on the basis of a phenomenological approach[2,27-31]. Some investigators, for example, Il'yushin and Pobedrya[2] and Moskvitin[3], introduced the concept of the vulnerability of the material ω; the physical significance of the vulnerability is not defined, but it is assumed that during the breakdown process the ω increases from 0 to 1 and that on breakdown $\omega = 1$.

On the basis of general considerations, according to which the rate of change of vulnerability should increase with increase of σ and should tend to a maximum reached directly before macroscopic breakdown, it has been suggested that the kinetic equations for the vulnerability be formulated as follows[27,28]:

$$\frac{d\omega}{dt} = A\sigma^{\beta}/(1-\gamma\omega)^{p}, \qquad (4)$$

where A, p, β, and γ are constants.

Since it has been noted[2] that Eqn.(4) does not agree well with experimental data for $\sigma \neq$ const., it has been suggested[29] that a new parameter q, the rate of change of which is related to the rate of change of σ, be introduced into this formula.

The theory of long-term strength described in the monograph of Il'yushin and Pobedrya[2], introduces the concept of the vulnerability (susceptibility to damage) tensor $P(p_{ij})$ with the components

$$p_{ij} = \int_0^t \varphi_{ijkl}(t-\tau)\,\sigma_{kl}(\tau)\,d\tau, \qquad (5)$$

and it is suggested that in the absence of stresses during a time interval $0 \leq t \leq t'$ all the components of the tensor P are zero, i.e. the breakdown of a "non-ageing" material is considered.

Although breakdown is considered in the above and similar studies as a process developing as a function of time, its physicochemical nature is not taken into consideration. This is responsible for limitations in the employment of relations of this kind, which are characteristic of phenomenological theories[32].

Attempts have been made frequently to create a mathematical procedure for the description of the kinetics of breakdown which would be able to take into account adequately and physicochemical processes occurring in the solid when the latter is acted upon by external mechanical forces[4,33-45]. However, while postulating a particular dependence on temperature and applied stress of the probability of the breakdown of strained interatomic bonds, the authors of these studies confined themselves to determining the type of relation $t_r(t, \sigma)$; furthermore, they considered (with a single exception[46]) only simple kinetic schemes. In some of these studies arbitrary and sometimes contradictory assumptions were made: in particular, in formulating the expression for the rate of rupture of strained bonds at constant T and σ, account was taken of the dependence of this rate on the current concentration of the strained bonds, but the increased number of ruptured bonds was disregarded[41-43].

Together with the differential relations for the description of the bulk-phase breakdown, integral equations have also been proposed[4,47,48]. Thus, in predicting the lifetime of polymers on extension with time-dependent stress and temperature, the principle of the summation of the contributions to breakdown is used in the form of the relation

$$\int_0^{t_r} \frac{dt}{t_r[\sigma(t), T(t)]} = 1, \qquad (6)$$

called Bailey's integral. Eqn.(1) or the expression

$$t_r = B\sigma^{-b} \exp \frac{U_0}{RT}, \qquad (7)$$

proposed for the description of the lifetime of elastomers[12], is then used normally as the function $t_r(T, \sigma)$. However, it has been noted that, in this approach to the prediction of the useful lifetime of polymeric materials under load, the error is low only for a single application of a load with a complex relation $\sigma(t)$ and also for the application of a load for a small number of cycles[4,47,48]. It must be emphasised that the use of integral relations of type (6) for the description of the kinetic process under variable conditions, which determine its rate (particularly for the determination of t_r with $\sigma \neq$ const. or $T \neq$ const) is possible, according to the principal postulates of chemical kinetics, only when the rate of the given process is independent of the degree of completion of the process.

A sufficient amount of experimental data, demonstrating convincingly the common features of the mechanisms of different types of degradation of polymers, particularly mechanical breakdown and thermal degradation, has now accumulated. The application of modern physicochemical research techniques and comparison of the experimental relations governing mechanical breakdown and thermal degradation made it possible to show that, in polymers acted upon by stretching stresses, chemical reactions take place whose nature is identical to that of the reactions occurring in the thermal degradation of the polymers[4]. Thus, in many of the instances investigated, the activation energy for the mechanical breakdown of the polymer U_0 proved to be close to the activation energy for its thermal decomposition E_T[4,49-52]. The identity of the intermediate and final products of these processes has been observed[4,53-60] and it has been shown that the variation of the molecular weight distribution is identical[4,61-62]; the increase of the lifetime following the introduction of inhibitors and antioxidants[21,63-65] and the decrease of the lifetime after the addition of sources of free radicals[4,66,67] have been demonstrated.

Thus the mechanical breakdown of polymers can be regarded as a chemical reaction involving the dissociation of interatomic bonds subjected to a mechanical load and the rate of dissociation of the strained bonds is determined not only by the temperature and degree of reaction, as in thermal degradation, but also by the magnitude of the stretching stress. We may note that an analogous influence on the rate of the process is shown by mechanical stresses also for other types of degradation of polymers (hydrolytic[68-70], thermo-oxidative[71], and photothermal[4]). The mechanical initiation of chemical reactions in solids has been examined in a series of studies[72-75].

Thus, from the standpoint of chemical physics, the degradation of polymers is a multifactorial process, the rate of which depends on temperature, the action of various chemical agents (water, oxygen, etc.), irradiation, and mechanical stresses. Depending on the combination of these factors acting on the polymer, it is possible to distinguish thermal, thermo-oxidative, hydrolytic, photothermal, and other types of degradation, and among them different types of mechanical degradation of polymers (mechanothermal, mechanothermo-oxidative, mechano-hydrolytic etc.). In conformity with the foregoing, one can assume that mechanical stresses (and apparently also irradiation[76]) cannot alter the mechanism of the reactions involving the degradation of polymers and that the corresponding types of mechanical degradation include the same elementary stages as degradation in the absence of stresses; however, the ratio of the rates of the individual stages changes significantly under these conditions as a function of the active factors determined by external conditions. For example, mechanical stresses under the conditions of a radical chain degradation mechanism activate the chain initiation process and apparently, to a lesser extent, the chain propagation process. Accordingly, the rate of chain initiation is much higher as a rule in photothermal degradation than in thermal degradation of polymers.

Thus in the most general case the problem of predicting the lifetime of a polymeric object requires, firstly, the determination of the chemical mechanism of the degradation of the given polymer, and the elucidation of the set of elementary stages of the process and of the dependence of the rates of these stages on the temperature T and the stress σ, the irradiation intensity I, and the concentrations c_i of the possible reactants and reaction products, and secondly, the determination from the operating conditions and regime for the given object of the laws governing the variation of $T(t)$, $\sigma(t)$, $I(t)$, and $c(t)$ at the characteristic points of the object. The determination of the stability of the polymeric object

must be based on the solution of the appropriate equations for the degradation kinetics subject to the observed laws governing the time variation of T, σ, I, and c_i.

In the general case this problem is extremely complex; comparatively simple special cases of the problem have now been analysed[77-88]. In the analysis it was assumed that the influence of the mechanical field on the rate of reaction reduces to the alteration of the energy barrier to the dissociation of the interatomic bond E_0. We may note that calculations performed taking into account the interaction between the atoms with the aid of the Morse potential[44,89-91] established that the dependence of the energy barrier E on the tension f in the chemical bond is non-linear, but allows a linear fit within a comparatively wide range of values of f. Then, assuming that the load is uniformly distributed along all the bearing bonds and taking into account the fact that, for a constant σ, the accumulation of breaks in the bonds leads to an increase of the tension in the surviving bonds, one can write

$$E(\sigma) = E_0 - \alpha\sigma n_0/n, \qquad (8)$$

where n_0 is the initial concentration of the bearing bonds, n the current concentration of the bearing bonds, and α a coefficient determined by the nature and structure of the substance.

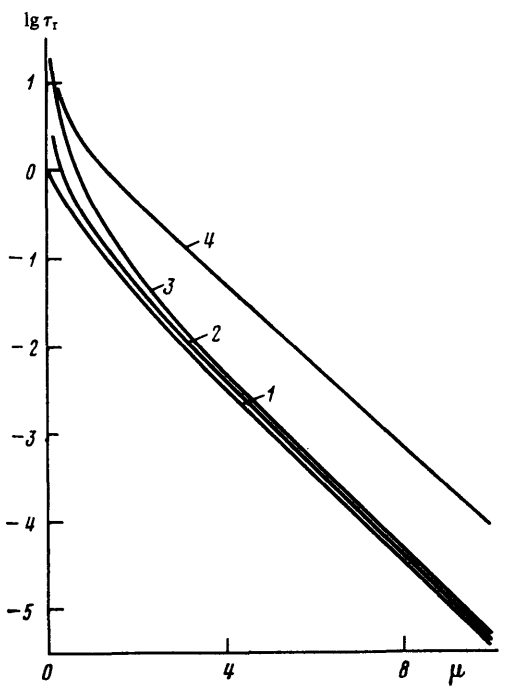


Figure 2. The $\lg \tau_r(\mu)$ relation for $\phi(\Pi) = 1$ (curve *1*), $1-\Pi$ (curve *2*), $(1-\Pi)^2$ (curve 3), and $(1-\Pi)(0.01+\Pi)$ (curve *4*).[77,78]

In the case of a simple irreversible reaction, the rate of mechanical degradation at constant T and σ can be described by the following dimensionless equation[77-79]:

$$\frac{d\Pi}{d\tau} = \varphi(\Pi)\exp\frac{\mu}{1-\Pi}, \qquad (9)$$

where $\Pi = 1-n/n_0$ is the relative concentration of the broken bearing bonds (the degree of accumulation of defects), $\mu = \alpha\sigma/RT$ the parameter characterising the intensity of the mechanical field, $\phi(\Pi)$ the kinetic law governing the reaction, $\tau = ktn_0^{m-1}$ the dimensionless time, $k = k_0\exp(-E_0/RT)$ the rate constant for the chemical reaction, k_0 the pre-exponential factor, and m the order of the reaction.

Eqn.(9) can be readily integrated. The dimensionless lifetime τ_r (corresponding to $\Pi = 1$) is determined solely by μ and $\phi(\Pi)$, i.e. the dependence of $\tau_r(\mu)$ for the given type of $\phi(\Pi)$ is universal. The $\lg \tau_r(\mu)$ curves plotted for different $\phi(\Pi)$ are non-linear for low values of μ and, when $\mu > 2$, they can be described with satisfactory accuracy by a linear equation (Fig.2), i.e. the following expression can be formulated in a dimensional form for the time variation in the region of high stresses ($\mu > 2$):

$$t_r = \frac{a}{k_0}\exp\frac{E_0 - b\alpha\sigma}{RT}, \qquad (10)$$

the expression being analogous to Eqn.(1). In the region where $\mu < 2$ the observed $\tau_r(\mu)$ relations are described satisfactorily by Eqn.(7). We may note that the deviation of the $\lg t_r(\sigma)$ relation from linearity under the conditions of low stresses has been observed experimentally in all the cases investigated[4].

The $\Pi(\tau)$ kinetic curves are of the self-accelerating type regardless of the form of $\phi(\Pi)$ and it is possible to distinguish qualitatively two stages in the development of the process: at the beginning a comparatively slow increase in the concentration of the ruptured bearing bonds, proceeding almost at a constant rate, followed by a rapid "avalanche like" increase. The degree of accumulation of defects Π^* for which there is a transition from the slow to the rapid stage of the process diminishes with increase of the parameter μ. The kinetic curves for the formation of volatile products[92] and for the change in light transmission[93] in the mechanothermal degradation of polystyrene are identical in form to the $\Pi(\tau)$ curve for a simple irreversible reaction.

The rate of thermal degradation of polymers is frequently described by equations for *two simultaneous first-order reactions*, which can be accounted for by the presence in the initial polymer of kinetically non-equivalent so-called strong and weak bonds. the difference between the activation energies for the radical-chain thermal degradation involving initiation via the strong and weak bonds being capable of reaching from 1–3 to several tens kcal mol^{-1}, while the initiation of degradation via the rupture of weak bonds give rise to a conversion of the polymer up to 10–30%.[40-52,94-96]

The equations for the mechanothermal degradation in the case under consideration can be formulated in a dimensionless form in the following way[78,79]:

$$\frac{d\Pi_1}{d\tau} = (1-\Pi_1)\exp\frac{\mu_1}{1-\Pi}, \qquad \frac{d\Pi_2}{d\tau} = \varkappa(1-\Pi_2)\exp\frac{\mu_2}{1-\Pi}, \qquad (11)$$

where $\Pi_1 = 1-n_1/n_0$ is the extent of accumulation of defects in the strong bonds, $\Pi_2 = 1-n_2/n_0$ the extent of accumulation of defects in the weak bonds, $\tau = k_1 t$ the dimensionless time, $\varkappa = k_2/k_1$ a parameter equal to the ratio of the rate constants for the degradation of the weak and strong bonds, $\Pi = c\Pi_1 + (1-c)\Pi_2$ the overall extent of accumulation of defects, and c the fraction of the strong bonds.

For comparatively low values of $\varkappa$(~10), the $\Pi(\tau)$ curves do not differ qualitatively from the corresponding curves in the case of a single simple reaction. For $\varkappa > 10^2$–10^3, the kinetic $\Pi(\tau)$ curves have three sections: initially the rate of accumulation of defects gradually diminishes with time, then there is

a more or less low-slope section of the curve, and at the end of the process the accumulation of defects proceeds at a very high rate. The first stage is largely determined by the rupture of the weak bonds: hence the $\Pi_2(\tau)$ relation can be described by a first-order equation. The length of the low-slope section of the $\Pi(\tau)$ curve diminishes with decrease of c and, when $c < 1-\Pi^*$, the $\Pi(\tau)$ curve degenerates into one characteristic of the model with kinetically equivalent bonds. The lifetime τ_r is then determined by the kinetic parameters of the weak bonds.

For low values of κ, the $\lg \tau_r(\mu)$ relation for all values of the parameter c retains the same nature as in the case of a simple unidirectional reaction. When the fractions of the weak and strong bonds are approximately equal, then, for sufficiently high values of $\kappa(\kappa \geq 10^3)$, the relation becomes non-linear over a wider range of variation of the parameter μ and can be described by two linear sections, the slope of the linear section of the $\lg \tau_r(\mu)$ relation being higher for low values of μ than for high values of μ.

The hypothesis that the mechanothermal degradation is reversible has been put forward in connection with the discussion of certain characteristics of the variation of the lifetime of solids of different chemical types observed under the conditions of relatively small stresses and high temperatures[97]. Previously an analogous degradative recombination mechanism had been proposed to describe the so-called chemical flow of cross-linked elastomers[98]. For a reversible reaction, the rate of mechanothermal degradation can be described by the following dimensionless equation[78-81]:

$$\frac{d\Pi}{d\tau} = (1-\Pi)^{m_1} \exp\left(\frac{\mu}{1-\Pi}\right) - \frac{\Pi^{m_2}}{\kappa}, \qquad (12)$$

where $\tau = k' t n_0^{m_1-1}$ is the dimensionless time, $\kappa = k' n_0^{m_1-1}$. .$^2/k''$ a dimensionless parameter characterising the ratio of the dissociation (k') and recombination (k'') rate constants, and m_1 and m_2 are the orders of the bond dissociation reaction and of the reaction involving the recombination and rupture of bonds respectively.

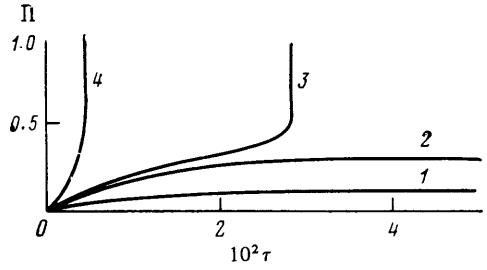


Figure 3. Kinetic curves for the accumulation of defects $\Pi(\tau)$ with $m_1 = 1$, $m_2 = 2$, $\kappa = 1.7 \times 10^{-3}$ and different values of μ: *1*) 2; *2*) 3; *3*) 3.1; *4*) 4.[78,79]

For this system, described by Eqn.(12), there exists a range of parameters μ and κ in which there is a possibility of a transition from a stationary to a non-stationary regime for a small change in external conditions, i.e., critical phenomena can arise. The specific form of the critical conditions $\mu_{cr} = \mu(\kappa)$ for specified pairs of values m_1 and m_2 can be readily found with the aid of Semenova's method. The nature of the $\Pi(\tau)$ curves changes sharply when μ passes through μ_{cr}: for $\mu < \mu_{cr}$, a stationary concentration of the ruptured bonds is established and there is no breakdown (the region of safe stresses); for $\mu > \mu_{cr}$, the process terminates with complete rupture of the bearing bonds (Fig.3). The influence of the reaction involving the recombination of the ruptured bonds on τ_r is significant only for values of μ slightly exceeding μ_{cr}: in this case the time taken to traverse a small (with respect to the values of Π) region, where the overall rate of breakdown is minimal, makes the main contribution to the lifetime of this specimen. For large values of μ (when $e^{\mu} \gg \kappa^{-1}$), the influence of the recombination of the ruptured bonds on the mechanothermal degradation becomes insignificant, and the $\tau_r(\mu)$ relation can be represented by Eqn.(10), obtained for a simple unidirectional reaction (Fig.4). We may note that the existence of safe stresses has been observed experimentally in the study of the mechanothermal degradation of cross-linked elastomers[99].

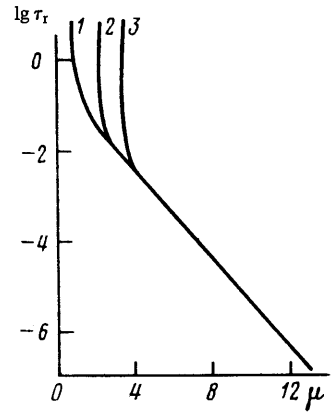


Figure 4. The $\lg \tau_r(\mu)$ relation with $m_1 = 1$, $m_2 = 2$, and different values of κ: *1*) 0.2; *2*) 10^{-2}; *3*) 10^{-3}.[78,79]

A radical-chain mechanism was proposed for the first time by Zakrevskii[46] in order to describe the kinetic characteristics of the breakdown of polymers. However, it dealt only with the initial stage of the process and no account was taken of the redistribution of the load on the surviving bearing bonds with increase of the number of ruptured bonds. The breakdown process proceeding via a radical-chain mechanism has been modelled in a number of studies[82-85]. The kinetic scheme for the process examined by Deyun et al.[83] includes the following stages: (1) the stress-activated initiation of the kinetic chain via the rupture of strained bonds in the macromolecules P_n, leading to the formation of terminal radicals R_t; (2) the depolymerisation of R_t as a result of the abstraction of the monomer P_2; (3) chain transfer in the interaction of R_t with P_n involving the formation of a central radical R_{ce}; (4) the stress-activated decomposition of R_{ce} with formation of R_t and molecules containing a double bond: (5) the migration of the free valence in R_{ce}, hindered by stresses, as a result of which R_{ce} is converted into R_t; (6) termination of the kinetic chain via the disproportionation or recombination of R_t.

Analysis of the corresponding kinetic equations using the method of quasi-stationary concentrations showed that, depending on the ratio of the parameters of the above equations, it is possible to distinguish three ranges of stresses

within the limits of which the $t_r(T, \sigma)$ relation is described by Eqn.(1) but with different values of U_0, t_0, and γ for each section, the values being complex combinations of the corresponding parameters of the elementary stages (see Table). A characteristic feature of the model of the breakdown of polymers under consideration is the establishment of quasi-stationary radical concentrations for relatively low stresses (regimes I and II); here the rate of mechanothermodegradation in regime I is limited by the decomposition of R_{ce} (stage 4), and that in regime II is limited by chain transfer (stage 3). For fairly large stresses (regime III), the radical concentrations are non-stationary throughout the process whose rate is determined by the initiation stage; thus in regime III the radical-chain process mechanism degenerates into a radical mechanism. The existence of the above three regimes in the mechanothermodegradation of polymers has been confirmed in a whole series of studies[62,100-107] and both types of breaks in the $\lg t_r(\sigma)$ relation, indicated in Fig.5, were noted. The presence of such breaks is usually attributed not to a radical-chain process mechanism but to the existence of a functional relation between the coefficient γ of Eqn.(1) and the temperature and stress due to the sharp alteration of the mobility of the side groups of the macromolecules[100,102].

Relation between the parameters of Eqn.(1) for the time variation of the strength and the constants of the elementary stages of mechanothermodegradation proceeding via a radical-chain mechanism*.[84]

Regime	U_0	t_0	γ
I	$\frac{E_{01}-E_{06}}{2}+E_{03}+E_{04}-E_{05}$	$\frac{(k_{06}/k_{01}P_0)^{0.5}RTk_{05}}{2^{1.5}k_{03}k_{04}n_0^{2.5}(0.5\alpha_1+\alpha_4+\alpha_5)\sigma}$	$\frac{\alpha_1}{2}+\alpha_4+\alpha_5$
II	$\frac{E_{01}-E_{06}}{2}+E_{03}$	$\frac{(k_{06}/k_{01}P_0)^{0.5}RT}{2^{1.5}k_{03}n_0^{1.5}\alpha_1\sigma}$	$\frac{\alpha_1}{2}$
III	E_{01}	$\frac{RT}{k_{01}n_0\alpha_1\sigma}$	α_1

*E_{0i}, k_{0i}, and α_i are respectively the activation energy, pre-exponential factor, and the structure-sensitive coefficient of the ith elementary stage and P_0 is the initial concentration of macromolecules.

The results of the calculation by the tabulated formulae of the values of U_0 and t_0 for a series of polymers [polyethylene, polypropylene, poly(vinyl chloride), polystyrene, poly(methyl methacrylate), and polyacrylonitrile], obtained using the literature values of the rate constants for the elementary stages of the thermal degradation of the corresponding polymers, in most cases agree satisfactorily with the experimental values of U_0 and t_0.[82] Thus the difference between the values of U_0 obtained in the study of the lifetime of the same polymer can be accounted for by the change in the rate-determining stages of mechanothermodegradation involving a radical-chain mechanism, when the stress is altered. In this connection one should note that comparison of the activation energies for thermal degradation and mechanothermodegradation (with the exception of regime I) is fairly conventional.

According to Regel' et al.[4], the quantity $t_0 = 10^{-12}-10^{-13}$ s for polymers, which is attributed to the period of the thermal vibrations of the atoms[108]. Thus the $t_r(T, \sigma)$ relation, defined by Eqn.(1), in essence involves only two constants (U_0, γ) characterising the polymer. However, the results of the analysis (see Table) have shown that such universality of the values of t_0 should not occur for mechanothermodegradation via a radical-chain mechanism. Indeed, for polymers listed above, calculation in the case of regimes I and III yields values of t_0 differing significantly from $10^{-12}-10^{-13}$ s. Apparently t_0 is frequently[4] assumed to be equal to 10^{-13} s in order to facilitate the calculation. One should also note that the use of the method of secants for the determination of t_0, recommended by Regel' et al[4], involves a long-range double extrapolation of experimental data on the logarithmic scale, which can also be a source of errors. These principles probably lead in many instances to the "pole redisplacement" effect[4].

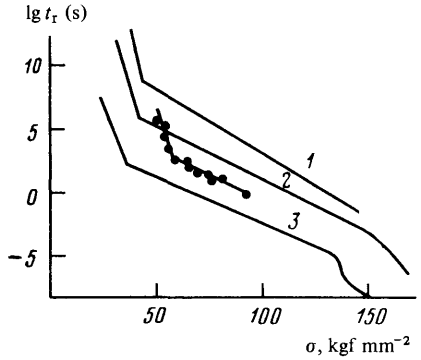


Figure 5. The $\lg t_r(\sigma)$ relation for polypropylene; calculation[84] using the tabulated formulae at different temperatures (K): *1*) 250; *2*) 300; *3*) 400. Circles—experimental data[4] at 300 K.

In the presence of a monofunctional stable radical In, termination of the kinetic chain is possible when In interacts with R_t or R_{ce}. It has been shown[85] that in this case there is a possibility of two regions in which inhibited and non-inhibited mechanothermodegradation develops, whose boundary is defined by the equation

$$[\mathrm{In}]^* = \frac{2(k_1k_6P_0\exp\mu)^{0.5}}{k_7+k_8k_7'/\left[k_4\exp\frac{\alpha_4\mu}{\alpha_1}+k_5\exp\left(-\frac{\alpha_5\mu}{\alpha_1}\right)\right]}, \qquad (13)$$

where k_7 and k'_7 are the rate constants for the interaction of In with R_t or R_{ce} respectively.

Depending on the ratio of the parameters of Eqn.(13), the critical concentration of the inhibitor [In]* either increases monotonically with increase of μ, passes through a minimum, or passes through a local maximum and then through a minimum. The nature of the [In]* (μ) curve determines the form of the relation $\lg \tau_r(\mu)$ (Fig.6). For given inhibitor concentration, there exists a maximum stress for which the inhibitor influences the breakdown process; starting from a certain inhibitor concentration, this test depends little on the latter. The qualitative nature of the theoretical $\lg t_r(\sigma)$ relation agrees with experimental data obtained in a study[62] of the breakdown of nitrocellulose in the presence of the 4-ethyl-4-hydroxy-2,2,6,6-tetramethylpiperidenyloxy-radical.

An analysis of the characteristics of the mechanothermodegradation taking into account the distribution of macromolecules with respect to chain lengths has been carried out[82] for a kinetic process mechanism involving the following stages: (1) initiation of the kinetic chain by the rupture of strained bonds in the macromolecules P_n* (n is the number of atoms in the chain of the macromolecule) with a rate constant k_1; (2) depolymerisation of the radical R_t with a rate constant k_2; (3) stress-activated chain transfer in the interaction of R_t with P_n involving the formation of R_{ce} and subsequent decomposition of the latter with a rate constant k_3; (4) termination of the kinetic chain via the disproportionation or recombination of R_t with a rate constant k_6. Unlike the kinetic degradation mechanism examined by Deyun et al[83], in this model the stages involving chain transfer and the decomposition of R_c have been combined into a single stage in order to simplify the calculation and the stage in which the free valence migrates is missing.

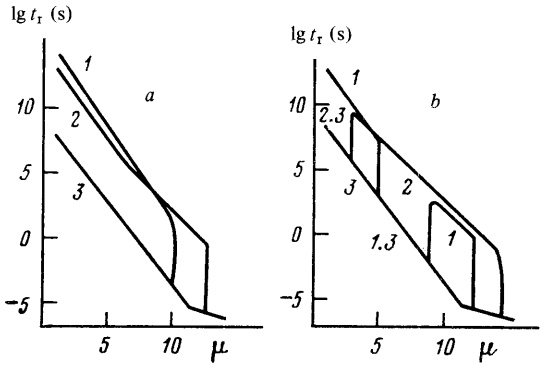


Figure 6. The lg $t_r(\mu)$ relation for the mechanothermodegradation of polymers in the presence of a monofunctional inhibitor[85] with $k_5/k_4 = 10^{10}$ and $\{k_1k_6[P_0]\}^{0.5}/k_7 = 5 \times 10^{-7}$: *a*) $k_3k'_7[P_0]/k_4k_7 = 10^4$ (curve *1*), 10^7 (curve *2*), and zero (curve *3*) and $[In] = 1.6 \times 10^{-4}$ (curve *1*), 1.6×10^{-5} (curve *2*), and zero (curve *3*); *b*) $k_3k'_7[P_0]/k_4k_7 = 10^7$ (curve *1*), 10^{10} (curve *2*), and zero (curve *3*) and $[In] = 10^{-5}$ (curve *1*), 2×10^{-7} (curve *2*), and zero (curve *3*).

The system of kinetic equations, formulated in accordance with the chosen reaction mechanism, agrees in broad outline with the system examined in the analysis of the thermodegradation of polymers[105]; the principal difference is that in mechanothermodegradation one takes into account the dependence of the rate of the initiation and chain transfer stages on the mechanical stresses. The system of equations has been converted into a dimensionless form by introducing the dimensionless time $\tau = k_1t$, the dimensionless concentrations of macromolecules $P_n(\tau) = \bar{P}_n(t)/\bar{P}_{n_0}(0)$ and radicals $R_n(\tau) = \bar{R}_n(t)/\bar{P}_{n_0}(0)$, and the dimensionless depolymerisation ($\kappa_2 = k_2/k_1$), chain transfer [$\kappa_3 = k_3\bar{P}_{n_0}(0)/k_1$], and chain termination [$\kappa_6 = k_6\bar{P}_{n_0}(0)/k_1$] rate constants ($n_0$ is the maximum number of atoms in the main chain of the macromolecule).

It has been shown that the kinetic curves for the variation of the overall concentration of radicals $R(\tau)$ are fairly complex (Fig.7). Radicals are initially accumulated at a decreasing rate; the subsequent shape of their $R(\tau)$ curves depends on the ratios of the parameter μ, κ_3, κ_6, and n_0. In a certain range of values of these parameters, it is possible to distinguish a section of the $R(\tau)$ curve along which the radical concentration remains virtually constant. The length of the quasi-stationary section is up to $(0.8-0.9)\tau_r$. The transition to the $R(\tau)$ curves without a quasi-stationary section takes place fairly abruptly as μ increases.

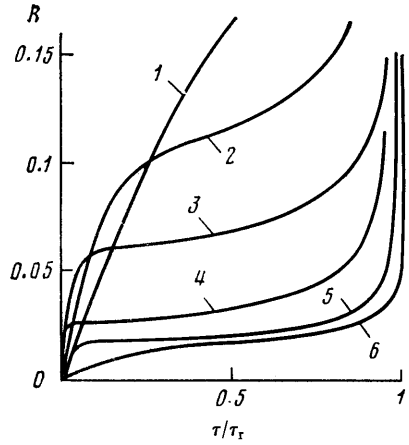


Figure 7. Kinetic curves for the variation of the overall concentration of free radicals $R(\tau)$ in the mechanothermodegradation of polymers by a radical-chain kinetic mechanism[84] with $n_t = 10$, $\alpha_3/\alpha_1 = 1$, $\kappa_2 = 10^2$, $\kappa_3 = 10$ (curves *1*–*5*) and 10^3 (curve *6*), $\kappa_6 = 10^6$ (curves *1*–*3*) and 10^8 (curves *4*–*6*), $\mu = 5$ (curves *1* and *4*–*6*), 4 (curve *2*), and 3 (curve *3*), and $n_0 = 100$ (curves *1*–*3* and *5* and *6*) and 200 (curve *4*) (n_t is the number of non-loaded atoms in the terminal sections of the main macromolecular chain).

The calculated $R(\tau)$ curves agree satisfactorily with the experimental characteristics of the accumulation of radicals in mechanothermodegradation[4,110]. The form of the calculated kinetic curves $P_n(\tau)$ depends on n; if n is small, then the induction period for the corresponding $P_n(\tau)$ curve is most distinct and the entire change in the concentration of the given product takes place virtually near the time of attainment of the maximum concentration P_n, which depends little on the process parameters and is largely determined by the value of n. We may note that the yield of the monomer $P_2(\tau_r)$ decreases with decrease of the parameter κ_2 and with increase of μ and κ_3. In the case of chain termination by the recombination of R_t the decrease of the number-average molecular weight $\bar{M}_n$ proceeds at a constantly increasing rate for all values of the parameter μ. On the other hand, if chain termination takes place via the disproportionation of R_t, then only for fairly large values of μ do the $\bar{M}_n(\tau)$ curves have the same form as in the previous case. For low values of the parameter μ, the kinetic curves $\bar{M}_n(\tau)$ have three sections: along the first and third sections $\bar{M}_n$ decreases at a gradually increasing rate, while along the second section the rate falls (Fig.8). The form of the kinetic $\Pi(\tau)$ curve is analogous to that of the $\bar{M}_n(\tau)$ curves.

IV. THE ROLE OF THE MECHANICAL MODEL IN THE KINETIC THEORY OF STRENGTH

The results of the analysis of certain kinetic models of the bulk-phase (quasi-homogeneous) breakdown, occurring over a wide range of conditions and regimes in the breakdown of polymers which are of practical importance, were examined above. Any theoretical model proposed to describe the breakdown kinetics involves (explicitly or implicitly) certain assumptions concerning the mechanical picture of the processes occurring in the loaded material, since each step involving the rupture of an interatomic bond constitutes at the same time a step in the rearrangement of the microstructure of the material.

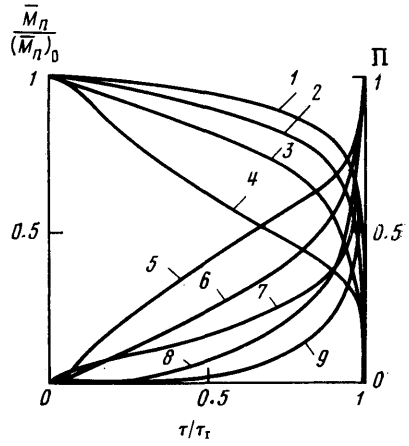


Figure 8. Kinetic curves for the variation of the number-average molecular weight (curves *1–4*) and for the degree of accumulation of defects (curves *5–9*) in the mechanothermodegradation of polymers by a radical-chain kinetic mechanism[84] with $n_t = 10$, $\alpha_3/\alpha_1 = 1$, $\kappa_2 = 10^2$, $\kappa_3 = 10$, and $\kappa_6 = 10^6$ (curves *1–5* and *7–9*) and 10^8 (curve *6*), $\mu = 3$ (curves *3–5* and *7*), 6 (curves *2, 6,* and *8*), and 9 (curves *1* and *9*), and $n_0 = 100$. The kinetic chain is terminated via recombination (curves *1–3, 5, 6, 8,* and *9*) and disproportionation (curves *4* and *7*).

Breakdown models, in which it is suggested that breakdown takes place throughout the bulk of the specimen, that the strength characteristics of the bonds are identical, and, in addition, that in most of the models mentioned above the load applied to the ruptured bonds is redistributed uniformly among the surviving bonds, have been examined in Refs. 33 to 45, 77–85, and others. Next it is assumed that the probability dp_i of the rupture of a bond under the influence of a force f_i during a time interval dt is described by an equation of the Arrhenius type:

$$dp_i = k_i \exp\left(-\frac{U_0 - \alpha f_i}{RT}\right) dt. \qquad (14)$$

Together with these models, others have been proposed[86,111] in which the non-equivalence of the chains with respect to strength characteristics and their non-uniform loading were assumed, but it was also postulated that the distribution of the load applied to the ruptured bonds among the residual surviving bearing bonds is uniform.

In particular, the influence of the non-uniformity of the load applied to the bonds on the kinetics of mechanothermodegradation was taken into account[86] subject to the following main assumptions: (1) throughout almost the entire lifetime of the specimen under load, the material remains linearly elastic; (2) a dimensionless parameter $x \geq 0$ can be assigned to each bond in such a way that all the strength characteristics (i.e. elastic constants and the parameters of the degradation kinetics) are functions of x and not of the time t; (3) the rupture of the bonds is described by the equation for an irreversible first-order reaction:

$$\dot{H}(x, t) = -H(x, t) k_0(x) \exp\{-[U_0(x) - \alpha(x)\Omega]/RT\}, \qquad (15)$$

where $H(x,t)$ is the density of the distribution of bonds with respect to x and Ω is the force acting on the bond.

If the rigidity of the bond is $\phi_1(x)$, then the stretching stress in the cross-section of the specimen is

$$\sigma(t) = \int_0^\infty H(x, t) \varphi_1(x) \varepsilon_{33}(t)\, dx, \qquad (16)$$

where ε_{33} is the elongation of the specimen.

Eqns. (15) and (16) can be written as follows in a dimensionless form:

$$\dot{h}(x, \tau) = -h(x, \tau) \varkappa(x) \exp[\omega(x) \varepsilon(\tau)], \qquad (17)$$

$$\mu(\tau) = \varepsilon(\tau) \int_0^\infty h(x, \tau) \varphi(x)\, dx, \qquad (18)$$

where $\tau = tk_0 \exp(-\tilde{U}_0/RT)$ is the dimensionless time, $\mu = \alpha\sigma/N_0RT$ the average dimensionless tension in the bonds, $h(x, \tau) = H(x, t)/N_0$ the relative density of the distribution of bonds with respect to the parameter x, $\kappa(x) = k_0(x)\exp.(\tilde{U}_0/RT)/\tilde{k}_0 \exp[U_0(x)/RT]$ the dimensionless breakdown strengths for thermal degradation, $\phi(x) = \phi_1(x) = \phi_1(x)N_0/A$ the dimensionless rigidity of the bonds, $\varepsilon = \varepsilon_{33}A/N_0RT$ the dimensionless deformation of the specimen, $\omega(x) = \Omega_1(x)RTN_0/A\tilde{\alpha}$ the dimensionless decrease of the activation energy, $\Omega_1(x)$ the decrease of the activation energy corresponding to $\varepsilon = 1$, N_0 the initial number of bonds in the given cross-section $\tilde{U}_0$, $\tilde{k}_0$, and $\tilde{\alpha}$ are certain characteristics of U_0, k_0, and α respectively, $A = \int_0^\infty H(x,0)\phi_1(x)dx$, and $\int_0^\infty h(x,0)\phi(x)dx = 1$.

Eqns. (17) and (18) make it possible to deduce the expression

$$\mu(\tau) = \varepsilon(\tau) \int_0^\infty h(x, 0) \varphi(x) \exp\left\{-\varkappa(x) \int_0^\tau \exp[\omega(x) \varepsilon(\tau')]\, d\tau'\right\} dx, \qquad (19)$$

which fully describes the evolution of a specimen for an arbitrary law governing the deformation or the application of a load. The study of Eqn. (19) showed that, for a constant load at fairly high values μ (in the sense that $e^\mu \gg 1$), we obtain

$$\tau_r = \tau_0 \exp(-\rho\mu), \qquad (20)$$

where $\rho \gg 1$, i.e. a non-distribution of the load among the bearing bonds leads to a decrease of the lifetime compared with a uniform distribution; at the same time, the $\tau_r(\mu)$ relation remains exponential.

The calculated evolution of the distribution function $h(x, \tau)$ reflects qualitatively the course of the breakdown process observed experimentally[4,112]. The shape of the $\varepsilon(\tau)$ creep curves for high values of μ depends on the form of the function $h(x, 0)$ (Fig. 9). If $h(x, 0)$ has a rectangular shape, then the $\varepsilon(\mu)$ curves consist of two sections, while in other cases they have three sections. For low values of the parameter μ, the creep curves cease to depend on the form of $h(x, 0)$;

in this case the decrease in the number of bearing bonds in consequence of purely thermal degradation makes a major contribution to the development of creep. The $\Pi(\tau)$ curves are similar in form to the $\varepsilon(\tau)$ curves. For high values of μ, the lifetime is determined by the rupture of a relatively small number of bearing bonds. The decrease in the rate of increase of the concentration of broken bonds for low values of μ is related to the decrease in the total number of bonds as a consequence of thermal degradation.

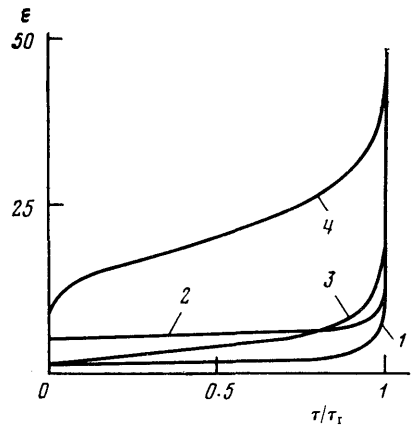


Figure 9. Creep curves $\varepsilon(\tau)$ for a non-uniform loading of the bearing bonds in mechanothermodegradation[86] with $\mu = 1$ (curve *1*), 5 (curve *2*), 1.2 (curve *3*), and 6 (curve *4*). The $h(x,0)$ curves *1* and *2* have a rectangular shape; the $h(x,0)$ curves *3* and *4* correspond to oriented capron[4,112].

One of the principal features of the mechanothermodegradation of real bodies is that the process as a rule develops initially as a homogeneous reaction, while in the concluding stage it is localised and terminates by the growth of a crack right through the specimen. Although the model discussed above and similar models[39,113] make it possible to explain qualitatively a whole series of features typical for mechanothermodegradation, they nevertheless do not provide an answer to the question which of the elementary steps in the breakdown process constitute the macroscopic breakdown of the given body[4,114] The initiation of a crack from single breaks, occurring on average uniformly throughout the bulk of the specimen, has still not been investigated. The study of the conditions under which the interaction of closely spaced continuity microdefects (bond breaks, submicrocracks) is significant and of the conditions under which breakdown occurs as a result of the growth of a single microdefect is complicated by the lack of effective solutions for the distributions of stresses and deformations in the vicinity of microdefects with allowance for the kinetics of the accumulation of microdefects and for the real structure of the polymer. The solution of the problem of the localisation of breakdown should, in principle, yield also an answer to the question how justified is the assumption, used in models describing quasi-homogeneous breakdown, that the transition from the bulk-phase breakdown to the growth of a crack right through the specimen coincides with a sharp increase of the rate of accumulation of defects.

In this connection mention should be made of the study[115] of the statistics of an *ensemble* of microdefects, the probability of the formation and growth of which depends on the local stresses in accordance with Eqn.(14). However, one then uses the solution of the problem of the distribution of stresses for an infinite crack extrapolated to the region of the typical dimensions of the microdefect. The same can also be said of a study[116] whose results are largely a repetition of those of the previous investigation. A direct solution of this problem by modelling the breakdown process using the Monte Carlo method on a computer has been attempted[117].

Several models, for instance[87,88,118-121], have been proposed to describe the kinetics of the growth of cracks right through the specimen. In most of these investigations the solutions of the theory of elasticity for a crack (section) through a continuous body were used together with particular assumptions whereby the specific features of the solution near the end of the crack (infinite stresses) can be eliminated. A correct formulation of the mechanical problem concerning the equilibrium governing the crack (it is assumed that a slowly growing crack corresponds to mechanical equilibrium) requires an explicit introduction of a parameter having the dimensions of length, i.e. it is necessary to invoke hypotheses concerning the structure of the material[118-121]. Together with the details of the structure of the material, the description of the kinetics of the growth of a crack right through the specimen requires the formulation of the kinetics of the elementary processes involving the rupture of interatomic bonds near the end of the crack, where, by virtue of the marked dependence of the rate of the process on the stresses, the breakdown is localised[87,88].

Thus the problems of the micromechanics of breakdown cannot be eliminated from kinetic models for the breakdown process. The attempts to disregard the structure of the material lead to implicit hypotheses concerning the structure[122] or the treatment remains open-ended[123].

---o0o---

A theoretical relation has been established for different kinetic degradation schemes[77-88] between the lifetime in mechanothermodegradation and the parameter μ characterising the intensity of the mechanical field. Comparison of the results of the calculation showed that the $\lg \tau_r(\mu)$ relations obtained are qualitatively the same in the region of small values of μ, although they differ quantitatively. For sufficiently large values of μ, the relation between the logarithm of the lifetime and the applied stress can be represented by a single straight line, i.e. can be described by Eqn.(1) only for a simple reaction mechanism. As a result of the occurrence of two parallel reactions, the above relation is in some cases represented by two linear sections over a wide range of stresses. For a radical-chain kinetic mechanism of the degradation process, the dependence of the logarithm of the lifetime on the stress is most complex and, with the exception of the initial section, is represented in the general case by three linear sections, the ratios of the slopes of which are 5 : 1 : 2 (when the structure-sensitive coefficients of the elementary stages are equal). For a reversible reaction, critical phenomona are possible in mechanothermodegradation, and the range of "safe" stresses is determined by the ratio of the rate constants for the forward and reverse reactions. The non-uniformity of the distribution of bonds with respect to tensions leads to a decrease of the lifetime without altering the general form of the $\lg \tau_r(\mu)$ relation.

The results of the theoretical analysis[77-88] agree with experimental data, which makes it possible to employ the mathematical procedures developed in the above studies for the prediction of the useful lifetimes of polymeric articles. The problem of the prediction of the stability of polymeric articles can be simplified in the case of a complex radical-chain mechanism and the prediction itself can be made more exact. Theoretical analysis shows that in this case one must employ in calculations of the lifetime not the rate constants for the individual elementary stages of the degradation process, which are as a rule still not known with adequate accuracy, but the corresponding functions of the above constants, in terms of which the parameters of the mechanothermodegradation equations are expressed. The functions of the constants can be determined with the necessary accuracy from experimental lifetimes of polymeric materials. In extrapolating the results thus obtained to the operating conditions of the corresponding polymeric article, it is, however, necessary to bear in mind that when the kinetic mechanism of the degradation process is complex, the combination of elementary constants determining the macroscopic parameters of the mechanothermodegradation (U_0, t_0, γ) varies with the applied stress.

REFERENCES

1. N.M.Emanuel', "Strukturno-Kineticheskie Aspekty Destruktsii i Stabilizatsii Polimerov, Karginskie Chteniya, 1977" (Structural-Kinetic Aspects of the Degradation and Stabilisation of Polymers, Kargin Lectures, 1977); Vysokomol.Soed., A19, 1903 (1977).
2. A.A.Il'yushin and B.E.Pobedrya, "Osnovy Mathematicheskoi Teorii Termovyazko-Uprugosti" (Fundamentals of the Mathematical Theory of Thermoviscoelasticity), Izd.Nauka, Moscow, 1970.
3. V.V.Moskvitin, "Soprotivlenie Vyazko-Uprugikh Materialov" (The Resistance of Viscoelastic Materials), Izd.Nauka, Moscow, 1972.
4. V.R.Regel', A.I.Slutsker, and E.E.Tomashevskii, "Kineticheskaya Priroda Prochnosti Tverdykh Tel" (The Kinetic Nature of the Strength of Solids), Izd.Nauka, Moscow, 1974.
5. A.Kelly, "Strong Solids" (Translated into Russian), Izd.Mir, Moscow, 1976.
6. V.P.Pukh, "Prochnost' i Razrushenie Stekla" (The Strength and Breakdown of Glass), Izd.Nauka, Moscow, 1973.
7. A.I.Lukomskaya and V.F.Evstratov, "Osnovy Prognozirovaniya Mekhanicheskogo Povedeniya Kauchukov i Rezin" (Methods for the Prediction of the Mechanical Behaviour of Raw and Cured Rubbers), Izd. Khimiya, Moscow, 1975.
8. A.L.Rabinovich, "Vvedenie v Mekhaniku Armirovannykh Polimerov" (Introduction to the Mechanics of Reinforced Polymers), Izd.Nauka, Moscow, 1970.
9. T.L.Smith and R.A.Dickle, Rubb.Chem.Technol., **43**, 714 (1970).
10. T.L.Smith, Rubb.Chem.Technol., **37**, 777 (1964).
11. S.N.Zhurkov and B.N.Narzullaev, Zhur.Tekh.Fiz., **23**, 1677 (1953).
12. G.M.Bartenev and Yu.S.Zuev, "Prochnost' i Razrushenie Vysokoelasticheskikh Materialov" (The Strength and Breakdown of Highly Elastic Materials), Izd.Khimiya, Moscow-Leningrad, 1964.
13. S.N.Zhurkov, Vestnik Akad.Nauk SSSR, No.3, 46 (1968).
14. R.J.Young and P.W.R.Beaumont, Polymer, **17**, 717 (1976).
15. W.L.Williams and F.N.Kelley, in "Polymer Network Structure and Mechanical Properties" (Edited by A.J.Chompff and S.Newman), Plenum Press, New York–London, 1971, p.193.
16. E.Orowan, Nature, **154**, 341 (1944).
17. J.B.Murgatroid, Nature, **154**, 51 (1944).
18. Yo Tokano and Shino Kondo, Polymer, **15**, 671 (1974).
19. N.N.Pavlov, Yu.B.Zaks, and E.N.Guseva, Symposium, "Svoistva i Primenenie Polimernykh Materialov pri Nizkikh Temperaturakh" (The Properties and Applications of Polymeric Materials at Low Temperatures), Izd. YaF Sibir.Otd.Akad.Nauk SSSR, Yakutsk, 1977, p.42.
20. N.N.Safonova, I.I.Frolova, V.I.Lebedeva, and A.I.Akhremenko, Symposium, "Svoistva i Primenenie Polimernykh Materialov pri Nizkikh Temperaturakh" (The Properties and Applications of Polymeric Materials at Low Temperatures), Izd. YaF Sibir.Otd.Akad.Nauk SSSR, Yakutsk, 1977, p. 56.
21. N.K.Baramboim, "Mekhanokhimiya Vysokomolekulyarnykh Soedinenii" (The Mechanochemistry of Macromolecular Compounds), Izd.Khimiya, Moscow, 1971.
22. O.N.Karpukhin, B.D.Goikhman, T.P.Smekhunova, L.P.Smirnov, and E.M.Slobodetskaya, Plast.Massy, No.11, 27 (1978).
23. N.N.Pavlov, V.A.Sade, and G.A.Kudryavtseva, Plast.Massy, No.3, 52 (1974).
24. E.L.Vinogradov, L.I.Godunova, A.M.Lobanov, and N.V.Lysenko, Plast.Massy, No.4, 44 (1976).
25. A.G.Kozlov, Symposium, "Svoistva i Primenenie Polimernykh Materialov pri Nizkikh Temperaturakh" (The Properties and Applications of Polymeric Materials at Low Temperatures), Izd.YaF Sibir. Otd.Akad.Nauk SSSR, Yakutsk, 1977, p.92.
26. A.A.Griffith, Phil.Trans.Roy.Soc., A221, 163 (1921)..
27. Yu.N.Rabotnov, "Polzuchest' Elementov Konstruktsii" (The Creep of Constructional Elements], Izd. Nauka, Moscow, 1966.
28. L.M.Kachanov, "Teoriya Polzuchesti" (Theory of Creep), Fizmatgiz, Moscow, 1960.
29. E.L.Lyubart, Mekhanika Tverdogo Tela, No.1, 141 (1974).
30. I.A.Birger, Problemy Prochnosti, No.11 (113) 3, (1978).
31. R.D.Maksimov and Yu.S.Urzhumtsev, Mekhanika Polimerov, 631 (1977).
32. Yu.S.Urzhuntsev, Zhur.Vses.Khim.Obshch.im. Mendeleeva, **23**, 310 (1978).
33. A.V.Tobolsky and H.Eyring, J.Chem.Phys., **11**, 125 (1943).
34. F.Bueche, J.Appl.Phys., **28**, 784 (1957).
35. A.I.Gubanov and A.D.Chevychelov, Fiz.Tverd. Tela, **5**, 91 (1963).
36. B.D.Coleman, J.Polymer Sci., **20**, 447 (1956).
37. A.D.Chevychelov, Fiz.Tverd.Tela, **5**, 1394 (1963).
38. H.H.Kausch, S.R.Joghe, and C.C.Hsiao, J.Appl. Phys., **38**, 201 (1970).
39. H.H.Kausch and C.C.Hsiao, J.Appl.Phys., **39**, 4915 (1968).
40. G.G.Hsiao, S.R.Moghe, and H.H.Kausch, J.Appl. Phys., **39**, 3857 (1968).

41. O.F.Shlenskii and V.V.Lavrent'ev, Mekhanika Polimerov, 668 (1970).
42. M.N.Bokshitskii, Mekhanika Polimerov, 654 (1970).
43. Yu.Ya.Gotlib and A.V.Dobrodumov, Vysokomol. Soed., **A20**, 854 (1978).
44. A.I.Gubanov and A.D.Chevychelov, Fiz.Tverd. Tela, 4, 928 (1962).
45. V.E.Gul', Mekhanika Polimerov, 489 (1972).
46. V.A.Zakrevskii, Vysokomol.Soed., **B13**, 105 (1971).
47. V.R.Regel', Mekhanika Polimerov, 98 (1971).
48. A.A.Askadskii, "Deformatsiya Polimerov" (Deformation of Polymers), Izd.Khimiya, Moscow, 1973.
49. A.V.Amelin, Yu.A.Glagoleva, A.F.Podo'skii, O.F.Pozdnyakov, V.R.Regel', and T.P.Sanfirova, Fiz.Tverd.Tela, **13**, 2726 (1971).
50. A.V.Amelin, O.F.Pozdnyakov, V.R.Regel', and T.P.Sanfirova, Fiz.Tverd.Tela, **12**, 2528 (1970).
51. A.V.Amelin, O.F.Pozdnyakov, and V.R.Regel', Mekhanika Polimerov, 467 (1968).
52. A.V.Amelin, Yu.A.Glagoleva, O.F.Pozdnyakov, and V.R.Regel', Vysokomol.Soed., A11, 1926 (1969).
53. W.J.Wettegren, W.E.Korsukow, and J.J.Nowak, Plaste und Kautschuk, No.2, 86 (1972).
54. V.A.Mal'chevskii and V.A.Zakrevskii, Izv.Vys. Ucheb.Zaved., Ser.Khim.i Khim.Tekhnol., **15**, 276 (1972).
55. A.V.Amelin, T.M.Muinov, O.F.Pozdnyakov, and V.R.Regel', Mekhanika Polimerov, 80 (1967).
56. A.M.Dubinskaya and P.Yu.Butyagin, Vysokomol. Soed., B9, 525 (1967).
57. V.A.Radtsig and P.Yu.Butyagin, Vysokomol.Soed., **A9**, 2549 (1967).
58. S.I.Veliev, V.I.Vettegren', and I.I.Novak, Mekhanika Polimerov, 433 (1970).
59. V.A.Zakrevskii and V.E.Korsukov, Vysokomol. Soed., **A14**, 955 (1972).
60. V.E.Korsukov and A.A.Shunkevich, Symposium, "Kinetika i Mekhanizm Khimicheskikh Reaktsii v Tverdom Tele" (Kinetics and Mechanisms of Chemical Reactions in Solid), Izd.Beloruss.Gos.Univ., Minsk, 1975, p.343.
61. A.Ya.Gol'dman, V.V.Matveev, and L.F.Shalaeva, Mekhanika Polimerov, 344 (1977).
62. M.A.Natov, S.V.Vasileva, and V.S.Kabaivanov, Vysokomol.Soed., A11, 1291 (1969).
63. V.A.Mal'chevskii and V.A.Zakrevskii, Mekhanika Polimerov, 342 (1978).
64. M.Robertson, B.Terselius, and J.-F.Jansson, "Abstracts of Short Communications at International Symposium on Macromolecular Chemistry, Tashkent, 1978", Vol.5, p.36.
65. A.M.Leksovskii, B.Gaffarov, and S.S.Khin'kis, Plast.Massy, No.10, 34 (1978).
66. O.A.Ledneva, Yu.A.Mikheev, and D.Ya.Toptygin, Vysokomol.Soed., A17, 546 (1975).
67. T.S.Popravko, Yu.A.Mikheev, D.Ya.Toptygin, and L.S.Zakina, Vysokomol.Soed., **A18**, 679 (1976).
68. V.A.Bershtein and L.M.Egorova, Vysokomol.Soed., **A19**, 1260 (1977).
69. L.V.Ivanova and G.E.Zaikov, Vysokomol.Soed., **A19**, 537 (1977).
70. V.A.Bershtein, L.M.Egorova, and V.V.Solov'ev, Mekhanika Polimerov, 854 (1977).
71. N.M.Livanova, N.Ya.Rapoport, V.B.Miller, and I.N.Musaelyan, Vysokomol.Soed., **A18**, 2260 (1976).
72. P.G.Fox, J.Materials Sci., **10**, 340 (1975).
73. F.Kh.Urakaev, O.F.Pozdnyakov, and V.V.Boldyrev, Symposium, "Kinetika i Mekhanizm Khimicheskikh Reaktsii v Tverdom Tele" (Kinetics and Mechanisms of Chemical Reactions in Solids), Izd.Beloruss.Gos. Univ., Minsk, 1975, p.341.
74. F.Kh.Urakaev, O.F.Pozdnyakov, V.V.Boldyrev, and Yu.P.Savintsev, Kinetika i Kataliz, **19**, 1442 (1978).
75. E.G.Avvakumov, "Mekhanicheskie Metody Aktivatsii Khimicheskikh Protsessov" (Mechanical Methods for the Activation of Chemical Processes), Izd.Nauka, Novosibirsk, 1979.
76. V.N.Panfilov and Yu.N.Molin, Uspekhi Khim., **47**, 967 (1978)[Russ.Chem.Rev., No.6 (1978)].
77. G.B.Manelis, L.P.Smirnov, and E.V.Polianchik, Dokl.Akad.Nauk SSSR, **215**, 1157 (1974).
78. G.B.Manelis, L.P.Smirnov, E.V.Polianchik, and S.N.Bloshenko, Vysokomol.Soed., **A19**, 86 (1977).
79. G.B.Manelis and L.P.Smirnov, Symposium, "Svoistva i Primenenie Polimernykh Materialov pri Nizkikh Temperaturakh" (The Properties and Applications of Polymeric Materials at Low Temperatures), Izd. YaF Sibir.Otd.Nauk SSSR, Yakutsk, 1977, p.17.
80. G.B.Manelis, Symposium, "Kinetika i Mekhanizm Khimicheskikh Reaktsii v Tverdom Tela" (Kinetics and Mechanisms of Chemical Reactions in Solids), Izd.Beloruss.Gos.Univ., Minsk, 1975, p.31.
81. G.B.Manelis, L.P.Smirnov, and E.V.Polianchik, Dokl.Akad.Nauk SSSR, **217**, 139 (1974).
82. E.V.Deyun, G.B.Manelis, and L.P.Smirnov, Dokl. Akad.Nauk SSSR, **237**, 859 (1977).
83. E.V.Deyun, G.B.Manelis, and L.P.Smirnov, "Tezisy Dokladov VII Vsesoyuznogo Soveshchaniya po Kinetike i Mekhanizmu Reaktsii v Tverdom Tele, Chernogolovka, 1978" (Abstracts of Reports at the VIIth All-Union Conference on the Kinetics and Mechanisms of Reactions in Solids, Chernoglovka, 1978), p.302.
84. E.V.Deyun, G.B.Manelis, and L.P.Smirnov, "Zakonomernosti Ob'emnoi Mekhanotermodestruktsii Polimerov pri Radikal'no-Tsepnoi Kineticheskoi Skheme" (Characteristics of the Bulk-Phase Mechanothermodegradation of Polymers Under the Conditions of a Radical-Chain Kinetic Mechanism), Preprint from OKIKhF Akad.Nauk SSSR, 1979.
85. E.V.Deyun, G.B.Manelis, and L.P.Smirnov, "Modelirovanie Ob'emnogo Razrusheniya Polimerov v Prisutstvii Monofunktsional'nogo Ingibitora" (The Modelling of the Bulk-Phase Breakdown of Polymers in the Presence of a Monofunctional Inhibitor), Preprint from OIKhF Akad.Nauk SSSR, 1979.
86. G.B.Manelis, E.V.Polianchik, and L.P.Smirnov, Vysokomol.Soed., **A20**, 125 (1978).
87. G.B.Manelis, E.V.Polianchik, and L.P.Smirnov, Symposium, "Kinetika i Mekhanizm Khimicheskikh Reaktsii v Tverdom Tele" (Kinetics and Mechanisms of Chemical Reactions in Solids), Izd.Beloruss.Gos. Univ., Minsk, 1975, p.338.
88. L.P.Smirnov and E.V.Polianchik, Tezisy Dokladov Vsesoyuznoi Nauchno-Tekhnicheskoi Konferentsii 'Svoistva i Primenenie Polimernykh Materialov pri Nizkikh Temperaturakh'" (Abstracts of Reports at the All-Union Science and Engineering Conference on "The Properties and Applications of Polymeric Materials at Low Temperatures"), Yakutsk, 1977, p.46.
89. J.H.de Boer, Trans.Faraday Soc., **32**, 10 (1936).

90. W.Kauzmann and H.Eyring, J.Amer.Chem.Soc., **62**, 3113 (1940).
91. E.E.Tomashevskii, Fiz.Tverd.Tela, **12**, 3202 (1970).
92. V.R.Regel' and T.M.Muinov, Fiz.Tverd.Tela, **8**, 2364 (1966).
93. B.Maxwell and L.F.Rahm, Ind.Eng.Chem., **41**, 1988 (1949).
94. N.Grassie, "Chemistry of High Polymer Degradation Processes" (Translated into Russian), Inostr.Lit., Moscow, 1959.
95. S.L.Madorsky, "Thermal Degradation of Organic Polymers" (Translated into Russian), Izd.Mir, Moscow, 1967.
96. H.Ellinek and Ting-Liu Ming, Khimiya i Tekhnologiya Polimerov, No.1, 126 (1967).
97. S.N.Zhurkov, Izv.Akad.Nauk SSSR, Neorg. Materialy, **3**, 1763 (1967).
98. V.A.Kargin and T.I.Sogolova, Dokl.Akad.Nauk SSSR, **108**, 662 (1956).
99. M.G.Fal'kovskii, V.I.Zheleznov, Yu.A.Antonov, L.D.Gal'perina, and N.F.Matveeva, Vysokomol.Soed., A17, 1678 (1975).
100. N.N.Peshchanskaya and V.A.Stepanov, Fiz.Tverd. Tela, **7**, 2962 (1965).
101. B.Shermatov, U.Sultanov, V.S.Kuksenko, and A.I.Slutsker, Vysokomol.Soed., **A18**, 1613 (1976).
102. E.A.Egorov, N.N.Peshchanskaya, and V.A.Stepanov, Fiz.Tverd.Tela, 11, 1325 (1969).
103. M.A.Natov and S.V.Vasileva, Vysokomol.Soed., **A11**, 1906 (1969).
104. G.M.Bartenev, Yu.V.Zelenev, and I.S.Lyakhovich, Mekhanika Polimerov, 886 (1971).
105. G.M.Bartenev, B.N.Narzullaev, V.A.Mirzoeva, and S.Yu.Mirzoev, Vysokomol.Soed., **A14**, 2022 (1972).
106. N.G.Erfan, G.M.Bartenev, B.N.Narzullaev, and B.M.Tulinov, Vysokomol.Soed., **A19**, 1528 (1977).
107. A.Ya.Gol'dman and V.V.Matveev, Vysokomol.Soed., B19, 156 (1977).
108. S.N.Zhurkov and V.E.Korsukov, Fiz.Tverd.Tela, **15**, 2071 (1973).
109. R.Simha, L.A.Wall, and P.J.Blatz, J.Polymer Sci., **5**, 615 (1950).
110. V.A.Zakrevskii and V.S.Kuksenko, Fiz.Tverd.Tela, **11**, 1940 (1969).
111. K.C.Valanis and O.Gilmazer, J.Polymer Sci.Phys., **15**, 1101 (1977).
112. V.I.Vettegren', Candidate's Thesis, The Physico-technical Institute, Leningrad, 1970.
113. V.P.Tamuzh and P.V.Tikhomirov, Mekhanika Polimerov, 227 (1973).
114. V.P.Tamuzh and V.S.Kuksenko, "Mikromekhanika Razrusheniya Tverdykh Polimerov" (The Micro-mechanics of the Breakdown of Solid Polymers), Izd.Nauka, Moscow, 1978.
115. Yu.A.Gotlib, A.V.Dobrodumov, A.M.El'yashevich, and Yu.V.Svetlov, Fiz.Tverd.Tela, **15**, 801 (1973).
116. P.V.Tikhomirov and S.P.Yushanov, Mekhanika Polimerov, 462 (1978).
117. A.V.Dobrodumov and A.M.El'yashevich, Fiz.Tverd. Tela, 15, 1891 (1973).
118. G.I.Barenblatt, V.M.Entov, and R.L.Salganik, Mekhanika Tverdogo Tela, No.6, 107 (1966).
119. G.I.Barenblatt, V.M.Entov, and R.L.Salganik, Mekhanika Tverdogo Tela, No.2, 148 (1967).
120. R.L.Salganik, Problemy Prochnosti, No.2, 79 (1971).
121. V.M.Entov, Mekhanika Tverdogo Tela, No.3, 111, (1976).
122. V.A.Petrov, Fiz.Tverd.Tela, **18**, 1290 (1976).
123. W.H.Gingman, J.Appl.Phys., 49, 2328 (1978).

Division of the Institute of
Chemical Physics, USSR Academy
of Sciences, Chernogolovka,
Moscow Region

Translated from *Uspekhi Khimii*, 49, 1594-1616 (1980) U.D.C. 541.128.24:547.313

Photochemical Oxidation of Polyolefins and Prediction of Their Useful Lifetime

E.M.Slobodetskaya (deceased)

By analysing the experimental data for individual elementary steps in the photochemical oxidation of pure polyolefins and by considering the kinetics of the process as a whole, it is shown that the latter is a chain reaction with degenerate photobranching by hydroperoxides and carbonyl compounds and quadratic chain termination. The available data are sufficient to describe the process at a quantitative level under any conditions. The use of this reaction as a model made it possible to elucidate the characteristic features of the photochemical oxidation of thermally stabilised and oriented polyolefins.
The bibliography includes 68 references.

CONTENTS

I. Introduction 771
II. Kinetics of the photochemical oxidation of polypropylene 771
III. Characteristics of the elementary steps and their influence on the photochemical oxidation of polyolefins 773
IV. The use of the model polypropylene photochemical oxidation reaction for the study of the influence of stabilisers and orienting extrusion on the photochemical oxidation of polyolefins and for predicting the useful lifetime of the polymers 775

I. INTRODUCTION

Polyolefins have been used traditionally to study the ageing of polymeric materials. Tens of original studies devoted to the degradation, oxidation, thermal, and photo- and radiation-induced ageing of polyolefins (PO) and several reviews are published annually. The interest in polyolefins as objects of study is due to a number of causes. On the one hand, polyolefins are some of the simplest polymeric molecules with thoroughly investigated low-molecular weight analogues—aliphatic hydrocarbons. On the other hand, polyolefins, particularly polypropylene (PP) are comparatively readily oxidised, which makes the problem of the stabilisation of these polymeric materials particularly urgent and at the same time facilitates the study of this process. Furthermore polyolefins are produced industrially on a wide scale and are used in practice in a comparatively pure form—in the presence of added stabilisers only. This permits an easy comparison of laboratory studies with the results of tests on a real polymeric material under natural conditions.

Polyolefins are usually employed at a temperature much higher than their glass point. Therefore, in describing the mechanism of the ageing of polyolefins, there are almost no difficulties characteristic of the description of solid-phase reactions. The formal process kinetics remain the same as in a viscous liquid or in the melt.

Several years ago, the present author published a review[1] in which a general mechanism of the entire polypropylene photooxidation process was "synthesised" on the basis of data for the mechanisms of individual elementary steps of the photochemical oxidation reaction and it was shown that the data available at the time for this process could be described at a quantitative level within the framework of the mechanism proposed. Despite the comparatively short period which has elapsed since the publication of the earlier review[1], a large amount of new experimental data, confirming the earlier hypothesis concerning the mechanism of the photooxidation of polypropylene has now accumulated. They now make it possible to regard the photochemical oxidation of polypropylene as a model reaction whose mechanism has been elucidated at a quantitative level.

The present review deals with the question of how this model reaction can be used to describe the kinetics of the variation of properties of polyolefins of practical importance, to elucidate the fundamental features of the mechanism of the action of various stabilisers, and to investigate the mechanism of the oxidation of polymers in an oriented state. The study of all these problems will permit a close approach to the performance of one of the fundamental tasks in the study of the ageing of polymers—the determination of the useful lifetime of polymeric materials—in the present instance those based on polyolefins.

II. KINETICS OF THE PHOTOCHEMICAL OXIDATION OF POLYPROPYLENE

By analysing the experimental data available at the time, it was shown in the earlier review[1] that the photochemical oxidation of polyolefins is a chain process with quadratic chain termination and degenerate photobranching by the hydroperoxide. The kinetic mechanism of this process can be formulated thus:

$$S \xrightarrow{w_0} PO_2^{\cdot}, \quad (1)$$

$$PO_2^{\cdot} + PH \xrightarrow{k_p} POOH + P^{\cdot}, \quad (2)$$

$$P^{\cdot} + O_2 \xrightarrow{k_2} PO_2^{\cdot},$$

$$PO_2^{\cdot} + PO_2^{\cdot} \xrightarrow{k_t} (C{=}O), \quad (3)$$

$$POOH + h\nu \xrightarrow{\alpha} PO^{\cdot} + OH^{\cdot} \xrightarrow{PH} (C{=}O) + 2PO_2^{\cdot}, \quad (4)$$

$$(C{=}O) + h\nu \xrightarrow{\alpha'} f\,PO_2^{\cdot}. \quad (5)$$

where S is the sensitiser present in the polymer and ensuring the primary initiation, $PO_2^{\cdot}$ are peroxy-radicals derived from the polymer PH, POOH is the hydroperoxide, (C=O) are carbonyl compounds, and f is the probability of the release of the radicals into the bulk phase on photolysis of the carbonyl compound. The rate constants for the corresponding reactions are indicated above the arrows, those for the photochemical reactions (α and α') characterising the probability of the decomposition of the given

substance per unit time under the influence of light having an intensity I subject to the condition that light is absorbed uniformly throughout the thickness of the specimen. The quantity α is related to the quantum yield of the decomposition into radicals ϕ and the extinction coefficient ε:

$$\alpha = \int \varphi I \varepsilon \, d\lambda. \qquad (6)$$

A change in the concentration of carbonyl compounds in the specimen is known to have no appreciable influence on the rate of photochemical oxidation[2,3] and the formation of radicals in the decomposition of C=O can therefore be neglected.

In this case the kinetics of the process are analogous to those of the familiar thermal oxidation of hydrocarbons[4]. If it is assumed that the principle of quasi-stationary concentrations of peroxy-radicals holds throughout the process, then, at a constant light intensity, the kinetics of the accumulation of reaction products are determined[1] solely by the parameter $k_p/\sqrt{k_t}$ and the probabilities of the photochemical decomposition of peroxides and carbonyl compounds—α and α':

$$[\mathrm{POOH}] = [\mathrm{POOH}]_\infty (1 - e^{-\alpha t/2})^2, \qquad (7)$$

$$[\mathrm{C{=}O}] = \frac{2\alpha}{\alpha'}[\mathrm{POOH}]_\infty \left(1 - e^{-\alpha t} - \frac{4\alpha'}{2\alpha' - \alpha}(e^{-\alpha t/2} - e^{-\alpha' t}) + \frac{\alpha'}{\alpha' - \alpha}(e^{-\alpha t} - e^{-\alpha' t})\right). \qquad (8)$$

For $\alpha' = 0$, we obtain

$$[\mathrm{C{=}O}] = 2[\mathrm{POOH}]_\infty (\alpha t - (3 - e^{-\alpha t/2})(1 - e^{-\alpha t/2})),$$

where

$$[\mathrm{POOH}]_\infty = (2k_p^2/\alpha k_t)[\mathrm{PH}]^2.$$

All the parameters in Eqns.(7) and (8) can be determined independently. It is known[5] that aliphatic hydroperoxides decompose into radicals in the step involving the absorption of each light quantum and α can therefore be calculated from spectroscopic data. Apart from spectroscopic data for carbonyl compounds, it is necessary to know the quantum yield ϕ_I of their decomposition via a Norrish type I reaction in order to determine α' †. The yields ϕ_I for different types of (C=O) in polyolefins are available in the literature (see, for example, Carlsson and Wiles[6] and Hartley and Guillet[7]).

The parameter $k_p/\sqrt{k_t}$ is determined from data for the initiated oxidation of the polymer. The calculation[1] yielded a satisfactory agreement with the results of experiments on the oxidation of pure polypropylene[8]; at that time only isolated data were available for the kinetics of the photochemical oxidation of polypropylene in which all the necessary characteristics of the process conditions were indicated: temperature and the intensity and spectral composition of the effective radiation.

Detailed studies have been made on the kinetics of the photochemical oxidation of polypropylene under the influence of light of different intensity and different spectral composition[9], the range of temperatures in which the parameters $k_p/\sqrt{k_t}$ were measured has been significantly extended, and the absolute values of the constants k_p and k_t have been determined (Table 1). All the results obtained concern the validity of the proposed mechanism. As an example, Fig.1 shows how the calculation agrees with data for the accumulation of (C=O) in the photochemical oxidation of different polypropylene specimens under the influence of light at a wavelength of 254 nm.

Table 1. Kinetic parameters of the oxidation of polypropylene* and the extinction coefficients of the branching products.

Parameter	Value	Refs.
$k_p/\sqrt{k_t}$, litre$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$	$17\ e^{-6630/RT}$	11
$k_p/\sqrt{k_t}$, litre$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$	$72\ e^{-8500/RT}$	9
k_p, litre mol^{-1} s^{-1}	$68 \cdot 10^{10}\ e^{-20840/RT}$	11
k_p, litre mol^{-1} s^{-1}	$28.8 \cdot 10^{11}\ e^{-22706/RT}$	9
k_t, litre mol^{-1} s^{-1}	$1.6 \cdot 10^{21}\ e^{-28500/RT}$	12
$k_p/\sqrt{k_t}$ at 20 °C, litre$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$	$2 \cdot 10^{-4}$	11
$k_p/\sqrt{k_t}$ at 20 °C, litre$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$	$4 \cdot 10^{-5}$	9
$k_p/\sqrt{k_t}$ at 20 °C, litre$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$	$1 \cdot 10^{-4}$	10
k_p at 20 °C, litre mol^{-1} s^{-1}	$2.4 \cdot 10^{-4}$	11
k_p at 20 °C, litre mol^{-1} s^{-1}	$9 \cdot 10^{-5}$	9
k_t at 20 °C, litre mol^{-1} s^{-1}	1.2	12
	0.15	2
$\varepsilon_{\mathrm{POOH}}$ at 254 nm, litre mol^{-1} cm^{-1}	12.5	5
$\varepsilon_{\mathrm{POOH}}$ at 313 nm, litre mol^{-1} cm^{-1}	0.252	5
$\varepsilon_{\mathrm{POOH}}$ at 365 nm, litre mol^{-1} cm^{-1}	0.01	5
$\varepsilon_{\mathrm{C=O}}$ at 254 nm, litre mol^{-1} cm^{-1}	8	5
$\varepsilon_{\mathrm{C=O}}$ at 313 nm, litre mol^{-1} cm^{-1}	10	5
$\varepsilon_{\mathrm{C=O}}$ at 365 nm, litre mol^{-1} cm^{-1}	0.44	5

*All the parameters were calculated taking into account the fact that the oxidation develops only in the amorphous component of the polymer[13].

Thus it has become possible to treat the photochemical oxidation of polypropylene from a single standpoint as a model process whose mechanism has been fully elucidated also at a quantitative level and the rate constants for all the elementary processes have been determined by independent methods. A characteristic feature of this process is a non-linear relation between the rate of reaction and the rate of formation of active centres. As a result of this non-linearity, the kinetics of the given process are qualitatively different from the kinetics of processes described as elementary nth order reactions.

For example, polypropylene does not absorb light at a wavelength greater than 200 nm; nevertheless, it is effectively oxidised under the influence of this light. The explanation is not inadequate purity of the polymer but the fact that the destruction of radicals proceeds via a second-order reaction. At low rates of initiation the oxidation chain length tends to affinity. Because of this, the solution of the differential equation describing the process kinetics is unstable at low rates of initiation and even at low rates of side processes the concentration of the hydroperoxide increases fairly rapidly; the quasi-stationary concentration of peroxy-radicals is also rapidly established.

A rigorous analysis of the kinetic scheme showed[14] that, for the majority of hydrocarbons and polymers, the decrease of the rate of primary initiation cannot alter significantly the induction period of the oxidation reaction, which is defined as the time required to accumulate the hydroperoxide at a concentration of $\sim 10^{-2}$ M.

† Norrish type II decomposition actually leads to the decomposition of the macromolecule and not to the consumption of the carbonyl group.

Another unusual consequence of the quadratic termination of the oxidation chains is a weak dependence of the stationary rate of photochemical oxidation on light intensity. Some time after the onset of oxidation (at $t \gg 1/\alpha$) the accumulation of the hydroperoxide virtually ceases completely and its quasi-stationary concentration is established. According to Eqn.(8), the concentration is inversely proportional to the light intensity. On the other hand, the rate of formation of carbonyl compounds, which under the given conditions is a measure of the rate of oxidation, is proportional to the concentration of the peroxide and the light intensity, i.e. [the hydroperoxide concentration] is independent of the light intensity#.

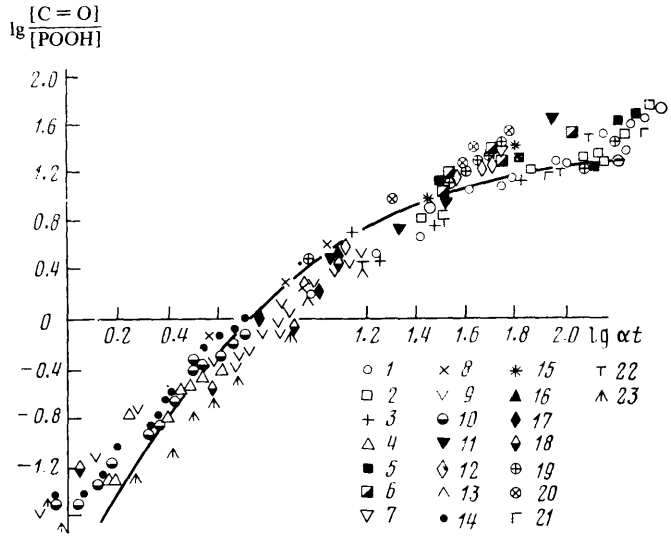


Figure 1. The logarithmic forms of kinetic curves for the accumulation of carbonyl compounds in the photochemical oxidation of different polypropylene specimens. Intensity of incident light 10^{-15} I (quanta cm^2 s^{-1}): 1), 5), 11), and 15) 4; 2), 6), 12), and 16) 2; 3), 7), 13), and 17) 0.5; 19) 0.7; 8) 0.44; 4), 9), and 18) 0.16; 10) and 14) 0.04; 20) 0.63; 21) 4; 22) 2; 23) 0.04 [21)–23) specimens consisting of large spherolites]; continuous line—calculation[9].

Within the framework of the mechanism under consideration, the stationary concentrations of the peroxide and carbonyl compounds are defined by the relations

$$[\mathrm{POOH}]_{\mathrm{stat}} = [\mathrm{POOH}]_\infty \frac{2\theta + f}{2\theta - f}, \qquad (9)$$

$$[\mathrm{C=O}]_{\mathrm{stat}} = [\mathrm{POOH}]_\infty \frac{\alpha}{\alpha'} 4 \frac{2\theta + f}{(\theta - f)^2}, \qquad (10)$$

where θ is the probability of the destruction of the carbonyl compound in the cage on decomposition via a Norrish type I reaction. With the aid of Eqns.(9) and (10), the values of θ and f have been determined for polypropylene[15] ($\theta = 0.75$ and $f = 0.15$).

It has been shown[16] that this treatment, which does not take into account the consumption of the substance oxidised, is valid only when one considers photochemical oxidation; in thermal oxidation $[\mathrm{POOH}]_\infty$ is usually comparable to [PH].

Thus the photochemical oxidation of polypropylene is a process which proceeds despite the fact that the initial substance does not absorb light and its stationary rate is independent of the light intensity.

III. CHARACTERISTICS OF THE ELEMENTARY STEPS AND THEIR INFLUENCE ON THE PHOTOCHEMICAL OXIDATION OF POLYOLEFINS

In the course of the study of the elementary reactions in polyolefins, certain features of their occurrence and quantitative characteristics were elucidated. This section deals with the conditions under which these features can influence the photochemical oxidation of polyolefins and the way in which this can be done.

1. Primary Initiation

According to a number of workers, the cause of the low stability of polyolefins with respect to the action of light is the sensitising role of impurities contaminating the polymer in the course of synthesis and processing[17,18]. Charge-transfer complexes between the polymer and oxygen[19–21], singlet oxygen donors[22–25], admixtures of aromatic compounds[26–28,34], residual amounts of catalysts[29–31], and unsaturated carbonyl compounds[18] have been considered as sensitisers of this kind. It has been shown that under certain conditions these compounds can serve as sources of free radicals. However, in estimating the influence of these impurities on the photochemical oxidation of polyolefins, it is necessary to compare the efficiency of their action with the efficiency of other stages of the process—in the first place the branching stage.

In the majority of cases such estimates were not made, which led to an apparent conflict between the available literature data. For example, it has been shown that, in the photolysis of aromatic[34] or carbonyl compounds, free radicals are formed. On the other hand it has also been shown that in many instances the presence of these impurities does not affect the photochemical oxidation[18]. This apparent contradiction is due to the fact that free radicals are formed from aromatic compounds at low temperatures in two-quantum processes, which do not occur in the photochemical oxidation of polyolefins close to room temperature. Carbonyl compounds are indeed sources of free radicals, but, together with these, photochemical oxidation of polyolefins gives rise to a much more effective source of free radicals—the hydroperoxide, and the role of sensitisation by carbonyl compounds is therefore insignificant.

A special analysis of the possible role of singlet oxygen donors in the photochemical oxidation of polyolefins and natural rubbers has been carried out[33]. It was assumed that the initiating function of $^1O_2$ consists in the fact that its interaction with unsaturated compounds can give rise to a hydroperoxide, which serves as an additional source of free radicals. It was shown[33] that the introduction of singlet oxygen donors does not accelerate the photochemical oxidation of the polymers investigated, occurring under the influence of ultraviolet radiation at fairly short wavelengths.

#In fact the increase of the concentration of carbonyl compounds is limited by their photochemical decomposition, which results in the formation of a certain amount of free radicals and this leads to some increase of the quasi-stationary concentration of the hydroperoxide.

On this basis, the authors[33] concluded that $^1O_2$ is not involved in the photochemical oxidation of natural rubbers and polyolefins. They showed[33] that this conclusion is valid only when the polymer is acted upon by ultraviolet radiation of sufficiently short wavelengths, which is effectively absorbed by the hydroperoxide. For a quantitative estimate of the influence of singlet oxygen, it is necessary to compare the rate w_0 at which it forms the hydroperoxide with the rate of its formation in the chain propagation reaction. For the photochemical oxidation of polypropylene, the influence of $^1O_2$ may be neglected if

$$\frac{k_p}{\sqrt{k_t}}\sqrt{2\alpha[\mathrm{POOH}]} \gg w_0. \qquad (11)$$

Consequently in the initial stages of the process the influence of singlet oxygen can be manifested throughout; it disappears under the condition

$$(1-e^{-\alpha t/2}) \simeq \frac{\alpha t}{2} \gg \frac{w_0 k_t}{2k_p^2}. \qquad (12)$$

Accordingly, the role of singlet oxygen donors can be neglected when the concentration of reaction products z exceeds a certain limit

$$[\mathrm{POOH}] > \frac{w_0^2 k_t}{2\alpha k_p^2}, \qquad (13)$$

$$z > \frac{w_0^2 k_t^2}{2\alpha k_p^4},$$

where z is the concentration of the products formed in the chain termination reaction.

The sensitising activity of the impurities generating free radicals can be estimated similarly. It has been shown[1] that the role of these impurities becomes insignificant when

$$\alpha t \gg \frac{\sqrt{w_i}}{k_p/\sqrt{k_t}}. \qquad (14)$$

Instead of Eqn.(13), we have in this case

$$[\mathrm{POOH}] > \frac{w_i}{2\alpha}, \qquad (15)$$

$$z > \frac{w_i^{3/2}}{\alpha k_p/\sqrt{k_t}}.$$

There are virtually no data at present based on a quantitative estimate of the role of sensitising impurities in photochemical oxidation. Therefore, as in the study of Karpukhin and Slobodetskaya[1], one can only say that, in the photochemical oxidation under the influence of ultraviolet radiation absorbed by peroxides, the role of sensitisation and $^1O_2$ is insignificant, since the available data can be accounted for without allowance for them and since the kinetic curves for the accumulation of the reaction products clearly reveal an acceleration of the process, which is impossible in the case of a process sensitised by impurities.

Photochemical oxidation cannot become sensitised under the influence of near ultraviolet (>360 nm) and visible light, which is not absorbed by hydroperoxides. This is indicated also by the examination of the criteria defined by Eqns.(12)–(15) which were discussed above.

2. Propagation and Termination of the Kinetic Chain

The kinetics of chain oxidation usually depend little on the absolute rate constants for chain propagation (k_p) and termination (k_t). When the principle of quasi-stationary radical concentrations holds, the kinetics are determined by the parameter $k_p/\sqrt{k_t}$. This parameter can be determined in different ways from the kinetics of the thermal and photochemical oxidation of polyolefins.

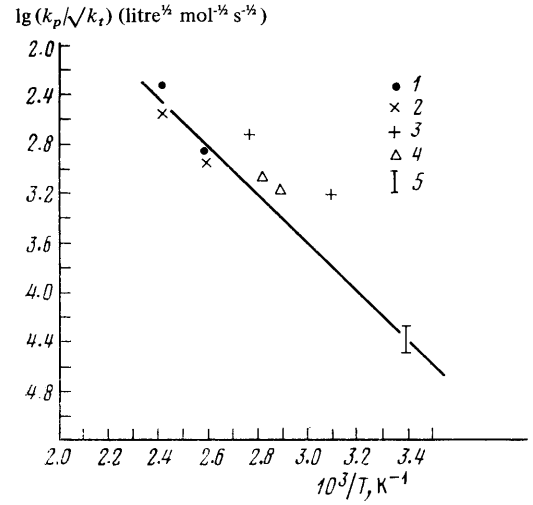


Figure 2. Temperature dependence of the parameter $k_p/\sqrt{k_t}$ for the oxidation of polypropylene according to different data: 1) Chien and Boss[68]; 2) Pudov et al.[16]; 3) Shanina et al.[11]; 4) Rapoport et al.[10]; 5) Karpukhin and Slobodetskaya[9].

The range of temperatures in which this parameter has been measured for polypropylene has been greatly extended recently. Fig.2 presents the data in terms of the variables of the Arrhenius equation. Evidently almost all the available data can be described by a single relation§; only at low temperatures is there some tendency towards an increase of the activation energy.

Table 2. The influence of the plasticiser and the hydroperoxide on the kinetic parameters of the oxidation of polypropylene[36].

Parameter*	Value of the parameter
	in the presence of 1 M *o*-dichlorobenzene
$k_p/(k_p)_0$	5.3
$k_t/(k_t)_0$	11
$(k_p/\sqrt{k_t})/(k_p/\sqrt{k_t})_0$	1.6
	in the presence of POOH**
k_t, litre mol^{-1} s^{-1}	170 (0.25); 12 (2.5); 5.2 (10)

*Subscript 0 refers to polypropylene without a plasticiser.
**The values of 10^2 [POOH] (M) are given in brackets.

§Only the data of Shanina et al.[11] deviate somewhat from the relation.

The absolute chain termination rate constants have been measured by EPR. It was observed that the rate of chain termination depends greatly on temperature[12,35] and is influenced by the molecular mobility of the medium[36] and the concentration of hydroperoxy-groups in the polymer[37]. The simultaneous measurement of the parameter $k_p/\sqrt{k_t}$ in the same systems showed[36] that all these factors have little effect on its value. The cause of this kind of compensation effect has not so far been established. Nevertheless the kinetics of the oxidation of polypropylene can be described under virtually any conditions using a single value of the parameter $k_p/\sqrt{k_t}$.

The parameters $k_p/\sqrt{k_t}$ for other polyolefins are much smaller. It is known that in the case of polyethylene (PE) the parameter has different values for low-pressure polyethylene (LPPE) and high pressure polyethylene (HPPE). This is explained by the fact that HPPE contains a greater number of tertiary hydrogen atoms, which react more effectively with the peroxy-radicals[38]. It is also known that a much smaller amount of hydroperoxides is formed in the photochemical oxidation of polyethylene than for polypropylene. This is associated with the lower value of the parameter $k_p/\sqrt{k_t}$ for polyethylene. In the thermal oxidation the parameter $k_p/\sqrt{k_t}$ for HPPE was measured in the melt[39]; furthermore, data have been published[40] on the accumulation of the HPPE hydroperoxide at 150–170 °C. The above parameter for HPPE was determined[41] from these results:

$$\frac{k_p}{\sqrt{k_t}}[\mathrm{PH}] = 34e^{-7000/RT}.$$

Photochemical oxidation of HPPE and LPPE was studied[41] at room temperature. The quantity $(k_p/\sqrt{k_t})[\mathrm{PH}]$ proved to be 1×10^{-4} (mol litre^{-1} s^{-1})$^{1/2}$, which virtually agrees with the value of this parameter extrapolated to room temperature in the study of Chokraborty and Scott[40].

3. Photobranching

The fundamental photoinitiation reaction in the photochemical oxidation of polyolefins is the photolysis of POOH. This reaction proceeds with a quantum yield of unity and with formation of two free radicals[5]. The presence of carbonyl compounds has no influence on the rate of this reaction. Thus a change in the concentration of carbonyl compounds by an order of magnitude does not affect the photolysis of POOH in polypropylene[42].

The absence of an initiating effect of (C=O) in polypropylene is associated with the low degree of liberation of radicals into space during their photolysis ($f_{20^\circ}=0.15$).[2] The situation is somewhat more complex in the case of polyethylene. Since the concentration of the hydroperoxide in polyethylene is very low and frequently cannot be determined analytically, it has been suggested in a number of studies that (C=O) is in fact a branching agent in polyethylene[43].

It is known[44] that, if 1% of C=O groups is introduced into polyethylene, the polymer becomes susceptible to decomposition by light and loses its strength characteristics much faster than pure polyethylene. On the other hand, it has been shown[40,45] that the rate of oxidation of specimens subjected to preliminary thermal oxidation varies in parallel with their hydroperoxide content (the hydroperoxide concentration in them was varied from 1×10^{-2} to 5×10^{-2} M). According to the data of Karpukhin et al.[41], when polyethylene is irradiated by light at a wavelength of 254 nm, the principal branching agents are also hydroperoxides. Analysis of literature data shows that the cause of this is (as for polypropylene) the low yield of radicals in the photolysis of carbonyl compounds (Table 3).

The observed contradictions can be resolved as follows. The photolysis of carbonyl compounds on irradiation of polyethylene by short-wavelength and particularly long-wavelength light proceeds extremely effectively. The photolysis of "central" ketones via a Norrish type II reaction involves the rupture of polymer chain. Thus the decomposition of the polymer takes place in two parallel processes: in the radical photochemical oxidation reaction and in the non-radical decomposition of ketones. Evidently the relative contributions of these processes will be determined by the irradiation conditions and by the concentration of ketones in the polyethylene. For example, calculation¶ for polyethylene used in practice, containing 10^{-2} M ketones, has shown that the role of the second process is small whatever the spectral composition of the incident light. When polyethylene containing ~0.5 M ketones is irradiated with long-wavelength light, the contributions of the two processes are comparable. This in fact explains the rapid decomposition of the ethylene–carbon monoxide copolymer. On the other hand, the degree of liberation of radicals into space during the photolysis of ketones is small; they make a small contribution to the rate of formation of radicals in polyethylene and a particular consequence of this is therefore that they have virtually no influence on the rate of photochemical oxidation of polyethylene.

Table 3. The quantum yields in the photochemical decomposition of aliphatic ketones in polyolefins.

Polymer	Ketone	φ_I	φ_{II}^*	f	$f\varphi_I$	Method of determination of φ	Refs.
PP	central	0.08	0.007	0.15	0.01	analysis of volatile products and weight loss on photolysis	6
PP	terminal	0.008	0.09	—	—	ditto	6
PE	central		0.025	—	0.003	change in molecular weight	46

*Here ϕ_{II} is the quantum yield of the decomposition via a Norrish type II reaction.

Thus the above analysis of data for the mechanisms and the quantitative characteristics of the elementary reactions which may occur in the photochemical oxidation of polyolefins showed that, under the usual conditions, the kinetics of this process are determined solely by the characteristics of the photochemical decomposition of hydroperoxides and carbonyl compounds and by the parameter $k_p/\sqrt{k_t}$.

IV. THE USE OF THE MODEL POLYPROPYLENE PHOTOCHEMICAL OXIDATION REACTION FOR THE STUDY OF THE INFLUENCE OF STABILISERS AND ORIENTING EXTRUSION ON THE PHOTOCHEMICAL OXIDATION OF POLYOLEFINS AND FOR PREDICTING THE USEFUL LIFETIME OF THE POLYMERS

The knowledge of the mechanism of the photochemical oxidation of pure polypropylene at a quantitative level makes it possible to use this reaction as a model whereby one

¶For the calculation, see E.M.Slobodetskaya, T.V.Magomedova, O.N.Karpukhin, and V.G.Protasov, Vysokomol.Soed. (in the Press).

can elucidate the details of more complex processes occurring both in the given polymer matrix and in other matrices with a similar structure.

1. Characteristics of the Oxidation of Oriented Polyolefins

Orienting extrusion is widely used in industry to obtain highly modular or specially strong fibres and films[47], which are used in various branches of technology. In particular, oriented polypropylene (OPP) films are used as packing materials in the food industry, for the packing of hygroscopic reagents and medicines, as insulating and protecting materials, etc.[48] The practical employment of these materials has shown that, compared with isotropic polypropylenes (IPP), they have not only more effective physicomechanical properties but are also more resistant to thermal oxidation[47]. A number of studies have been published recently whose authors attempt to discover the causes of this unusual structural stabilisation[49–51].

It is shown below that the data for the mechanism of the photochemical oxidation of isotropic polyolefins have been used to explain the fundamental stages of the oxidation of oriented polymers (OPO).

Polyolefins are semicrystalline polymers, the degree of crystallinity of which is usually in the range 60–70%. When crystalline polyolefins are extruded, their crystalline and amorphous components are oriented and the orientation of crystallites is virtually completed for low extrusion factors ($\bar{\lambda} = 4-5$), while for high extrusion factors all the changes occur in the amorphous part of the material[52].

The oriented fibres and films have a fibrillar structure, i.e. the polymer consists of microfibrils ~100 Å in diameter and several microns long, in which the amorphous and crystalline components alternate. The average periodicity in the polyolefin fibrils (the so-called long period) is ~100 Å and depends mainly on the extrusion temperature. The fraction of amorphous regions in the long period is inversely proportional to the degree of crystallinity of the polymer and usually amounts to 0.3–0.5 of the latter in industrial polyolefins. The composition of the crystallite usually includes several macromolecules. Consequently a large number of molecules in the amorphous region are "transient", i.e. pass from one crystallite to another through the amorphous layer. Indeed, according to Marikhin[53] 80–90% of the molecules in the amorphous region are transient and only 10–20% form the free ends and loops of the polymeric molecules projecting outside the limits of a single crystallite. Thus various parts of almost every macromolecule are incorporated simultaneously in several crystallites and contain several transient chains. The presence of a large number of transient chains is responsible for the increase in the stength of oriented polymers relative to isotropic polymers; according to Zhurkov et al.[52], the strength of fibres varies in parallel with the degree of orientation of macromolecules in the amorphous part.

Since the crystalline component of the specimens is not oxidised because the oxygen molecule cannot penetrate a crystallite, the oxidation of oriented polyolefins develops in their amorphous region[13]. According to Tochin et al.[54], considerable changes in the diffusion coefficients and in the solubility of gases in the amorphous portion of oriented polyethylene are observed only for $\bar{\lambda} > 12$. This shows, that, for $\bar{\lambda} = 4-5$, the orientation involves only a small fraction of the transient chains, while the rest remain in the same state as before orientation. When the oriented polymer is heated to a high temperature, its amorphous component undergoes partial disorientation, the degree of which depends on the annealing conditions—temperature, duration of annealing, and the strain in the macromolecule. This disorientation is caused by the "tearing out" of the transient chains from the crystallites or their "slip" relative to one another. Isometric annealing also leads to the disorientation of the amorphous part of the polymer, but here the width and the thickness of the specimen contract. The disorientation of the amorphous component of oriented polyolefins is indicated by the decrease of their contraction strain[55], the extent of which can serve as a measure of the orientation of the amorphous component of the polymer.

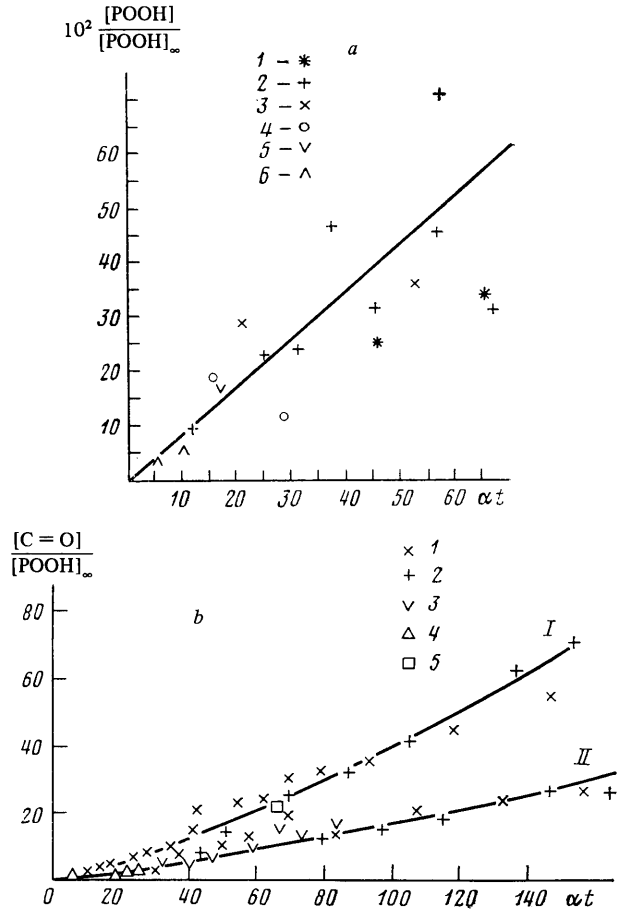


Figure 3. Kinetics of the accumulation of POOH (*a*) and carbonyl compounds (*b*) in the photochemical oxidation of OPP by light at a wavelength of 254 nm.[15] *a*) Intensity of incident light 10^{-15} *I* (quanta cm^2 s^{-1}): 1) 3.3; 2) 1.5; 3) 0.75; 4) 0.6; 5) 0.46; 6) 0.15; extrusion factor $\bar{\lambda} = 4-5$; *b*) intensity of incident light 10^{-15} *I* (quanta cm^2 s^{-1}): 1) 4; 2) 1; 3) 0.74; 4) 0.3; 5) 0.08; extrusion factor $\bar{\lambda}$: I) 4–5; II) 9–10.

A characteristic feature of the oxidation of oriented polypropylene compared with the isotropic material (IPP) is that, other conditions being equal, POOH accumulates in it at a much lower concentration. The decrease of the rate of accumulation of POOH is not related to the overall decrease of the rate of the process, which also occurs in thermal

oxidation, but is due to a qualitative change in the composition of the oxidation products.

In thermal oxidation of oriented polypropylene the yield of hydroperoxide per mole of absorbed oxygen decreases from virtually unity for IPP to 0.13 for OPP with $\bar{\lambda}=4-5$ and to 0.05 for OPP with $\bar{\lambda}=9$.[51] In the photochemical oxidation of OPP with $\bar{\lambda}=4-5$ the rate of accumulation of POOH at the beginning of the process decreases compared with IPP by a factor of hundreds, while the rate of formation of carbonyl compounds hardly changes (Fig.3). Isometric annealing at 165 °C fully eliminates the characteristics of the oxidation of OPP.[50] These results show that the changes in the physical structure of the amorphous component of polypropylene alter radically the mechanism of the oxidation process.

The small change in the rate of accumulation of carbonyl compounds on photochemical oxidation of OPP compared with IPP in the almost complete absence of POOH at the beginning of the process can be explained by assuming that in this case the photochemical decomposition of carbonyl compounds becomes an important source of free radicals or that the carbonyl compounds are formed in the chain propagation reaction on photochemical oxidation of OPP. The increase of the release of radicals into space on photolysis of strained polymers is indicated by the results of studies[57-59], where the increase of the concentration of radicals on photolysis of strained PA and PMMA compared with unstrained polymers was observed by EPR. The degree of liberation of radicals into space in the photolysis of ketones in OPP was determined[15] on the assumption that two kinds of carbonyl compounds are present in the OPP. Some of the carbonyl groups are distributed along the extended polymer chains and in their photochemical decomposition $f=2$, while others are distributed along non-extended chains and have the same properties as in IPP. The effective value of f was found by comparing the rate of accumulation of carbonyl compounds with the current concentration of POOH in the OPP. It was found that f increases compared with IPP almost by an order of magnitude and reaches $f=2$ at the beginning of the process.

As a result of the appearance of a second source of free radicals in the OPP, namely carbonyl compounds, the orientation of polypropylene does not always increase its stability. Thus, under the influence of light with $\lambda=254$ nm, the rates of accumulation of carbonyl compounds in OPP ($\bar{\lambda}=4.5$) and in IPP are virtually the same, while under the influence of light with $\lambda>300$ the photochemical oxidation of OPP is significantly faster than that of IPP.[56] This result can be readily explained by the fact that the extinction coefficients of POOH and carbonyl compounds at a wavelength of 254 nm are almost identical, while at $\lambda>300$ nm carbonyl compounds absorb light almost 20 times more effectively than POOH (Table 1).

In the thermal oxidation of polyolefins orientation always increases their stability, since a new source of free radicals does not appear in this process.

In the course of the oxidation of OPP the oriented macromolecules are ruptured with a consequent gradual disorientation of the amorphous component (chemical relaxation); the rate of accumulation of POOH increases, its yield per mole of absorbed oxygen also increases[50], while the effective liberation of free radicals into space in the photochemical decomposition of carbonyl compounds diminishes[56]. However, despite the fact that extensive and varied data have been obtained for the oxidation of OPP, at the present time the mechanism of this process has not been established at a quantitative level and only its fundamental features are clear.

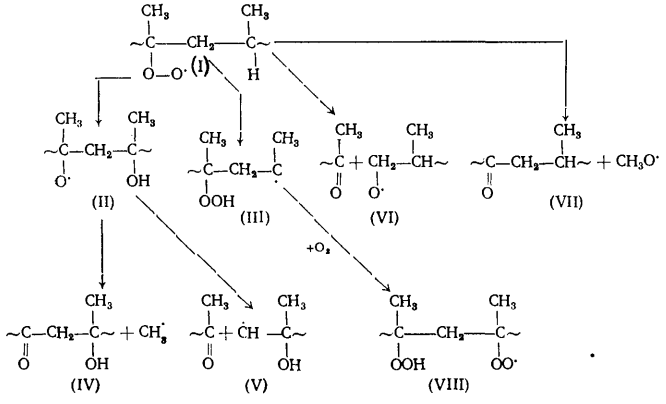
1. OPP is oxidised via a chain mechanism with quadratic chain termination.

2. The formation of free radicals by the photochemical decomposition of carbonyl compounds plays an important role in the photochemical oxidation of OPP, so that, depending on the intensity and spectral composition of the light acting on the polymer, the orientation of polypropylene can lead to both a decrease and an increase of the rate of photochemical oxidation, while thermal oxidation of polypropylene is always inhibited when the latter is oriented.

3. In the course of oxidation there is a gradual disorientation of the amorphous component of the OPP and the qualitative differences in the oxidation of OPP and IPP gradually diminish.

The results could be seemingly accounted for on the hypothesis that the oriented transient chains in OPP play a role akin to inhibitors which terminate the oxidation chains. However, under the conditions of this process mechanism, the kinetics of the photochemical oxidation should be determined by the dose of the light incident on the specimen, since in linear chain termination the rate of formation of any reaction product is linearly related to the rate of initiation. Furthermore, this conclusion is inconsistent with the available experimental data. Thus in the photochemical oxidation of OPP the efficiency of the formation of carbonyl compounds (per quantum of the light incident on the specimen) is higher the lower the irradiation intensity[56]. This result can be explained only by assuming that the branched products (carbonyl compounds) accumulate in the chain propagation reaction with quadratic termination or in accordance with a more complex kinetic mechanism in which the interaction between the reaction products plays an important role. This mechanism of the formation of carbonyl compounds in the chain propagation reaction can be set up by postulating that the peroxy-radical group on the strained chain is unstable and isomerises or decomposes, yielding ultimately a carbonyl compound.

Formally one can postulate the following different pathways leading to such isomerisation:



The consecutive isomerisation of the radicals (I) → (III) → (II), involved in competition with the oxidation of radical (III) leading to the formation of POOH (VIII) has been considered[49-51]. The authors believe that their observation of an increase of the yield of hydroperoxide per mole of absorbed oxygen with increase of O_2 pressure from 150 to 600 mmHg constitutes proof of this mechanism[60]. This conclusion appears to be ambiguous, since oxygen accelerates the oxidation of any alkyl radicals and the increase of the yield of POOH can be accounted for by competition between the oxidation of labile alkyl radicals and their interaction with strained polymer chains. The rate constant for the latter reaction should greatly exceed that for the

chain propagation in IPP, since otherwise the rates of oxidation of OPP and IPP would differ insignificantly, because the majority of chains in OPP are unstrained. Therefore the role of the competition between these reactions should be effective at considerably higher oxygen pressures than in the case of competition between analogous reactions in IPP involving an unstrained chain. This reaction is known[4] to be significant in IPP only at $p_{O_2} < 100$ mmHg. At higher p_{O_2} the influence of oxygen is determined by the competition between the reactions involving the formation of block hydroperoxides and the transfer of valence by the alkyl radical to another macromolecule[60]. In the oxidation of OPP these reactions are apparently less important, since the formation of POOH does not constitute the main pathway to the oxidation of OPP.

2. Prediction of the Kinetics of the Variation of the Practically Important Properties of a Polyolefin on the Basis of the Known Mechanism of Its Ageing

The data described above show that studies of the mechanism of the ageing of polyolefins have usually been directed towards the investigation of the changes in their chemical composition. Studies were made of the interconversion of the active centres propagating the process and of the accumulation of reaction products. However, for practical purposes, the variation of the physicomechanical characteristics of polyolefins is usually of interest and not the variation of their composition.

At the same time it is known that the kinetics of the variation of the physicomechanical properties of polyolefins are frequently not determined by the variation of their composition. Evidently, the variation of the physicomechanical properties of polyolefins and the variation of their composition in the course of ageing are caused by the same elementary processes, so that, in order to predict the kinetics of the variation of the practically important properties of the polymer, it is necessary to discover which elementary process is the primary determinant of its properties. This was achieved in the study of the photochemical oxidation of polypropylene and polyethylene.

A characteristic feature of this process is the fact that the reaction products accumulate more effectively at lower light intensities, where the branching product (the hydroperoxide) is formed in a process with longer chains. The available literature data show[41] that this feature holds qualitatively when one considers the kinetics of the variation of the molecular weight and the mechanical characteristics [the strength σ and the elongation on rupture ε (%)] of polypropylene and polyethylene.

The nature of the relation between the physicomechanical properties of polyolefins and their composition and the causes of the differences in the form of the kinetic curves for the variation of ε(%) in the case of specimens prepared in different ways are unknown, but the available data are in good qualitative agreement with the data for the mechanism of the photochemical oxidation of polyolefins. The lower the light intensity, the greater the chain length in the formation of the branching product (POOH), and consequently the higher the efficiency of all the processes occurring in the polymer.

Fig.4 presents the same relations for polypropylene obtained by plotting along the abscissa axis the amount of radicals formed in the specimen by a given instant and not the amount of light incident on the specimen:

$$\Omega = \int_0^t (2\alpha[\text{POOH}] + f\alpha'[\text{C=O}])\,dt. \qquad (16)$$

Evidently, in terms of these coordinates, the data obtained at different light intensities fit the same relation. The quantity Ω can be calculated with the aid of a system of equations for any variable operating conditions, while the relation between ε(%), σ and Ω, can be obtained empirically for different polypropylene specimens.

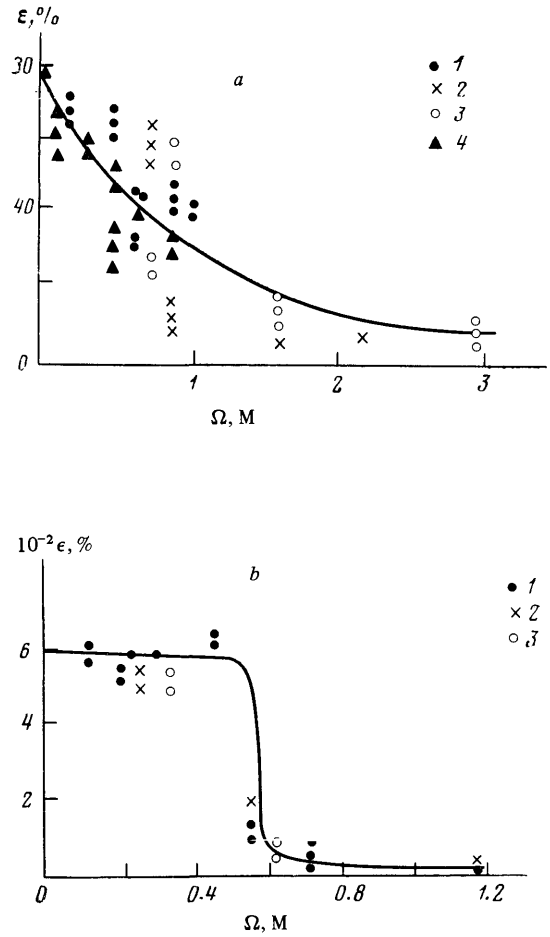


Figure 4. Dependence of the relative elongation on the dose of radicals Ω: *a*) triply oriented and annealed specimen; *b*) IPP. Intensity of incident light 10^{-15} I (quanta cm^2 s^{-1}): 1) 4; 2) 0.7; 3) 0.24; 4) 4 (in the presence of 0.15 M Methylox)[9].

Polyethylene is a much more stable polymer than polypropylene and its photochemical decomposition time is several times longer than the time required to decompose polypropylene. Analysis of Eqn.(16) shows that, for high values of t, the rate of accumulation of Ω is independent of the intensity of the incident light. Fig.5 illustrates the kinetics of the variation of ε(%) and σ for polyethylene at different light intensities. Evidently the results fit a single relation, as in the case of polypropylene. Thus on the basis of the known mechanism of the accumulation of the products of the photochemical oxidation of pure polyolefins,

it was possible to describe the kinetics of the variation of their physicomechanical characteristics.

As stated above, the mechanism of the photochemical oxidation of OPP has not been established at all hitherto. Nevertheless it has been shown[15] that the variation of the physicomechanical characteristics of OPP is correlated with the variation of Ω. The difference relative to the oxidation of IPP discussed above consists in the fact that Ω was calculated from experimental kinetic curves for the accumulation of POOH and carbonyl compounds and not on the basis of a known oxidation mechanism. Thus, even when the mechanism of the photochemical oxidation of the polymer is not known completely, it is possible to describe the kinetics of the variation of its physicomechanical properties in this process.

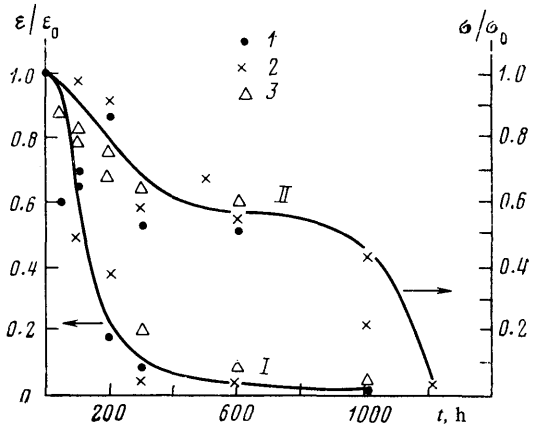


Figure 5. Dependence of the relative elongation (I) and strength (II) on the radical dose in the photochemical oxidation of HPPE.[41] Intensity of incident light 10^{-15} I (quanta cm^2 s^{-1}): 1) 2; 2) 1; 3) 0.3.

3. Photochemical Oxidation of Polypropylene Thermally Stabilised by Sterically Hindered Phenols

The example of the photochemical oxidation of pure polypropylene discussed above is to a large extent of academic interest. Only polypropylenes containing thermal and light stabilisers, which increase their useful lifetime, are used in practice. The widely employed stabilisers of the phenolic type are acceptors of the free radicals which inhibit the dark stages of the oxidation process. At the same time these stabilisers absorb the short-wavelength component of sunlight fairly effectively and function as photosensitisers of the oxidation process. Therefore, in the study of the photochemical oxidation of polymers in the presence of phenols, it is necessary to take into account not only the inhibiting effect of the antioxidant but also its initiating capacity. Furthermore, one must take into account the initiating activity of the inhibitor conversion products. For example, it has been shown[61] that the methylenequinone formed in the oxidation of ionol can dehydrogenate decane, increasing at the same time the rate of initiation. The mechanism of the sensitisation of the photochemical oxidation by phenols is complex and has not so far been ultimately established[62,63].

The photochemical transformation of the thermal stabiliser Methylox [the methyl ester of β-(3,5-di-t-butyl-4-hydroxyphenyl)propionic acid] in polypropylene has been investigated[63]. It was shown that the photochemical oxidation of Methylox results in the formation of two different photochemically active products A and B. Product A absorbs light in the longer-wavelength part of the spectrum than Methylox and many of its characteristics (the form of the absorption spectrum, the quantum yield of the photochemical decomposition) correspond to 2,6-di-t-butyl-4-methylmethylenequinone. Product A sensitises the photochemical decomposition of Methylox. Under the influence of light, products A and B decompose with different quantum yields and in the presence of large radiation doses both products are consumed almost completely and the specimen ceases to absorb light with $\lambda > 220$ nm.

Despite the very complex mechanism of the photochemical transformation of phenols in the polymer, the knowledge of the principal features of the mechanism of the photochemical transformation of pure polypropylene made it possible to discover the fundamental stages of the process which determine the photochemical decomposition of the thermally stabilised polymer.

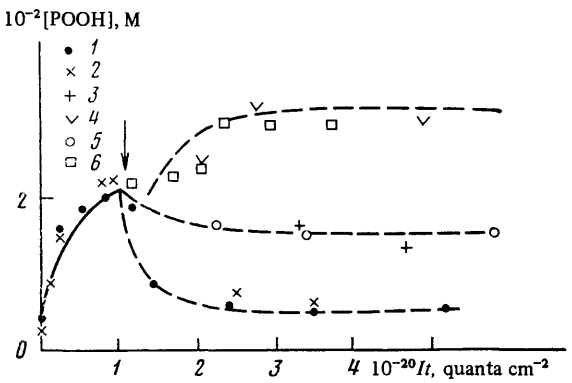


Figure 6. Kinetic curves for the accumulation of POOH in specimens containing 0.15 M Methylox[63]. Intensity of incident light 10^{-15} I (quanta cm^2 s^{-1}): 1) and 2) 4; 3) and 5) 1.4; 4) and 6) 0.7. The calculated curves are shown dashed. In plotting curves *3* and *4* the irradiation dose $It = 1.2 \times 10^{20}$ quanta cm^{-2} was attained at $I = 4 \times 10^{-15}$ quanta cm^2 s^{-1}. The arrow indicates the instant at which Methylox is consumed.

Fig.6 illustrates the kinetics of the variation of the concentration of POOH in the photochemical oxidation of polypropylene thermally stabilised by Methylox. Evidently, at different light intensities the amount of accumulated POOH at the beginning of the process is determined by the amount of light incident on the specimen. By the time of the virtually complete consumption of the phenol, the kinetic curves describing the variation of the POOH concentration begin to diverge. At low light intensities POOH continues to accumulate, while at high light intensities the POOH concentration falls.

The observed features can be readily explained within the framework of the kinetic mechanism of the photochemical oxidation of pure polypropylene with a certain initial concentration of POOH accumulated at the beginning of the process. If the initial POOH concentration is higher than the limiting value for the given intensity, then, after the consumption of the phenol, the POOH concentration will diminish; if it is lower, then POOH will continue to accumulate. The kinetics of the variation of the POOH concentration should then be described by the equation

$$[\mathrm{POOH}] = [\mathrm{POOH}]_\infty (1-(1-\sqrt{[\mathrm{POOH}]/[\mathrm{POOH}]_\infty}) \times e^{-\alpha t/2})^2. \quad (17)$$

Fig.6 shows that Eqn.(17) describes satisfactorily the kinetics of the accumulation of POOH after the consumption of Methylox. This shows that the products of the photochemical transformation of Methylox do not function as sensitisers of the photochemical oxidation process.

The variation of the physicomechanical properties of the thermally stabilised polypropylene is described by the same relation as for the pure polymer; the dose of the radicals formed in the photochemical decomposition of POOH is then calculated from the data for the kinetics of the variation of the concentration of POOH. The identity of the two relations (for the pure and thermally stabilised polymers) show that the variation of the physicomechanical properties is determined in both cases by the kinetics of the same radical reactions.

Thus, in order to develop a method for predicting the kinetics of the variation of the properties of thermally stabilised polypropylene, it is only necessary to calculate the kinetics of the consumption of Methylox and to discover at which concentration of the latter the process mechanism begins to be described by the kinetic mechanism for the photochemical oxidation of pure polypropylene. The latter problem is solved relatively simply: it is sufficient to assume that, as long as Methylox is present in the polymer, it is consumed both via its intrinsic photochemical decomposition and in terminating all the oxidation chains initiated as a result of the decomposition of POOH. Presumably, as long as the polymer contains Methylox, POOH is not effectively consumed in the photochemical decomposition steps, since it is constantly regenerated by the interaction of Methylox with peroxy-radicals.

On the basis of the foregoing, it is possible to obtain the following system of differential equations describing the kinetics of the formation of POOH in polypropylene in the presence of Methylox:

$$\frac{d[\mathrm{M}]}{dt} = -\alpha_\mathrm{M}[\mathrm{M}],$$
$$\frac{d[\mathrm{POOH}]}{dt} = f_\mathrm{M}\alpha_\mathrm{M}[\mathrm{M}], \quad (18)$$

where [M] is the concentration of Methylox, f_M the yield of hydroperoxide per Methylox destruction step, $\alpha_\mathrm{M} = \int_\lambda \phi_\mathrm{M}\varepsilon_\mathrm{M} I d\lambda$, ε_M the extinction coefficient of Methylox, and ϕ_M the quantum yield in the consumption of Methylox. The quantity ϕ_M has been included in the integral, since the consumption of Methylox is not an elementary photochemical reaction[63] and ϕ_M can therefore depend on the wavelength of the acting radiation. Under the influence of light with $\lambda = 254$ nm, we have $\phi_\mathrm{M} = 2.7 \times 10^{-2}$ and $f_\mathrm{M} = 0.14$.

After the consumption of the thermal stabiliser, the kinetics of the variation of the POOH concentration are described by Eqn.(17) for an initial non-zero POOH concentration calculated with the aid of Eqn.(18).

Thus, despite the fact that the mechanism of the sensitising effect of phenols in the polyolefin has not been established and the nature of the relation between the composition of the photochemical oxidation products and the kinetics of the variation of the physicomechanical properties of the polymer is unknown, it was possible to put forward, on the basis of ideas concerning the fundamental features of the process mechanism, a method for the prediction of the kinetics of the variation of the properties of a thermally stabilised polymer.

4. Prediction of the Useful Lifetimes of Polyolefins under Natural Conditions

The elucidation of the mechanism of the photochemical oxidation of polypropylene and the determination of the correlation between the kinetics of this process and the kinetics of the variation of the physicomechanical properties led to the formulation of the problem of the calculation of the rate of change of these properties in the course of the natural ageing of polypropylene.

As shown above, the kinetics of the variation of the physicochemical mechanical properties of polypropylene are determined unambiguously by the amount of radicals formed in the polymer throughout the process—the dose of the radicals Ω. Consequently the determination of the useful lifetime of polypropylene reduces to the calculation of Ω under the operating conditions. Two problems arise in the calculation of this quantity.

1. Eqns.(7) and (8), describing the kinetics of the photochemical oxidation of polypropylene, are non-linear and the kinetics of the variation of Ω under conditions varying with time cannot therefore be reduced to the kinetics of the variation of this quantity under equivalent conditions which are constant in time. Indeed, under variable conditions, even when the condition of a quasi-stationary concentration of free radicals holds, the kinetics of the variation of Ω in the photochemical oxidation of IPP are desdribed by the integral equation

$$\Omega = \int_0^t e^{-D}\left(\int_0^t k_p[\mathrm{PH}]\sqrt{\alpha/k_t}\, e^{D/2} dt\right)^2 \alpha\, dt, \quad (19)$$

where $D = \int_0^t \alpha dt$. Evidently one cannot replace the variable characteristics of the conditions by average quantities. In this case one can speak of an average temperature, provided that the intensity of the light and the temperature are in no way correlated. The average light intensity can in principle characterise the quantity D; however, the light intensity also enters into the integrand independently of D.

Analogous relations should apparently hold also in thermal oxidation. The activation energies for the thermal decomposition of POOH and for the process described by the integrand may not be the same; this means that the process kinetics cannot be described within the framework of the same activation energy and it is therefore also not always possible to adjust the thermal process to an equivalent temperature.

The above calculation is illustrated in Fig.7, where the kinetic curves for the variation of Ω at different constant light intensities are shown. In the calculation it was assumed† that the light intensity varied periodically; during approximately one tenth of the period, the light intensity

†O.N.Karpukhin and E.M.Slobodetskaya, J.Polymer Sci., Polymer Chem.Ed., 17, 3687 (1979).

was I_0 (and $\alpha = \alpha_0$), while in the course of the remaining nine tenths of the period it was 100 times lower.

It is seen from the data presented that, under the conditions of a variable intensity the process proceeds in accordance with a qualitatively different law. The limiting rate of increase of Ω, which is independent of light intensity under constant conditions, under variable conditions does depend on the law governing the time variation of I. In the example under consideration it is almost three times smaller than for the average intensity.

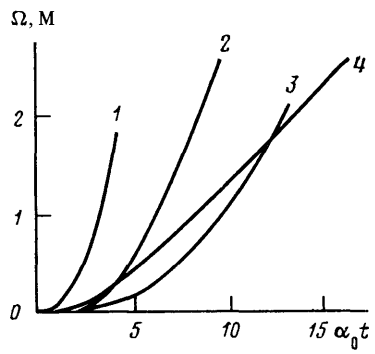


Figure 7. Calculated curves based on the measurement of Ω in the photochemical oxidation of polypropylene for variable (cruve 4) and constant (curves 1–3) light intensities[64]. The law governing the variation of I is described in the text: 1) $0.1I_0$; 2) $0.03I_0$; 3) $0.015I_0$.

Thus the calculation requires data for the dynamics of the variation of the light intensity and temperature in the course of ageing and not simply the average characteristics of the operating conditions of the polyolefin.

2. Modern computer techniques permit the calculation of Ω after substituting in the initial system of equations the primary data for the variation of the temperature and the intensity and spectral composition of the effective radiation. However, it has been found that, apart from Moscow, systematic regular measurements (over a period of many years) of the ultraviolet component of sunlight, which largely determines Ω, have hardly been made anywhere.

It is therefore necessary to resort to the advances in modern meteorology in order to set up a program for the calculation of Ω on the basis of the available meteorological data. This program includes the following initial data[64]: (a) the physicochemical characteristics of the process (the rate constants for the elementary reactions of the Arrhenius form, the absorption spectra, and the quantum yields of the decomposition of POOH and carbonyl compounds); (b) the spectral characteristics of the sun and the Earth's atmosphere (the spectrum of the sun at the outer edge of the atmosphere, the absorption spectrum of the ozone layer of the atmosphere, and the characteristics of the light scattering by the atmosphere); (c) the results of meteorological observations (temperature, thickness of the ozone layer, and the characteristics of the cloud cover); (d) geographical coordinates of the site where the tests are performed and the geometry of the arrangement of the polymer specimens (the angle with respect to the horizon and the direction of inclination).

In the calculation it was assumed that the variation with respect to the spectral composition of the solar radiation occurs only due to the change in the effective thickness of the ozone layer, while clouds play the role of an absolutely grey light filter. Fig.8 presents kinetic curves, calculated from meteorological data (Moscow, 1974)[64], for the variation of Ω and the accumulation of the products of the oxidation of free horizontally arranged polypropylene specimens exposed on the first of each month. Evidently the useful lifetime of the specimens varies with the time of the beginning of the exposure, since during cold months the photochemical oxidation is extremely slow. Fig.8 also shows that the same value of Ω, i.e. the same degree of change in the mechanical properties of polypropylene, is obtained at different concentrations of hydroperoxy- and carbonyl groups.

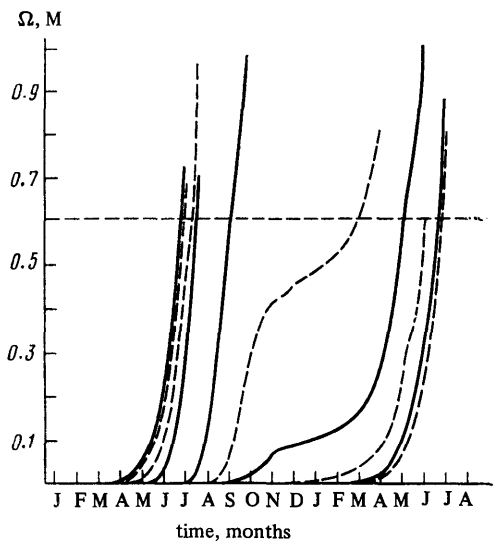


Figure 8. Calculated kinetic curves for the variation of Ω on exposure of polypropylene. Ω = 0.6 M corresponds to the loss of useful operating properties by the polypropylene.

A special computational experiment shows[64] that, in order to determine the useful lifetime of the polymer in the given case, one can employ the average monthly temperatures and average monthly coefficients of the screening of ultraviolet radiation by clouds. The average monthly coefficient of the screening of ultraviolet radiation by clouds K is calculated from the empirical formula proposed by Belinskii et al:[65]

$$K = \frac{n_1 + 0.8n_2 + 0.6n_3 + 0.35n_4}{N},$$

where N, n_1, n_2, n_3, and n_4 are respectively the total number of days, the total number of clear days, the number of days with a variable cloud cover, the number of cloudy days, and the number of days without sunshine. The quantities n_1, n_2, n_3, and n_4 are recorded systematically in the course of meteorological observations.

Comparison of the results of the calculation with the results of tests under natural conditions showed that the experimental useful lifetime is systematically shorter than the calculated lifetime. This arises apparently because the temperature of the exposed polymer specimens is always higher than the temperature of the ambient layer, since they are heated as a result of the absorption of light by the support on which the specimen rests. According to the results of Kurzhenkova and Pashchenko[66], for example, films stretched on agricultural implements age preferentially at the sites of contact with the frame, which is due to the higher temperature at these sites compared with the free film. It has been shown[67] that the film exposed under natural conditions on a black support is heated to 40–50 °C, while on a white support its temperature is 25–27 °C. It is also known that the films used for fencing in seed beds are at a temperature higher by 10–15 °C than that of the surrounding medium[67].

Thus the data presented show that in the given case the exact determination of the useful lifetime of the polymeric material is limited by the lack of exact data concerning its operating conditions.

REFERENCES

1. O.N.Karpukhin and E.M.Slobodetskaya, Uspekhi Khim., 42, 391 (1973)[Russ.Chem.Rev., No.3 (1973)].
2. V.L.Bodneva, O.N.Karpukhin, and E.M.Slobodetskaya, Vysokomol.Soed., B19, 276 (1977).
3. D.J.Harper and J.F.McKellar, Chem.Ind.(London), 848 (1972).
4. N.M.Emanuel', E.T.Denisov, and Z.K.Maizus, "Tsepnye Reaktsii Okisleniya Uglevodorodov v Zhidkoi Faze" (Liquid-Phase Chain Oxidation Reactions of Hydrocarbons), Izd.Nauka, Moscow, 1969.
5. J.G.Calvert and J.N.Pitts, "Photochemistry" (Translated into Russian), Izd.Mir, Moscow, 1968.
6. D.J.Carlsson and D.M.Wiles, Macromolecules, 2, 587 (1969).
7. G.H.Hartley and J.E.Guillet, Macromolecules, 4, 232 (1972).
8. J.A.Melchore, Ind.Eng.Chem., 1, 165 (1968).
9. O.N.Karpukin and E.M.Slobodetskaya, Vysokomol. Soed., A16, 1624 (1974).
10. N.Ya.Rapoport, V.B.Miller, A.G.Goniashvili, and M.S.Akutin, Vysokomol.Soed., A20, 1432 (1978).
11. E.L.Shanina, V.A.Roginskii, and V.B.Miller, Vysokomol.Soed., A18, 1160 (1976).
12. V.A.Roginskii and V.B.Miller, Dokl.Akad.Nauk SSSR, 215, 1164 (1974).
13. N.E.Korduner, T.A.Bogaevskaya, B.A.Gromov, V.B.Miller, and Yu.A.Shlyapnikov, Vysokomol. Soed., B12, 693 (1970).
14. O.N.Karpukhin, Kinetika i Kataliz, 17, 589 (1976).
15. O.N.Karpukhin, E.M.Slobodetskaya, I.R.Mardaleishvili, and A.N.Neverov, Vysokomol.Soed.(in the Press).
16. V.S.Pudov, B.A.Gromov, E.G.Sklyarova, and M.B.Neiman, Neftekhimiya, 3, 743 (1963).
17. D.J.Carlsson and D.M.Wiles, J.Macromol.Sci., C14, 65 (1976).
18. N.S.Allen and J.F.McKellar, Brit.Polymer J., 9, 302 (1977).
19. T.Tsubomura and R.S.Mulliken, J.Amer.Chem.Soc., 82, 5166 (1960).
20. J.C.W.Chien, J.Phys.Chem., 69, 4317 (1965).
21. T.Tsuji and T.Seihi, J.Polymer Sci., B8, 817 (1970).
22. D.J.Carlsson and D.M.Wiles, Rubber Chem.Technol., 47, 999 (1974).
23. D.J.Carlsson and D.M.Wiles, J.Polymer Sci., Polymer Letters Ed., 11, 759 (1973).
24. A.M.Trozzolo and F.H.Winslow, Macromolecules, 1, 98 (1968).
25. M.L.Kaplan and P.G.Kelleher, J.Polymer Sci., 9, 565 (1971).
26. R.H.Partridge, J.Chem.Phys., 45, 1679 (1966).
27. J.Boustead and A.Charlesby, Europ.Polymer J., 3, 459 (1967).
28. A.P.Pivovarov, Yu.G.Gak, and A.F.Lukovnikov, Vysokomol.Soed., A13, 2110 (1971).
29. O.Chiccetti and F.Gratani, Europ.Polymer J., 8, 561 (1972).
30. L.Balaban, J.Majer, D.Resary, and L.Shoma, Kunststoffe, 60, 341 (1970).
31. O.Chiccetti, Adv.Polymer Sci., 7, 70 (1970).
32. N.S.Allen, J.Homer, and J.F.McKellar, J.Appl. Polymer Sci., 20, 2553 (1976).
33. V.B.Ivanov, M.N.Kuznetsova, L.G.Angert, and V.Ya.Shlyapintokh, Dokl.Akad.Nauk SSSR, 228, 1144 (1976).
34. L.M.Baider, Candidate's Thesis, Moscow State University, Moscow, 1969.
35. L.A.Davis, C.A.Pampillo, and T.C.Chiang, J.Polymer Sci., A2, 11, 841 (1973).
36. E.L.Shanina, V.A.Roginskii, and V.B.Miller, Vysokomol.Soed., B19, 447 (1977).
37. V.A.Roginskii, E.L.Shanina, and V.B.Miller, Vysokomol.Soed., A20, 265 (1978).
38. A.P.Gol'denberg and S.A.Pirozhnaya, "Molekulyarnaya Spektroskopiya" (Molecular Spectroscopy), Izd.Leningrad.Gos.Univ., 1960.
39. F.Tudos, T.Kelen, and M.Iring, Europ.Polymer J., 12, 35 (1976).
40. K.B.Chokraborty and G.Scott, Europ.Polymer J., 13, 731 (1976).
41. O.N.Karpukhin, E.M.Slobodetskaya, and T.V.Magomedova, Vysokomol.Soed., B22, 595 (1980).
42. D.J.Carlsson and D.M.Wiles, Macromolecules, 2, 597 (1969).
43. C.H.Chew, L.M.Gan, and G.Scott, Europ.Polymer J., 13, 361 (1976).
44. V.Pozzi, A.E.Silvers, and L.Giuffre, J.Appl. Polymer Sci., 19, 923 (1975).
45. M.U.Amin, G.Scott, and M.K.Tillekeratne, Europ. Polymer J., 11, 85 (1975).
46. G.H.Hartley and J.E.Guillet, Macromolecules, 1, 413 (1968).
47. I.K.Yartsev and V.I.Pilipovskii (Editors), "Polipropilen" (Polypropylene), Izd.Khimiya, Moscow, 1967.
48. Brit.Plast., 35, No.1, 32 (1962).
49. N.Ya.Rapoport and V.B.Miller, Dokl.Akad.Nauk SSSR, 227, 911 (1976).
50. N.Ya.Rapoport, N.M.Livanova, and V.B.Miller, Vysokomol.Soed., A18, 2045 (1976).
51. N.Ya.Rapoport and V.B.Miller, Vysokomol.Soed., A18, 2343 (1976).
52. S.N.Zhurkov, I.I.Novak, B.Ya.Levin, A.V.Savitskii, and V.I.Vettegren', Vysokomol.Soed., 7, 1203 (1965).
53. V.A.Marikhin, Fiz.Tverd.Tela, 19, 1036 (1977).
54. V.A.Tochin, I.N.Musaelyan, D.N.Sapozhnikov, R.A.Shlyakhov, and K.T.Masolimov, "III Vsesoyuznaya Konferentsiya 'Diffuzionnye Yavleniya v Polimerakh'" (The IIIrd All-Union Conference 'Diffusion Phenomena in Polymers'), Riga, 1977, p.73.

55. N.M.Livanova, N.Ya.Rapoport, V.B.Miller, and I.N.Musaelyan, Vysokomol.Soed., A18, 2260 (1976).
56. O.N.Karpukhin, E.M.Slobodetskaya, and A.N.Neverov, Dokl.Akad.Nauk SSSR, 236, 677 (1977).
57. G.G.Samoilov and E.E.Tomashevskii, Fiz.Tverd.Tela, 10, 3039 (1968).
58. G.G.Samoilov and E.E.Tomashevskii, Fiz.Tverd.Tela, 10, 1729 (1968).
59. T.B.Boboev, V.R.Regel', T.P.Sanfirova, and N.N.Chernyi, Mekhanika Polimerov, 661 (1968).
60. S.G.Kiryushkin and Yu.A.Shlyapnikov, Dokl.Akad. Nauk SSSR, 220, 1364 (1975).
61. G.S.Popova, Candidate's Thesis, Leningrad Polytechnic Institute, 1975.
62. E.M.Slobodetskaya and O.N.Karpukhin, Vysokomol. Soed., B18, 184 (1976).
63. E.M.Slobodetskaya, M.G.Vorob'ev, and O.N.Karpukhin, Vysokomol.Soed., A17, 1533 (1975).
64. O.N.Karpukhin, E.M.Mostovaya, B.V.Novozhilov, and E.M.Slobodetskaya, Plast.Massy (in the Press).
65. V.A.Belinskii, M.P.Garadzha, L.N.Mezhennaya, and E.I.Nezval', "Ul'trafioletovaya Radiatsiya Solntsa i Neba" (Ultraviolet Radiation from the Sun and Sky), Izd.Moskov. Gos.Univ., 1968.
66. M.S.Kurzhenkova and T.E.Pashchenko, "Sbornik Trudov po Agronomicheskoi Fizike" (Collected Reports on Agronomical Physics), Gidrometeoizdat, Leningrad, 1976, No.36, p.121.
67. V.A.Kolyaseva, I.N.Kotovich, T.E.Pashchenko, and V.E.Emel'yanova, "Sbornik Trudov po Agronomicheskoi Fizike" (Collected Reports on Agronomical Physics), Gidrometeoizdat, Leningrad, 1976, No.36, p.130.
68. C.J.W.Chien and C.R.Boss, J.Polymer Sci., A1, 5, 3091 (1967).

Institute of Chemical Physics,
USSR Academy of Sciences,
Moscow

Translated from *Uspekhi Khimii*, 49, 1617 - 1647 (1980) U.D.C. 547.944/945

Synthesis of Bisbenzylisoquinoline Alkaloids

O.N.Tolkachev, E.P.Nakova, and R.P.Evstigneeva

Methods for the synthesis of bisbenzylisoquinoline alkaloids and also 1-benzylisoquinoline bases, which are biogenetic precursors of the dimeric alkaloids, are surveyed in the biogenetic sequence of the alkaloids. Not only total but also partial and biomimetic syntheses of bisbenzylisoquinoline bases are covered. A list of 153 references is included.

CONTENTS

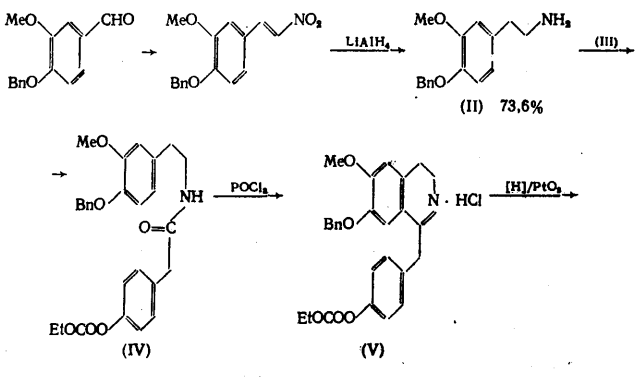
I. Introduction 784
II. Synthesis of coclaurine and its derivatives 784
III. Synthesis of bisbenzylisoquinoline alkaloids containing one diphenyl ether link 785
IV. Synthesis of bisbenzylisoquinoline alkaloids containing two diphenyl ether bridges 787
V. Synthesis of bisbenzylisoquinoline alkaloids containing three diphenyl ether links 795

I. INTRODUCTION

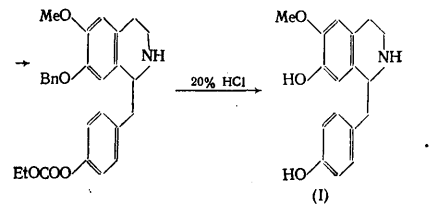
Bisbenzylisoquinoline alkaloids form a large group (>150) of naturally occurring compounds in which two benzylisoquinoline moieties are joined by one, two, or three ether links. More rarely a diphenylated carbon–carbon bond is encountered. The number and positions of the ether links are used to classify these alkaloids[1], and this classification has great value for the choice of method of synthesis. During recent years great attention has been paid to these alkaloids in connection with the discovery of their great and diverse biological activity—antitubercular, anti-inflammatory, antitumour, etc. (see reviews[2–4]).

II. SYNTHESIS OF COCLAURINE AND ITS DERIVATIVES

Since coclaurine (I) and its derivatives accompany bisbenzylisoquinoline alkaloids in plants, besides being precursors and also structural fragments, their synthesis is a necessary stage in obtaining the dimeric alkaloids. The method of synthesising coclaurine suggested originally consists in the condensation of *p*-benzyloxy-*m*-methoxyphenethylamine (II) with *p*-chloroformylphenyl ethyl oxalate (III), Bischler–Napieralski cyclisation of the resulting amide (IV) to give the dihydroisoquinoline derivative (V), reduction of the double bond over platinum dioxide, and removal of the protective groups by acid hydrolysis[5]:†



† Here and subsequently the abbreviations Me = CH_3, Et = C_2H_5, and Bn = $C_6H_5CH_2$ are employed.



This scheme has since been only slightly modified. For example, racemic coclaurine has been synthesised via the corresponding dibenzyl derivative, with the free amine (II) replaced by its *N*-formyl derivative[6]; the double bond in the dihydroisoquinoline derivative is then reduced with zinc dust in acetic acid. It has also been proposed[7] to use homovanillylamine for condensation with the acid component followed by temporary protection of the phenolic hydroxyl in the resulting amide by acetylation, which makes it possible to have fewer stages and increase the overall yield of coclaurine.

Several coclaurine derivatives—intermediates in the synthesis of bisbenzylisoquinoline alkaloids—have been synthesied similarly[8–10]. The initial amines are obtained by reducing the corresponding nitrostyrenes with lithium tetrahydroaluminate[5,11], over palladium–carbon to the oxime and then over platinum dioxide to the amine[5] or over palladium black to homovanillylamine[12]. It has been proposed[13,14] to reduce an unsubstituted or a substituted nitrostyrene with amalgamated zinc dust in acid. The reduction of *p*-benzyloxy-*m*-methoxyphenylacetonitrile with lithium tetrahydroaluminate has been described[15]. Cyclisation to dihydroisoquinoline is effected with phosphoryl chloride in various solvents, e.g. toluene[5], chloroform[6,15], or acetonitrile[16], in the last of which a good yield was obtained. Phosphorus pentachloride[15] and other phosphorus compounds, such as polyphosphoric acid and phosphorus pentoxide[17], have also been used as condensing agents.

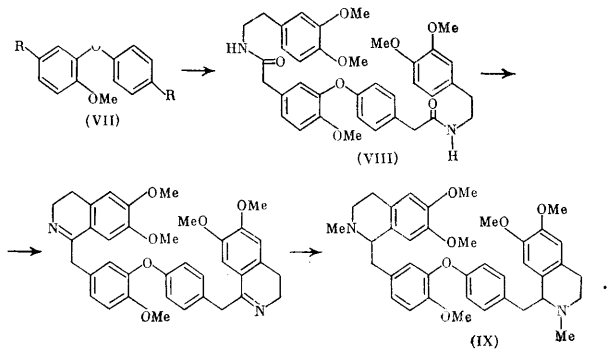
The synthesis of (±)-coclaurine has been accomplished also by Arndt–Eistert condensation of a 4-methylsulphonyloxy-ω-diazoketone with (II) to give the corresponding amide[18].

(±)-*N*-Methylcoclaurine has been obtained by the methylation of coclaurine with formaldehyde and formic acid[19], and also by reduction of the urethane derivative of dibenzylcoclaurine with lithium tetrahydroaluminate followed by hydrogenolysis[20]. Resolution of *N*-methylcoclaurine into optical antipodes was achieved by means of (+)- and (−)-di-*p*-tolyltartaric acids[21]. (±)-Armepavine and its derivatives have been resolved similarly[22,23].

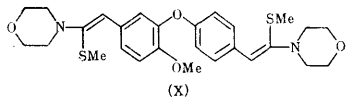
III. SYNTHESIS OF BISBENZYLISOQUINOLINE ALKALOIDS CONTAINING ONE DIPHENYL ETHER LINK

The simplest bisbenzylisoquinoline alkaloids are bases of monoether type—magnoline and dauricine—at which were aimed the first synthetic attempts. There exist two fundamental synthetic routes to such alkaloids—(*a*) from substituted diphenyl ethers by the addition of appropriate isoquinoline fragments using known methods and (*b*) by linking substituted benzylisoquinoline bases by means of ether bridges.

The first attempt to synthesise a bisbenzylisoquinoline alkaloid was made in 1935,[24] when a scheme was worked out for obtaining *O*-methyldauricine (IX)# via the intermediate 4-methoxy-3-phenoxybenzene-1,4'-dicarboxylic acid (VII: R =COOH), which was converted into the acid chloride, aldehyde, azlactone, and then the bisacetic acid (VII: R = CH_2. .COOH); the isoquinoline fragments were obtained by Bischler–Napieralski cyclisation of the corresponding bishomoveratrylamides (VIII) with subsequent conversion into the tetrahydro-*N*-methylisoquinoline derivative by the usual method:



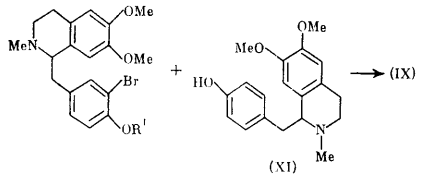
Since, however, the required compound was non-crystalline, it was converted into a methine base identical with the compound obtained from the natural alkaloid[24]. This scheme was subsequently improved by modifying the method of obtaining the initial acid (VII: R = CH_2COOH): *o*-methoxydiphenyl ether was chloromethylated, the halogen atom replaced by a cyano-group, and the latter was hydrolysed[28]; alternatively the corresponding diacetyl derivative was subjected to the Willgerodt–Kindler reaction, and the resulting bisthiomorpholide was hydrolysed[29]. The intermediate bisamide (VIII) has been obtained also by condensing homoveratrylamine with the bisenaminothioether structure[30]



Application of this scheme to the benzylated diacid gave a diastereomeric dauricine mixture[31]. Another scheme for the synthesis of (±)-dauricine was based on the Arndt–Eistert reaction of a bisdiazoketone with homoveratrylamine[32,33], which also gave a diastereomeric racemic mixture.

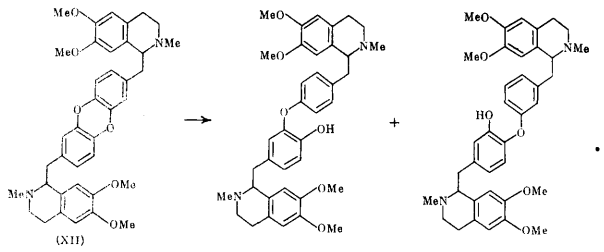
O-Methyldauricine was originally obtained by methylating natural dauricine with diazomethane. It was first detected in plant sources (*Colubrina asiatica*, etc.) only in 1970.[25–27]

Racemic magnoline was synthesised from appropriate benzyl or ethoxycarbonyl derivatives of the acid (VII).[34–36] In view of the difficulties encountered in removing the benzyl group, preference was given to the ethoxycarbonyl group. A diastereomeric mixture of (±)-cuspidaline was synthesised similarly[37,38]. A different route—condensation of (–)-armepavine with (–)-1-*m*-bromo-*p*-methoxybenzyl-1,2,3,4-tetrahydro-6,7-dimethoxy-2-methylisoquinoline, obtained by the bromination of armepavine (XI)—was used to synthesised *O*-methyldauricine in 24% yield[39]:



(±)-Dauricine[31,40,41], daurinoline[42], magnoline[43], (±)-magnoline[44], and berbamunine[45] have been obtained by the same synthetic method.

Dauricine is formed, together with an isomer differing in the position of the ether link, when the dibenzodioxin ring of compound (XII) undergoes fission in the presence of sodium in liquid ammonia[46]:

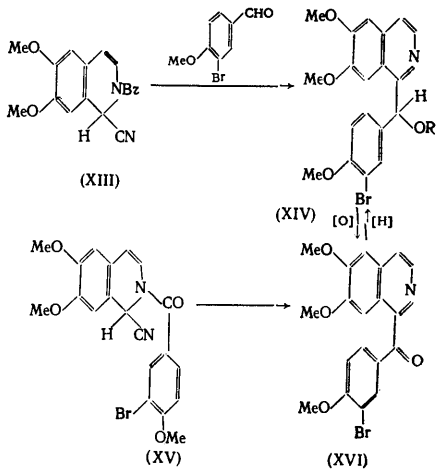


The intermediate (XII) was synthesised from the corresponding diacetyldibenzodioxin via the stages of bisthiomorpholide, diacid, diamide, bisdihydrosioquinoline derivative, and dihydric secondary base.

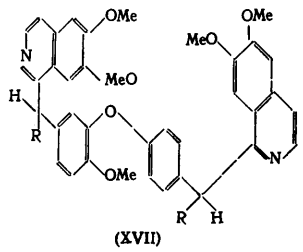
Dauricine has been obtained, in low yield, also by selective demethylation with butylmagnesium bromide of the methoxy-group in the diphenyl ether portion of *O*-methyldauricine[47].

An original sythesis of *O*-methyldauricine[48,49] consisted in reaction between 2-benzoyl-1,2-dihydro-6,7-dimethoxyisoquinolyl cyanide (Reissert's compound, XIII) and *m*-bromo-*p*-methoxybenzaldehyde, hydrolysis of the resulting *O*-benzoyl derivatives (XIV: R = C_6H_5CO) to the carbinol (XIV: R = H) in 87% yield, and reduction of this product with zinc dust in hydrobromic acid to 1-*m*-bromo-*p*-methoxybenzyl-6,7-dimethoxyisoquinoline (yield 78%), whose methiodide was reduced with sodium tetrahydroborate to 1-*m*-bromo-*p*-methoxybenzyl-1,2,3,4-tetrahydro-6,7-dimethoxy-2-methylisoquinoline and then condensed with (±)-armepavine, as mentioned above; in a modification of this synthesis 1-*m*-bromo-*p*-methoxybenzoyl-1,2-dihydro-6,7-dimethoxyisoquinolyl cyanide (XV) was converted into 1-*m*-bromo-*p*-methoxybenzoyl-6,7-dimethoxyisoquinoline (XVI) in the presence of sodium hydride in dimethylformamide (yield 49%)

and then reduced to the carbinol with sodium tetrahydroborate:

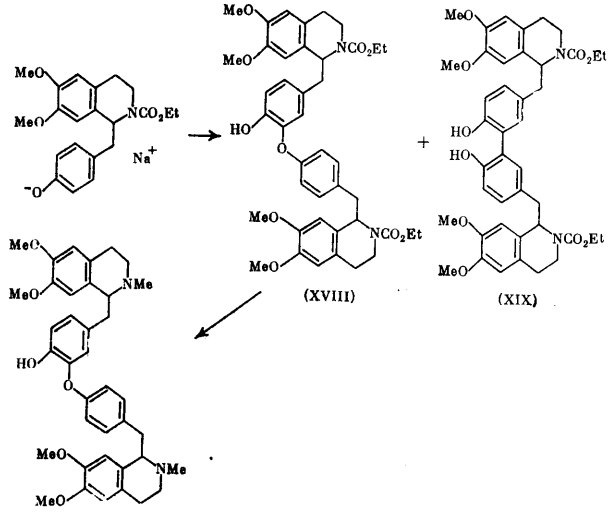


A shorter synthetic route to (±)-*O*-methyldauricine involves condensation of the diphenyl ether (VII: R = CHO) with Reissert's compound to give the bisisoquinoline base

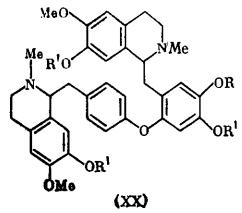


with R = C_6H_5COO in 83% yield. The latter was hydrolysed with aqueous–alcoholic alkali to the diol (XVII: R = OH), which was reduced with zinc dust in a mixture of hydrobromic and acetic acids to give a 91% yield of a product from which the methiodide was obtained and further reduced with sodium tetrahydroborate to an 81% yield of *O*-methyldauricine (overall yield 52% based on Reissert's compound)[48]. Yet another alternative was to condense Reissert's compound with 5,4'-bischloromethyl-2-methoxydiphenyl ether (VII: R = CH_2Cl) and hydrolyse the product with aqueous–alcoholic alkali to the bisisoquinoline derivative (XVII: R = H), whose methiodide was similarly reduced to *O*-methyldauricine[50].

Theoretical interest attaches also to the biomimetic synthesis of (±)-dauricine by the electrochemical oxidation of salts of *N*-ethoxycarbonyl-*N*-norarmepavine to the compound (XVIII) followed by reduction of the ethoxycarbonyl to an *N*-methyl group; the dimer (XIX) was isolated as a by-product[51]:



Magnolamine is an alkaloid closely similar to those already discussed: it differs in the presence of an additional oxygen function and in the location of the diphenyl ether link. It was originally assumed to contain four hydroxy-groups (XX: R = R' = H) [52–55]

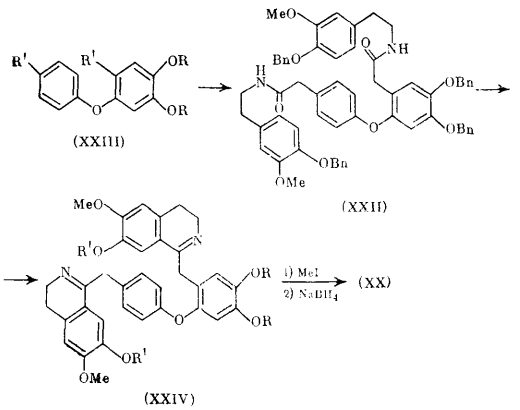


but it has now been proved that only three hydroxyls are present (XX: R = CH_3; R' = H).[56]

The antipode and the diastereomer of methylmagnolamine have been obtained by the condensation of (–)-6'-bromolaudanosine (XXI) with respectively (–)- and (+)-armepavine, which confirmed the *SS*-configuration of the natural alkaloid [57,58]. Similarly, condensation of the corresponding benzylated components[59] gave a stereoisomeric mixture of the tetraol having the formula originally suggested for magnolamine. Ullmann condensation in its classic form gives a very low yield (~2%). Replacement of copper powder and pyridine by pentafluorophenylcopper enables the yield of the methyl ether of magnolamine to be raised to 53%. In this case the reaction involves intermediate formation of copper phenoxide[60].

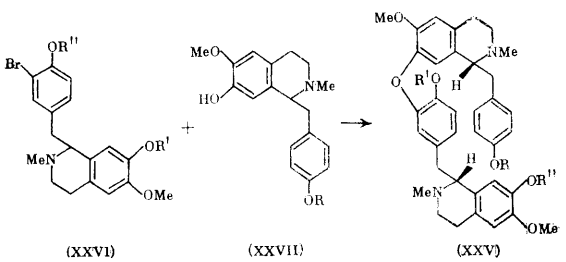
A total synthesis of a diastereomeric mixture of "magnolamine" (XX: R = R' = H) (*O*-demethylmagnolamine) was also accomplished by route (*b*) [see below], in which the bisamide (XXII) was obtained by the Arndt–Eistert method from

(II) and the bisdiazoketone (XXIII: $R = C_6H_5CH_2$; $R' = N_2CHCO$):



As in other cases, the diastereomeric mixture could not be resolved[51,62]. The tetradehydro-derivative (XXIV: $R = CH_3$: $R' = C_6H_5CH_2$) was also synthesised by a method involving formation of an intermediate bisamide[63]. Here the initial dicarboxylic acid (XXIII: $R = CH_3$; $R' = CH_2COOH$) was obtained in two ways—(*a*) chloromethylation of *mp*-dimethoxydiphenyl ether with subsequent replacement of the chlorine atoms by cyano-groups followed by hydrolysis, and (*b*) Ullmann condensation of two substituted esters of phenylacetic acids.

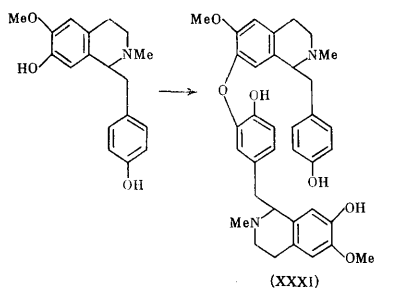
Another type of monoether base, in which benzylisoquinoline fragments are linked "head to tail", is represented by liensinine (XXV: $R = R' = H$; $R'' = CH_3$) and isoliensinine (XXV: $R = CH_3$; $R' = R'' = H$). The former was synthesised by condensation of the bromobenzylisoquinoline component (XXVI: $R' = CH_3$; $R'' = C_6H_5CH_2$) with the *p*-benzyl ether or the *p*-toluene-*p'*-sulphonic ester of *N*-methylcoclaurine (XXVII):[64,65]



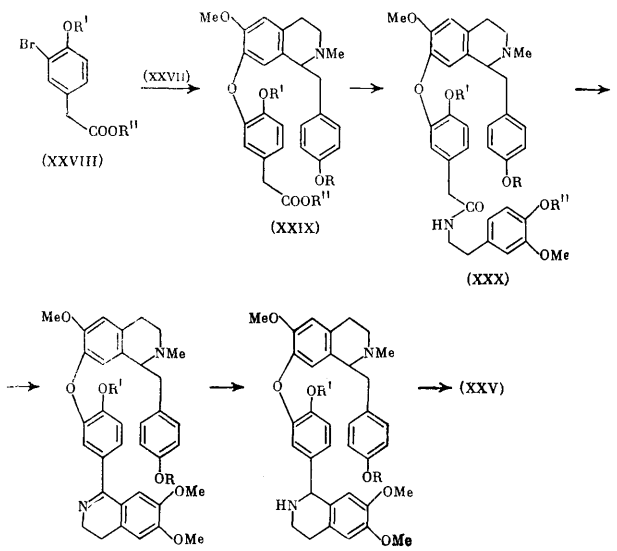
Condensation of the bases (XXVI: $R' = R'' = C_6H_5CH_2$) and (XXVII: $R = CH_3$) or their optically active forms gave (±)- and (−,−)-isoliensinine[65–69].

In another synthesis (Scheme 1) the *p*-methyl ether of *N*-methylcoclaurine (XXVII: $R = CH_3$) is condensed with the bromophenylacetic ester (XXVIII: $R' = CH_3$; $R'' = CH_3$, C_2H_5), and then the diphenyl ether (XXIX: $R = R' = CH_3$; $R'' = H$, CH_3, C_2H_5) is converted by the action of homoveratrylamine into the amide (XXX), which after cyclisation to the dihydroisoquinoline derivative, reduction, and *N*-methylation gives *OO'*-dimethyl-liensinine[70].

The enzymatic oxidative dimerisation of *N*-methylcoclaurine has been achieved, with the isolation of 7″-*O*-demethylliensinine (XXXI) together with the corresponding trimer[71]:



Scheme 1



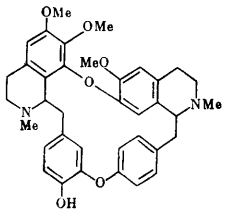
IV. SYNTHESIS OF BISBENZYLISOQUINOLINE ALKALOIDS CONTAINING TWO DIPHENYL ETHER BRIDGES

This group of alkaloids, which are formed in plants by enzymatic double dehydrogenation of two molecules of coclaurine or its derivatives, can be divided into four types of compounds differing in the location of the ether bonds.

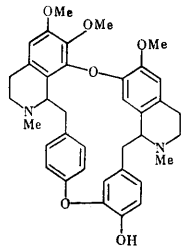
1. Oxyacanthine–Berbamine Type of Alkaloids

This group of natural bases includes the structural isomers berbamine (XXXII) (*RS*), oxyacanthine (XXXIII) (*SR*), their stereoisomers—pycnamine (XXXII) (*RR*) and repandine

(XXXII), (*SS*)—and also their derivatives.



(XXXII)



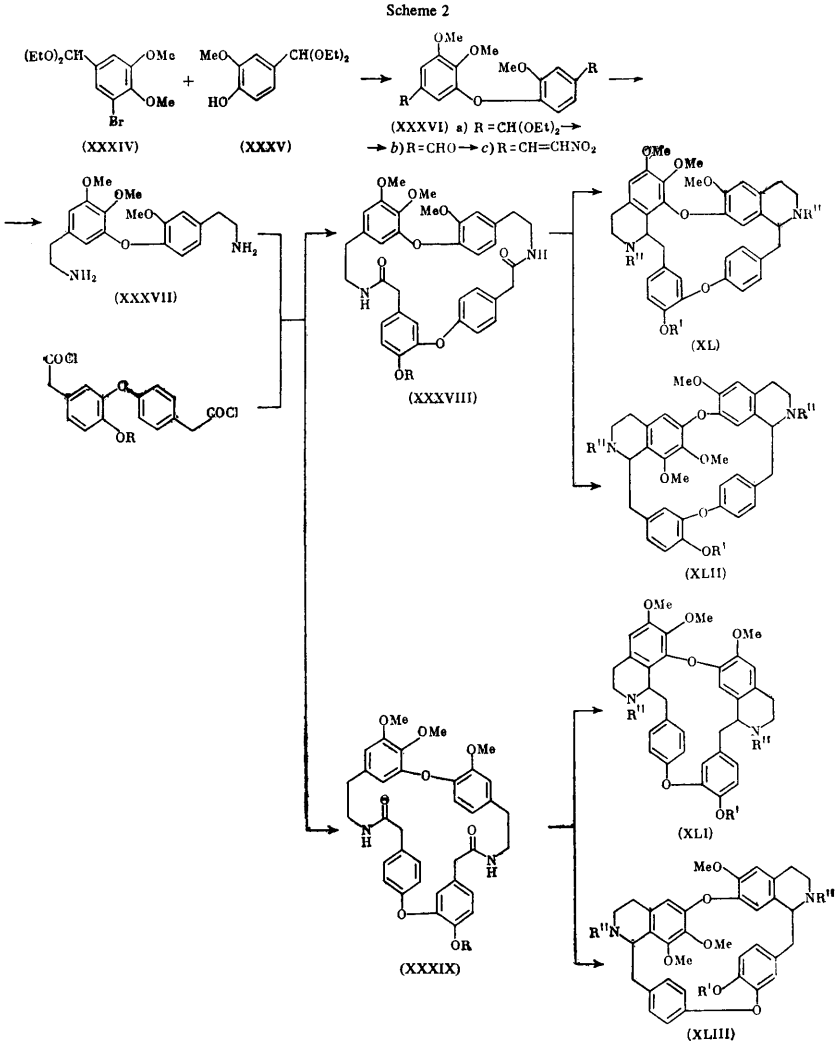
(XXXIII)

The synthesis of berbamine and oxyacanthine (Scheme 2) consists in condensation of the acetals of 5-bromoveratraldehyde and vanillin (XXXIV and XXXV) to give the diacetal (XXXVIa) of diphenyl ether (in 53% yield), which is converted by acid hydrolysis into the dialdehyde (XXXVIb) and then into the oxybisnitrostyrene (XXXVIc). The latter is reduced with lithium tetrahydroaluminate to the diamine (XXXVII).

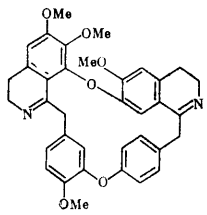
The Schotten–Baumann reaction with 2-benzyloxy-4',5-oxybisphenylacetyl chloride gives an isomeric mixture of the amides (XXXVIII) and (XXXIX), which are separated chromatographically and then subjected to Bischler–Napieralski cyclisation. Each amide forms a mixture of isomeric dihydroisoquinoline bases, which are converted without resolution into the methiodides, reduced, and then debenzylated. After cyclisation of the final products the compounds (XL)–(XLIII) were isolated, two of which were identified with berbamine and oxyacanthine[72,73].

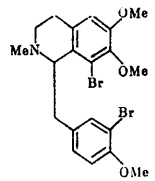
The non-phenolic alkaloids obaberine (*O*-methyloxyacanthine) and tetrandrine have been synthesised by a similar route[74]. In this case the bisamide (XXXVIII: $R = CH_3$), after cyclisation to the bisdihydroisoquinoline bases, was first reduced to the tetrahydroisoquinoline derivatives, which were separated and then methylated. One of the final compounds was identified with *O*-methyloxyacanthine. Tetrandrine was obtained (Scheme 2) from the other bisamide (XXXIX: $R = CH_3$). In the early attempts to synthesise this alkaloid by a similar scheme the dihydroisoquinoline derivatives could not be isolated[75–78]. Other schemes were also proposed, in which the initial diacid was obtained e.g. by Willgerodt rearrangement of the corresponding acetophenone

Scheme 2



[75,79]. Direct condensation of *p*-hydroxyphenylacetic and *m*-bromo-*p*-methoxyphenylacetic esters gives a low yield of the expected diphenyl ether. Obtaining the acid component by Arndt–Eistert chain lengthening has no advantages over the first method[81]. The second component for the synthesis—the diamine (XXXVII)—was also obtained by several methods, e.g. from the corresponding diacid (formed in low yield by Ullmann condensation of substituted aromatic esters) by reduction of ester to hydroxymethyl groups, replacement of the hyroxyls by chlorine and then by cyano-groups, and subsequent reduction with lithium tetrahydroaluminate[80–82]. On the other hand, the dialdehyde (XXXVIb), obtained from the corresponding acid dichloride by Rosenmund reduction, was further converted via the corresponding nitrostyrene (as described above) into the diamine (XXXVII).[75,81] This compound was synthesised from the corresponding bispropionic acid via the isopropylidene hydrazide[83].

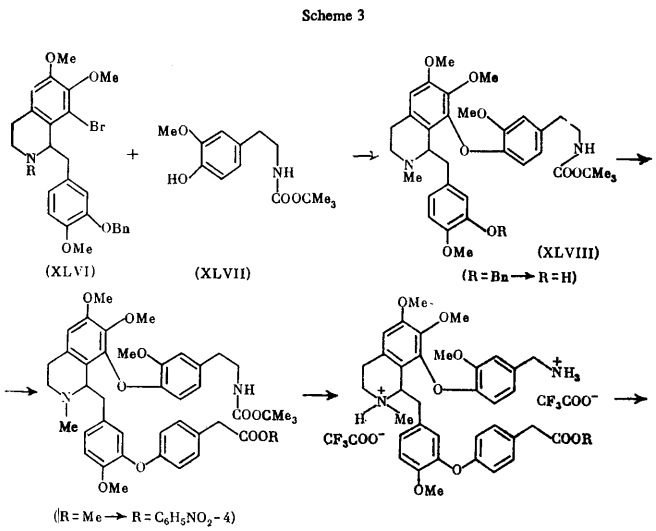

(XLIV)

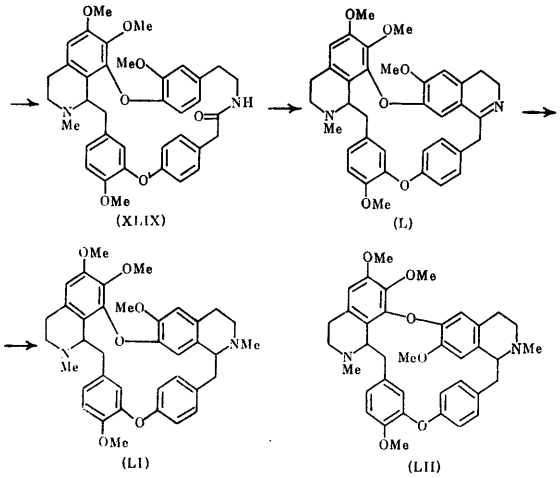

(XLV)

The alkaloid stebisimine, a bisdehydro-derivative (XLIV) isolated from *Stephania japonica*[84], was identified with an intermediate in the synthesis of obaberine[85,86].

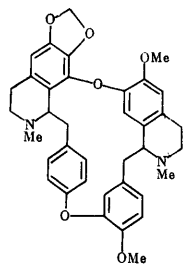
Another synthesis of tetrandrine was the condensation of *N*-methylcoclaurine with its 3′,8-dibromo-*OO*′-dimethyl derivative (XLV).[87] However, all syntheses of this type are at present merely of theoretical interest, because of the very low yields.

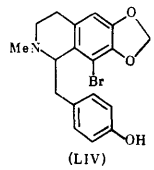
Scheme 3

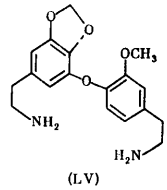

(R = Me → R = $C_6H_5NO_2$-4)


(XLIX) (L) (LI) (LII)

The first total synthesis of the optically active alkaloids—tetrandrine, isotetrandrine, and pheanthine—was accomplished in 1968 from *O*-benzyl-8-bromolaudanine (XLVI: R = H) (Scheme 3),[88,89] which was obtained from 5-bromohomoveratrylamine and *O*-benzylhomoisovanillic acid by classic methods. The tetrahydroisoquinoline derivative was resolved into its optical antipodes by means of (+)-tartaric acid, and after *N*-methylation subjected to Ullmann condensation with t-butyl *N*-*p*-hydroxy-*m*-methoxyphenethylcarbamate (XLVII) to give the diphenyl ether (XLVIII: R = $C_6H_5CH_2$) in 50% yield. After debenzylation (by hydrogenolysis) and condensation with methyl *p*-bromophenylacetate the protecting group in the diphenyl ether was removed, and the cycloamide (XLIX) isolated in 54% yield. Cyclisation to the dihydroisoquinoline (L), reduction, and *N*-methylation gave a mixture of isotetrandine and pheanthine (LI), which were separated by crystallisation of the picrates. (±)-Tetrandrine, which had previously been resolved[90], and *O*-methylthalicberine (LII) [91] were synthesised similarly. Japanese chemists have patented this synthesis of tetrandrine, isotetrandrine, and pheanthine[92].


(LIII)

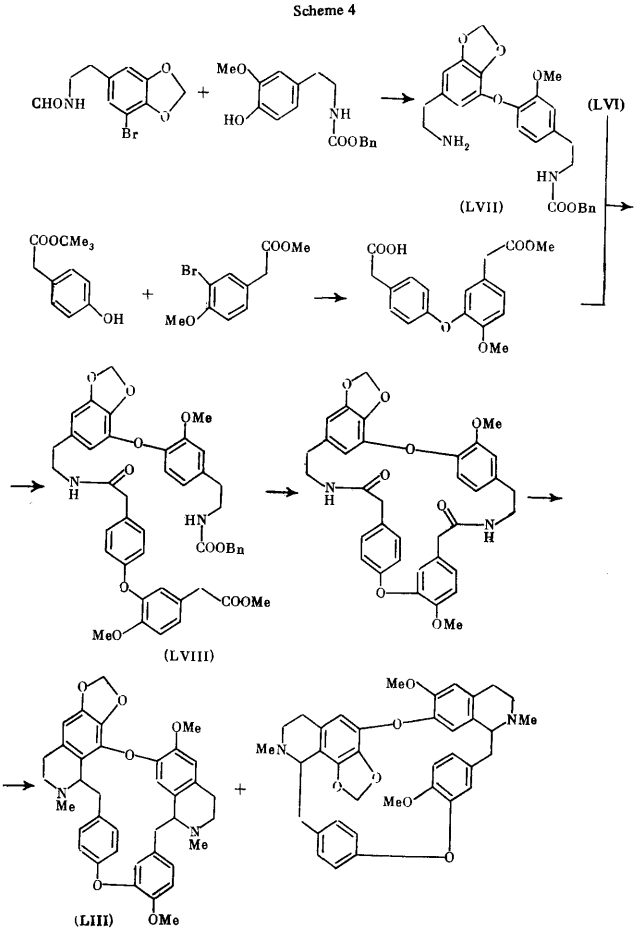

(LIV)


(LV)

The first attempts to synthesise the alkaloid cepharanthine (LIII) by double Ullmann condensation of the two tetrahydroisoquinoline fragments (LIV) and (XXVI: R′ = H; R″ = CH_3) were unsuccessful owing to difficulties in obtaining an 8-bromo-derivative with a methylenedioxy-group (LIV).[93] An attempt to synthesise this alkaloid by the scheme of double amide condensation of diacid and the diamine (LV) described

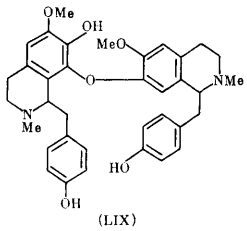
for tetrandrine gave a mixture of cyclobisamides, one of which when isolated could not be cyclised to the expected bis-dihydroisoquinoline[79,80,93–95]. Spectral results indicated that merely products of the oxidation and partial cyclisation of the bisamide had been isolated[96].

Scheme 4

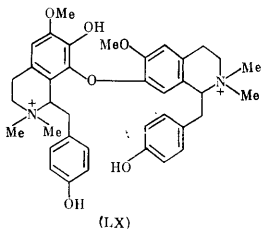


The first successful synthesis of cepharanthine was accomplished by Japanese workers, with successive formation of amide links to obtain the intermediate cyclobisamide[87,98]. Monosubstituted components—the monoether (LVI) and the benzyl *N*-aminoethylphenoxyphenethylcarbamate (LVII)—were synthesised for condensation in the presence of dicyclohexylcarbodi-imide to form initially the monoamide (LVIII) (Scheme 4). The second amide link was formed by means of activated esters. This multistage synthesis of cepharanthine has also been patented by Japanese workers[99]. As in the preceding syntheses, the Bischler–Napieralski cyclisation produces two isomeric dihydroisoquinoline bases, so that not only cepharanthine (LIII) but also its isomeric 6,7′-ether was isolated. Cepharanthine can be converted into obaberine (*O*-methylhydroxyacanthine) by removing the methylene group with a mixture of phloroglucinol and sulphuric acid and then methylating the phenolic product[100].

An attempted double oxidative coupling of *N*-methylcoclaurine units to form compounds of the oxyacanthine–tetrandrine series was unsuccessful. Use of potassium hexacyanoferrate-(III) as oxidant or enzymatic oxidation in the presence of hydrogen peroxide converts coclaurine derivatives or their quaternary ammonium salts merely into the 7′,8-dehydro-derivatives



(LIX)

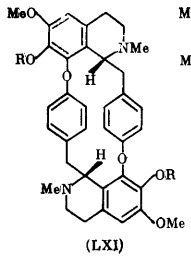


(LX)

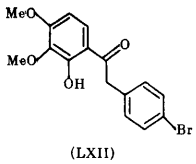
whose structures have been confirmed by synthesis[101–105].

2. Isochondrodendrine Alkaloids

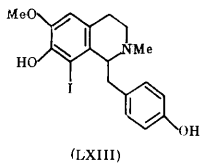
Alkaloids of this type include isochondrodendrine, its methyl ether cycleanine, insularine, etc. The *RR*-configuration has been established for the first two (LXI: R = H, CH_3), which have an axis of symmetry, in contrast to alkaloids of the berbamine–oxyacanthine series. Although alkaloids of the present type were the first to attract the attention of chemists, progress in this field has been achieved only recently. Their synthesis presented certain difficulties, since methods developed for the preceding type of bases proved relatively unsuitable. Several unsuccessful attempts were made to effect a double Ullmann condensation of (LXII) with the aim of obtaining the macrocyclic system forming the basis of isochondrodendrine[106]. An attempt to synthesise 8-iodo-*N*-methyl-coclaurine (LXIII), an intermediate in the synthesis of isochondrodendrine, was also unsuccessful[107].



(LXI)



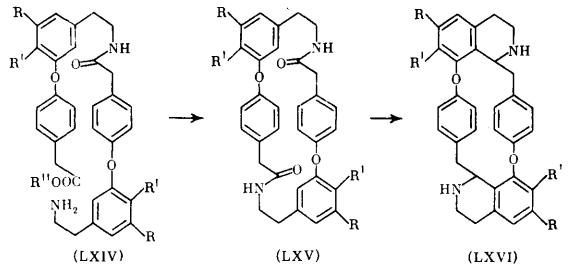
(LXII)



(LXIII)

A theoretical synthesis of isochondrodendrine alkaloids was suggested by Preobrazhenskii et al.[108] and accomplished on a model compound. The main stage was intramolecular cyclisation of the monoamide (LXIV) to the macrocyclic diamide (LXV), which was converted by cyclisation followed by

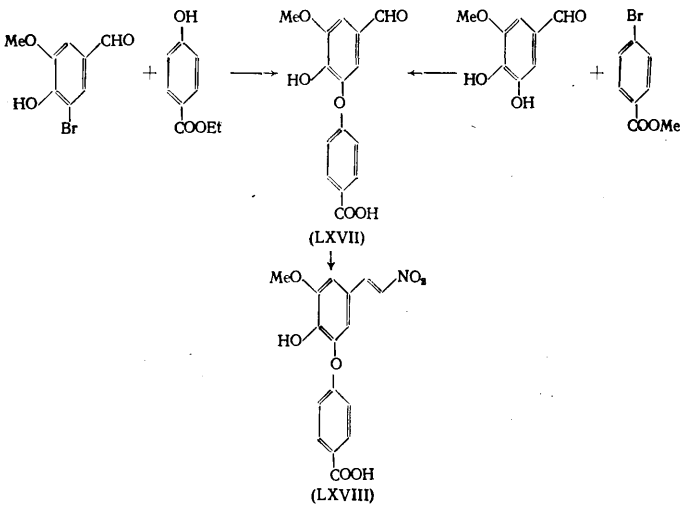
reduction into (LXVI: R = R' = H):



(LXIV) (LXV) (LXVI)

The initial diphenyl ethers were synthesised by condensing 5-bromovanillin with a *p*-hydroxybenzoic ester, or $O_{(3)}$-methylgallaldehyde with a *p*-bromobenzoic ester, to give *p*-5'-formyl-2'-hydroxy-3'-methoxyphenoxybenzoic acid (LXVII), which was converted by means of nitromethane into the corresponding nitrostyrene (LXVIII) (Scheme 5).[109] Alternatively, halogen activation was used to increase the yield of the products, by introducing a nitro-group into the halogenated component, and subsequently removing it. However, the additional operations required to eliminate the nitro-group from the nitrated diphenyl ether almost nullify the advantages of this method[109]. The nitrovinyl group can then be reduced over palladium black to an aminoethyl group[110].

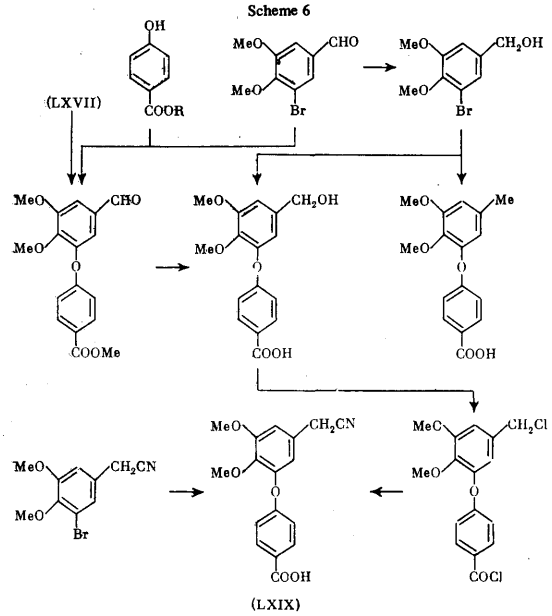
Scheme 5



(LXVII) (LXVIII)

p-5'-Cyanomethyl-2',3'-dimethoxyphenoxybenzoic acid (LXIX), identical with the product of the condensation of 3'-bromo-4',5'-dimethoxyphenylacetonitrile with a *p*-hydroxybenzoic ester, was synthesised by methylating the phenolic hydroxyl in (LXVII), reducing the formyl group to a hydroxymethyl group, and then replacing the hydroxyl by a chlorine atom followed by a cyano-group (Scheme 6). Other intermediates in the synthesis have also been obtained independently, as outlined in Scheme 6.[111]

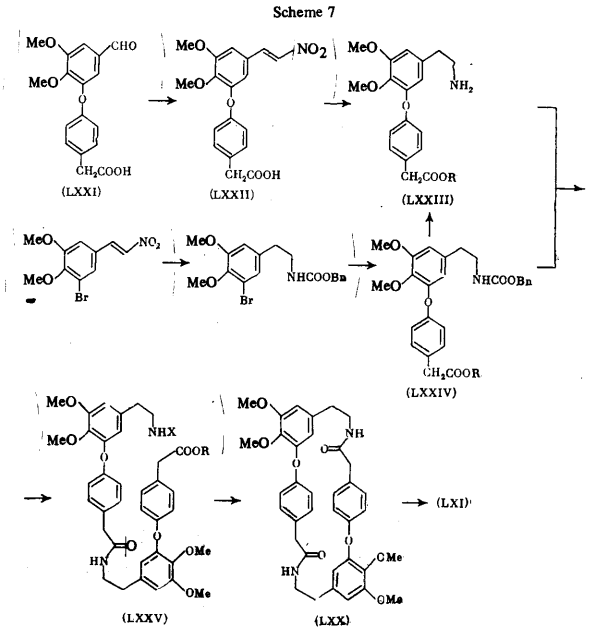
Scheme 6



(LXVII) (LXIX)

The two diphenyl ethers can be combined by Arndt–Eistert chain lengthening to give the cyclodiamide (LXV: R = R' = CH_3O). In view of the low overall yield, however, a search was made for more practicable methods of synthesis. In ticular, reduction of brominated nitrostyrenes with zinc amalgam was used to obtain 4-alkoxy-3-bromo-5-methoxyphenethylamines[13], which would yield 7-alkoxy-8-bromo-3,4-dihydro-1-*p*-hydroxybenzyl-6-methoxyisoquinolines[10], intermediates in the synthesis of these alkaloids. However, the cyclocondensation of (±)-8-bromoarmepavine was accompanied by debromination, so that only (±)-armepavine and (±)-*NOO'*-trimethylcoclaurine were isolated[112,113].

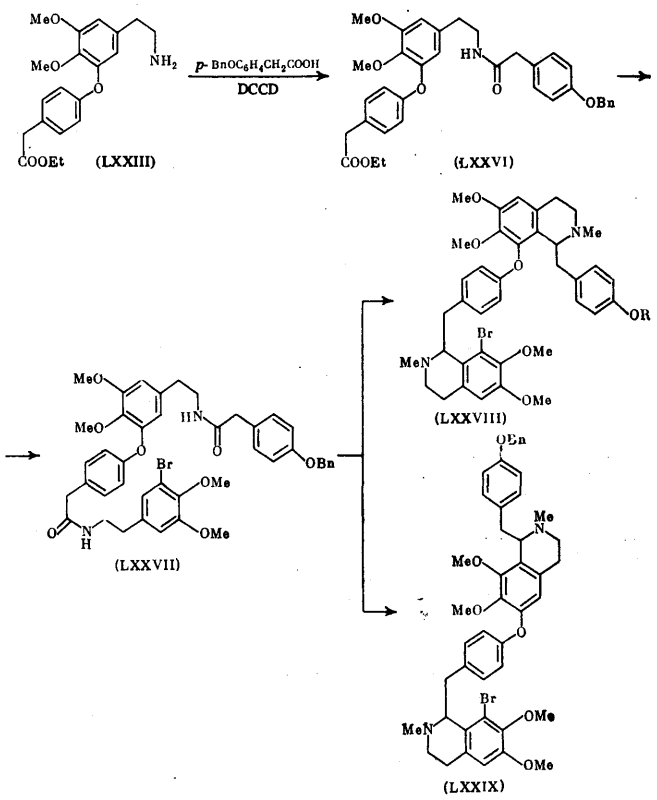
Scheme 7



(LXXI) (LXXII) (LXXIII) (LXXIV) (LXXV) (LXXVI) (LXI)

In the first of two independent syntheses of (±)-cycleanine (LXI: R = CH_3) via the cyclobisamide (LXX) the acetal of 5-bromoveratraldehyde was condensed with a *p*-hydroxyphenylacetic ester, and the resulting p-5'-formyl-2',3'-dimethoxyphenoxyphenylacetic acid (LXXI) was converted into the nitrostyrene (LXXII), which was reduced to the amino-acid (LXXIII) (Scheme 7). An ester of this acid was obtained by condensing benzyl *N*-5-bromohomoveratrylcarbamate with a *p*-hydroxyphenylacetic ester and then hydrogenolysing the carbamic ester (LXXIV). The two fragments (LXXIII) and (LXXIV) were condensed by means of dicyclohexylcarbodiimide in dichloromethane. The second amide link was formed by heating the *p*-nitrophenyl ester (LXXV) in the presence of pyridine and triethylamine[114–116].

Scheme 8

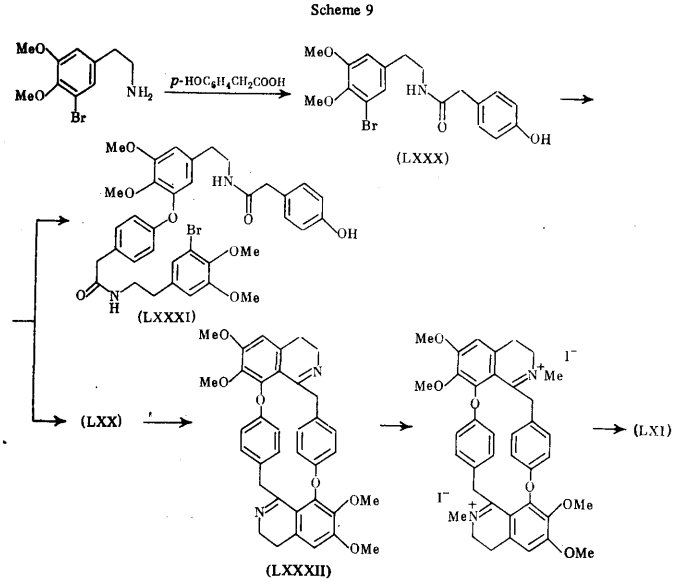


In another procedure[117] the initial amino-acid is condensed in the form of an ester [LXXIII] with *p*-benzyloxyphenylacetic acid, and the resulting amide (LXXVI) converted by reaction with 5-bromohomoveratrylamine into the diamide (LXXVII) which is cyclised, reduced, and methylated (Scheme 8). This yields a mixture of isomeric tetrahydroisoquinoline bases (LXXVIII) and (LXXIX), one of which was identified with the product of the condensation of (±)-8-bromoarmepavine with (±)-8-bromo-*NOO'*-trimethylcoclaurine in the presence of copper(II) oxide instead of metallic copper as catalyst. However, cyclocondensation of (LXXVIII: R = H) into cycleanine could not be achieved[112].

Scheme 9 outlines a successful double Ullmann cyclocondensation of the phenolic bromo-amide (LXXX), in which 5-bromohomoveratrylamine was condensed with *p*-hydroxyphenylacetic acid, and the potassium salt of the resulting bromo-amide (LXXX) was converted by an Ullmann reaction into a mixture of the cyclobisamide (LXX) and the open-chain diamide (LXXXI), which were easily separated by conversion of the latter into a salt[118]. The cyclic diamide was then subjected to Bischler–Napieralski cyclisation to give the bisdihydroisoquinoline derivative (LXXXII), whose methiodide was reduced to a mixture of tetrahydroisoquinoline bases that could be separated chromatographically. One of these showed the same chromatographic mobility as natural cycleanine.

Phenolic alkaloids—isochondrodendrine (LXI: R = H) and norcycleanine (7-*O*-demethylcycleanine)—have been obtained by the selective demethylation of cycleanine with hydrobromic acid[119].

Scheme 9



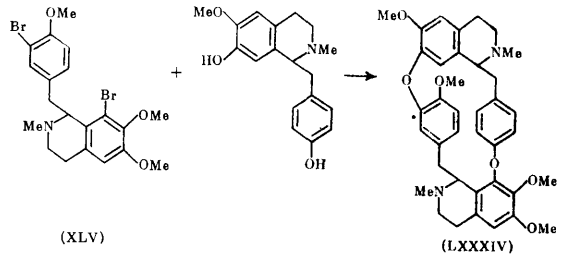
3. Curine–Tubocurarine Alkaloids

In contrast to the preceding group the present diether alkaloids are based on the unsymmetrical chondrodendrine (LXXXIII) skeleton. This group includes the alkaloids curine and the quaternary bases tubocurarine, chondrocurarine, etc. Tubocurarine chloride, the active principle of tubocurare, found application in surgical practice[120]. However, the relative inaccessability of this alkaloid and the great demand stimulated synthetic work on substitutes for curare, quaternary bisammonium salts, of which several thousands were obtained, most of them weaker than tubocurarine or having no advantages over the latter[121].

Two fundamentally different approaches have also been made to the synthesis of this group of alkaloids.

(*a*) Synthesis from benzylisoquinoline components

N-Methylcoclaurine (XI: R = H), obtained by the cleavage of isotetrandrine with sodium in liquid ammonia, was brominated at positions 3′ and 8 and then diazomethylated to give 3′,8-dibromo-*NOO*′-trimethylcoclaurine (XLV), which was condensed with the potassium salt of *N*-methylcoclaurine; *NOO*′-trimethylcoclaurine, isotetrandine, and dimethylcurine (LXXXIV) were found among the reaction products:

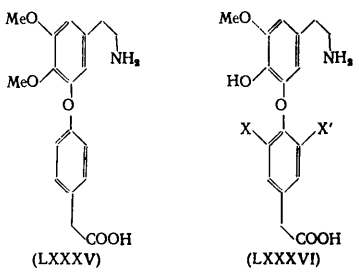


(XLV) (LXXXIV)

The use of laevorotatory components yielded (−,−)-*OO*′-dimethylcurine[122–124]. Phenolic components have also been employed for condensation, but the yield of the macroring is then very low. After methylation of the reaction products with diazomethane followed by chromatography diastereomeric racemates of *OO*′-dimethylcurine and of an acyclic base were isolated, the latter of which after debromination was identified with racemic *OO*′-dimethyl-liensinine.

(*b*) Synthesis from diphenyl ethers

The alternative synthesis of bisbenzylisoquinoline alkaloids from substituted diphenyl ethers has recently been applied to the oxyacanthine–berbamine series. However, the synthesis of amino-acid diphenyl ethers, of chondrodendrine and isochondrodendrine structural units, it made difficult by the inconvenience of obtaining them by the Ullmann reaction, because these alkaloids contain a hydroxyl next to the phenoxyphenyl link. It was shown experimentally that direct formation by the Ullmann reaction even of the simplest compounds of this type is devoid of preparative value owing to the very low yields[125]:

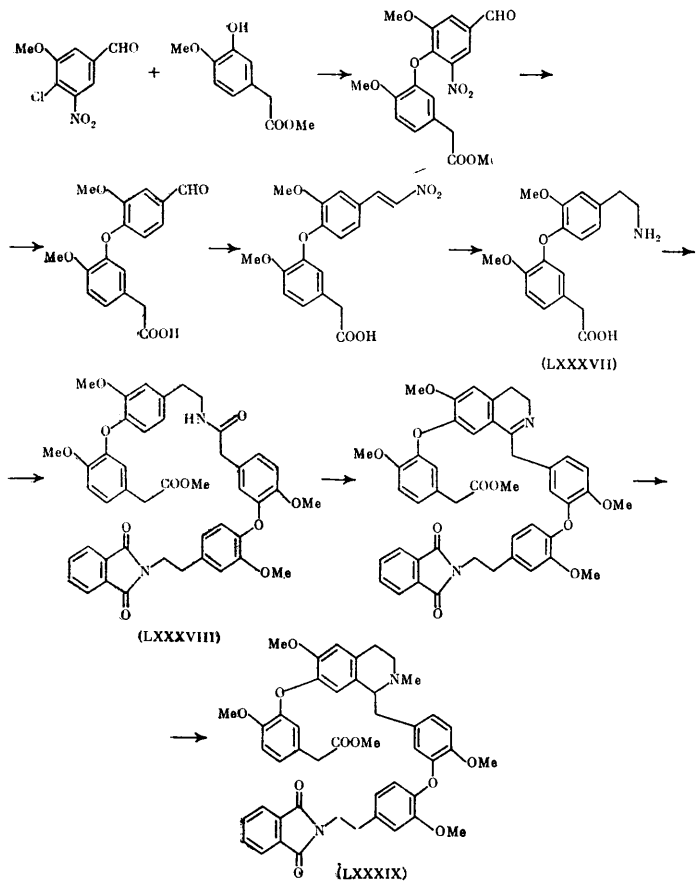


(LXXXV) (LXXXVI)

The structural formulae reveal that one diphenyl ether fragment is common to isochondrodendrine and curine, so that this moiety can be synthesised in the same way for the two alkaloids. Activation of aromatic halogen by means of groups such as nitro has been used to synthesise *p*-5′-aminoethyl-2′,3′-dimethoxyphenoxyphenylacetic acid (LXXXV) [126] and several of its phenolic analogues (LXXXVI),[127,128], as well as homologous acids (see above[109–111]).

The other component, *m*-*p*′-aminoethyl-*o*′-methoxyphenoxy-*p*-methoxyphenylacetic acid (LXXXVII), was also synthesised by the method of activated ethers from 4-chloro-3-methoxy-5-nitrobenzaldehyde and isohomovanillic acid (Scheme 10).[129,130] In all cases the activating group was removed by reduction to an amino-group, diazotisation, and subsequent treatment with hypophosphoric acid. The overall yield of the amino-acid (LXXXVII) was 12%. Further condensation of the corresponding ester with a phthalimide derivative gave the amide (LXXXVIII), which after cyclisation, reduction, and *N*-methylation was converted in low yield into the non-cyclised ether (LXXXIX).[130] It was also suggested that diphenyl ethers derived from phthalimidoamino-acids could be obtained via diaryliodonium salts, but the yield of a model compound was 6%.[131]

Scheme 10

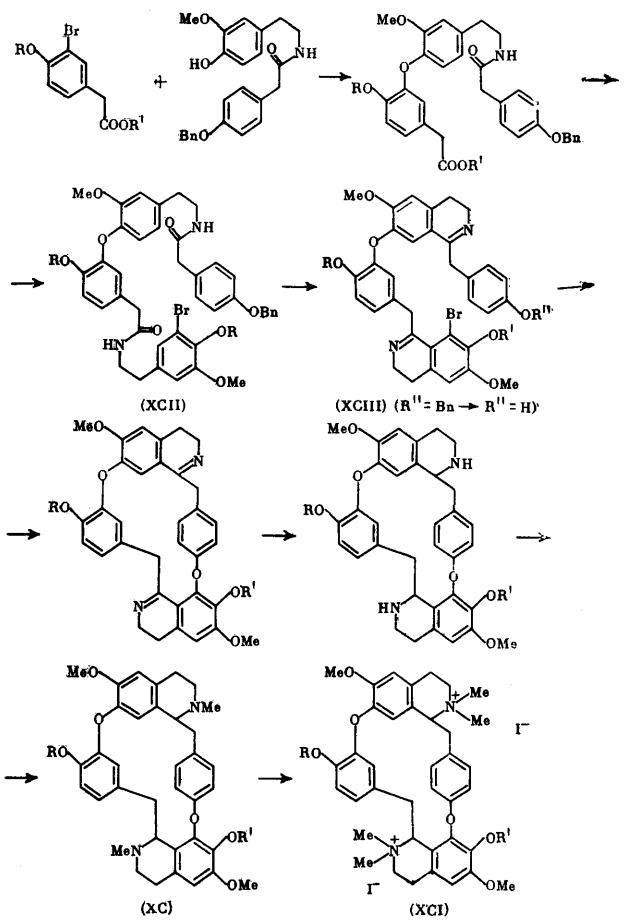


(LXXXVII) (LXXXVIII) (LXXXIX)

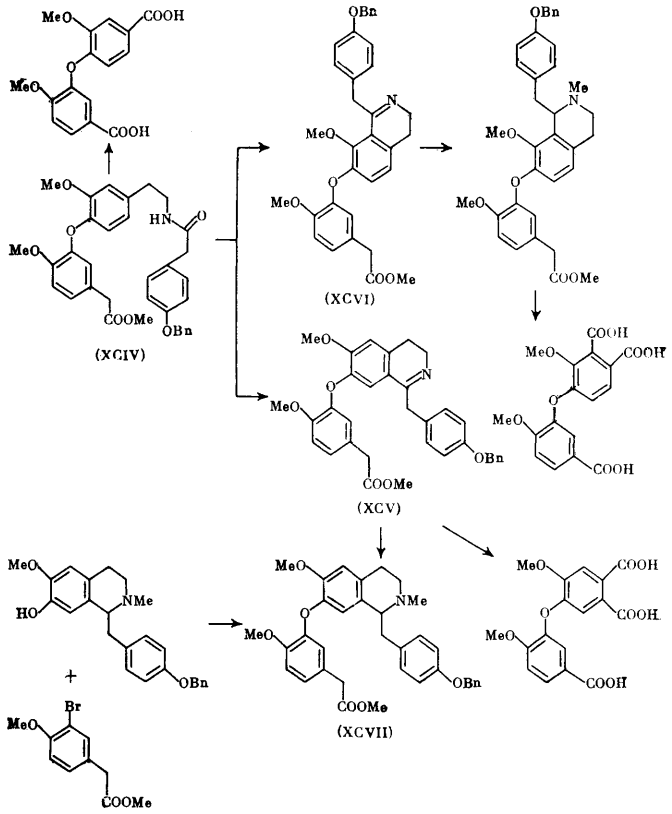
The total synthesis of racemic curine, i.e. (±)-chondrodendrine (XC: R = R′ = H), its ethers, and its quaternary salts (XCI: R = R′ = H, CH_3) is accomplished by successive chain extension followed by cyclisation of the diamide (XCII: R = R′ = CH_3, CH_3CO) to the bisdihydroisoquinoline base (XCIII: R = R′ = CH_3, CH_3CO), removal of the protecting groups, and formation of a second diphenyl ether bridge (Scheme 11).[132–137] It is noteworthy that the use of amides for Ullmann condensation enabled the required diphenyl

ethers to be obtained in good yield even when free phenolic hydroxyls were present in the compounds[138]. The amide protection of amino-groups in the Ullmann reaction later enabled Japanese workers to achieve the total synthesis of alkaloids of the oxyacanthine–tetrandrine group (see above). This scheme is simple to carry out, involves relatively few stages, and gives good yields at all stages. Diastereomeric compounds can be quite easily separated in the later stages by crystallisation of the salts. In the synthesis of (±)-chondrodendrine and its dimethiodide free hydroxy-groups must be protected by acetylation before Bischler–Napieralski cyclisation.

Scheme 11



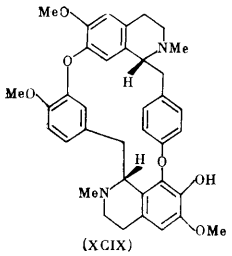
Scheme 12



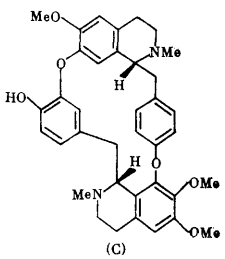
The acetamido-diphenyl ether (XCIV) was isolated in two forms, giving on cyclisation different dihydroisoquinoline derivatives (XCV) and (XCVI) (Scheme 12). The cyclisation products were identified by cross-synthesis of the compound (XCVII) and also of the oxidation products[139]. The same method was used to synthesise *NN'*-demethyl-4″-*O*-methyl chondrodendrine (*NN'*-demethylgaiatinine)[140]

The intermediate methyl *m*-l-*p'*-benzyloxybenzyl-1,2,3,4-tetrahydro-6-methoxy-2-methylisoquinolin-7-yloxy-*p*-methoxyphenylacetate (XCVII) has also been used in an alternative synthesis of *OO'*-dimethylchondrodendrine (XC: R = R' = CH_3) (Scheme 13).[141] *OO'*-Dimethyl-liensinine[70] and the non-cyclised analogue *OO'*-dimethyltubocurarine iodide[110] have been synthesised by the same route.

Demethylation of the methyl ether of curine with hydrobromic acid followed by separation of the demethylated products was reported[142], but the structures of the latter were not given. *RR*-12′-*O*-Methylcurine (4″-*O*-methylcurine) (XCIX) was obtained together with chondrofoline (C) by the partial methylation of (−)-curine with diazomethane[143].

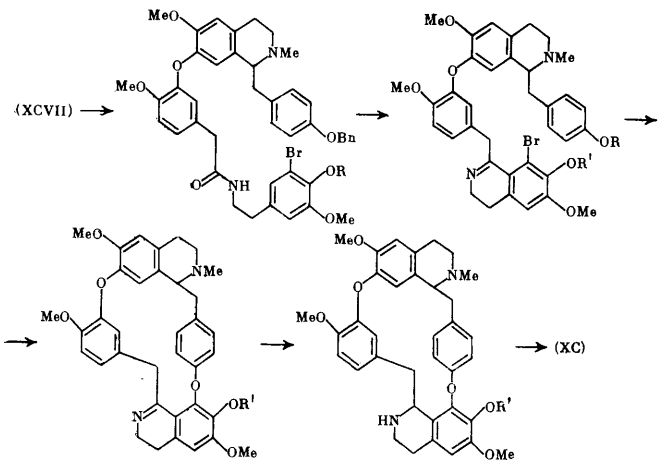


(XCIX)



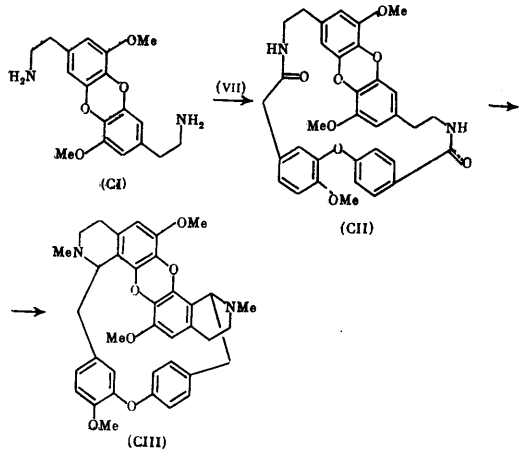
(C)

Scheme 13



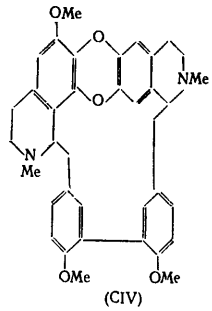
V. SYNTHESIS OF BISBENZYLISOQUINOLINE ALKALOIDS CONTAINING THREE DIPHENYL ETHER LINKS

This group of alkaloids includes micranthine, menisarine, and normenisarine, as well as trilobine and isotrilobine. The structure of menisarine has been confirmed by synthesis of a derivative[144–147]. The condensation of 2,7-bis-2′-aminoethyl-4,9-dimethoxydibenzo-5,10-dioxin (CI) with 4-methoxy-3-phenoxybenzene-1,4′-bisacetic acid at high dilution gave a macrocyclic bisamide (CII), which on cyclisation, reduction, and *N*-methylation was converted into a ditertiary base, identified with dihydro-*N*-methylmenisarine (CIII) obtained from natural menisarine:



(CI) (CII) (CIII)

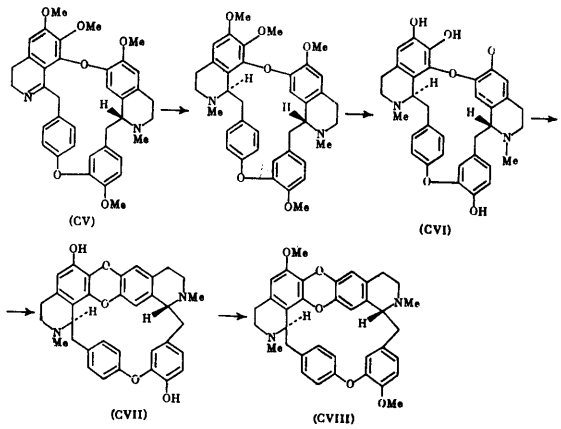
(±)-*O*-Methyltiliacorine



(CIV)

has been synthesised by an analogous scheme[148].

Scheme 14



(CV) (CVI) (CVII) (CVIII)

It is interesting to pass from the hydroxyacanthine to the trilobine group of alkaloids, which contains three diphenyl ether links. For example, (+)-epistephanine (CV), after reduction of the dihydroisoquinoline ring and *N*-methylation, was demethylated with hydrobromic acid at 100 °C to the tetraol (CVI), which when heated with this acid at 150 °C underwent dehydration to the prototrilobine derivative (CVII), diazomethylation of which gave (−)-isotrilobine (CVIII), the antipode of natural (+)-isotrilobine (Scheme 14)[149,150]. Repandine was similarly converted into isotrilobine[151,152], and dihydroepistephanine into the *N*-ethyl analogue of the antipode of trilobine[153].

---o0o---

During recent years synthetic schemes have been worked out for the chief bisbenzylisoquinoline alkaloids containing one, two, or three diphenyl ether links. The main criterion in the choice of method of synthesis is the biogenetic classification. At present most of these syntheses are merely of theoretical interest. However, the presence of high biological activity among bisbenzylisoquinoline alkaloids, e.g. antitumour and antitubercular in tetrandrine, etc., as well as their relative unavailability for practical use, makes further search desirable for practical methods of synthesis.

REFERENCES

1. M.Shamma and J.L.Moniot, Heterocycles, **4**, 1817 (1976).
2. M.Shamma, in "The Isoquinoline Alkaloids, Chemistry and Pharmacology", Acad.Press, New York, 1972, p.115.
3. N.M.Mollov, H.B.Dutschewska, and V.St.Georgiev, in "Recent Developments in the Chemistry of Natural Carbon Compounds", Akadémiai Kiadó, Budapest, 1971, Vol.4, p.195
4. O.N.Tolkachev, J.Sci.Ind.Res.India, **26**, 209 (1967).
5. J.Finkelstein, J.Amer.Chem.Soc., **73**, 550 (1951).
6. M.Tomita, K.Nakaguchi, and S.Takagi, Yakugaku Zasshi, **71**, 1046 (1951).
7. O.N.Tolkachev, L.V.Volkova, G.S.Vasil'ev, A.B.Prokhorov, N.S.Kulachkina, and N.A.Preobrazhenskii, Khim.Geterotsikl.Soed., 831 (1969).
8. O.N.Tolkachev, V.P.Chernova, Pao Fang-lin, E.V.Kuznetsova, and N.A.Preobrazhenskii, Zhur. Obshch.Khim., **36**, 1767 (1966).
9. O.N.Tolkachev, N.S.Butusova, and N.A.Preobrazhenskii, Khim.Geterotsikl.Soed., 310 (1967).
10. O.N.Tolkachev, E.B.Yagubskii, L.T.Dorofeeva, and N.A.Preobrazhenskii, Zhur.Obshch.Khim., 34, 548 (1964).
11. O.N.Tolkachev, V.G.Voronin, and N.A.Preobrazhenskii, Zhur.Obshch.Khim., **28**, 3320 (1958).
12. K.Kratzl and C.Billek, Monatsh., **83**, 1045 (1952).
13. O.N.Tolkachev, V.P.Chernova, E.V.Kuznetsova, Pao Fang-lin, and N.A.Preobrazhenskii, Zhur.Obshch. Khim., **34**, 545 (1964).
14. J.P.Sheth and O.N.Tolkachev, Indian J.Appl.Chem., **31**, 137 (1968).
15. I.Baxter, L.T.Allan, and G.A.Swan, J.Chem.Soc., 3645 (1965).
16. S.Teitel and A.Brossi, J.Heterocyclic Chem., **5**, 825 (1968).
17. H.Hellmann and W.Elser, Annalen, **639**, 77 (1961).
18. T.Kametani, S.Takano, K.Masuko, and S.Kuribara, Yakugaku Zasshi, **85**, 166 (1965).
19. T.Kametani, H.Yagi, and S.Kaneda, Chem.and Pharm. Bull.(Japan), **14**, 974 (1966).
20. M.P.Cava and K.T.Buck, Tetrahedron, **25**, 2795 (1969).
21. T.Kametani and H.Yagi, Chem.and Pharm.Bull., **15**, 1283 (1967).
22. D.G.Farber and A.Giacomazi, Chem.and Ind., 57 (1968).
23. J.Knabe and P.Horn, Arch.Pharm., **300**, 547 (1967).
24. H.Kondo, Z.Narita, and S.Uyeo, Ber., **68**, 519 (1935).
25. R.Tschesche, R.Geipel, and H.-W.Fehlhaber, Phytochemistry, **9**, 1683 (1970).
26. M.Tomita, Y.Okamoto, Y.Nagai, K.Kitayama, and H.Yanasawa, Yakugaku Zasshi, **90**, 1178 (1970).
27. S.R.Johns, J.A.Lamberton, C.S.Li, and A.A.Sioumis, Austral.J.Chem., **23**, 363 (1970).
28. I.N.Gorbacheva, G.V.Bushbek, L.P.Varnakova, L.M.Shulov, and N.A.Preobrazhenskii, Zhur.Obshch. Khim., **27**, 2297 (1957).
29. S.M.Kupchan and H.W.Altland, J.Medicin.Chem., **16**, 913 (1973).
30. O.N.Tolkachev, E.P.Nakova, A.I.Vukolova, G.I.Aranovich, and R.P.Evstigneeva, Zhur.Obshch.Khim., **44**, 410 (1974).
31. T.Kametani, S.Takano, R.Yanase, C.Kibayashi, H.Iida, S.Kano, and K.Sakurai, Chem.and.Pharm.Bull. (Japan), **14**, 73 (1966).
32. T.Kametani and K.Fukumoto, Tetrahedron Letters, 2771 (1964).
33. T.Kametani and K.Fukumoto, J.Chem.Soc., Suppl.II, 6141 (1964).
34. T.Kametani, R.Yanase, S.Kano, and K.Sakurai, Chem. and Pharm.Bull.(Japan), **15**, 56 (1967).
35. T.Kametani, R.Yanase, S.Kano, and K.Sakurai, J.Heterocyclic Chem., **3**, 239 (1966).
36. T.Kametani and K.Fukumoto, Tetrahedron Letters, 2771 (1964).
37. M.Tomita, K.Fujitani, Y.Masaki, and Y.Okamoto, Chem. and Pharm.Bull.(Japan), **16**, 70 (1968).
38. T.Kametani and F.Satoh, Chem.and Pharm.Bull. (Japan), **16**, 773 (1968).
39. M.Tomita, K.Ito, and H.Yamaguchi, Chem.and Pharm. Bull.(Japan), **3**, 449 (1955).
40. K.Fujitani, Y.Aoyagi, and Y.Masaki, Yakugaku Zasshi, **84**, 1234 (1964).
41. K.Fujitani, Y.Aoyagi, and Y.Masaki, Yakugaku Zasshi, **86**, 654 (1966).
42. T.Kametani, S.Takano, T.Kobari, H.Iida, and M.Shinbo, Chem.and Pharm.Bull.(Japan), **16**, 1625 (1968).
43. T.Kametani, H.Iida, and K.Sakurai, J.Chem.Soc.C, 500 (1969).
44. T.Kametani, H.Iida, and K.Sakurai, Chem.and Pharm Bull.(Japan), **16**, 1623 (1968).
45. T.Kametani, K.Sakurai, and H.Iida, Yakugaku Zasshi, **88**. 1163 (1968).
46. K.Fujitani and Y.Masaki, Yakugaku Zasshi, **86**, 660 (1966).
47. M.Tomita and Y.Watanabe, Yakugaku Zasshi, **74**, 1363 (1954).
48. F.D.Popp, H.W.Gibson, and A.C.Noble, J.Org.Chem., **31**, 2296 (1966).
49. H.W.Gibson, F.D.Popp, and A.C.Noble, J.Heterocyclic Chem., **3**, 99 (1966).
50. D.C.Smith and F.D.Popp, J.Heterocyclic Chem., **13**, 573 (1976).
51. J.M.Bobbitt and R.C.Hallcher, J.Chem.Soc.D, 543 (1971).

52. N.F.Proskurnina and A.P.Orekhov, Zhur.Obshch. Khim., **9**, 127 (1939).
53. N.F.Proskurnina, Zhur.Obshch.Khim., **16**, 129 (1946).
54. K.Ito, Farmatsiya, **21**, No.5, 70 (1972).
55. K.Ito and T.Aoki, Yakugaku Zasshi, **79**, 325 (1959).
56. L.K.Yakhontova, O.N.Tolkachev, D.A.Fesenko, M.E.Perel'son, and N.F.Proskurnina, Khim.Prirod. Soed., 234, No.2 (1977).
57. M.Tomita and K.Ito, Yakugaku Zasshi, **78**, 103 (1958).
58. M.Tomita and K.Ito, Yakugaku Zasshi, **78**, 605 (1958).
59. T.Kametani, H.Yagi, and S.Kaneda, Chem.and Pharm. Bull.(Japan), **14**, 974 (1966).
60. M.P.Cava and A.Afzali, J.Org.Chem., **40**, 1553 (1975).
61. T.Kametani and H.Yagi, Tetrahedron Letters, 953 (1965).
62. T.Kametani and H.Yagi, Chem.and Pharm.Bull.(Japan), **14**, 78 (1966).
63. I.N.Gorbacheva, M.I.Lerner, G.G.Zanesochnaya, L.P.Varnakova, and N.A.Preobrazhenskii, Zhur. Obshch.Khim., **27**, 3353 (1957).
64. Y.Y.Hsien, P.C.Pan, W.C.Chen, and Y.S.Kao, Sci. Sinica (Peking), **13**, 2020 (1964).
65. T.Kametani, S.Takano, K.Masuko, and F.Sasaki, Chem.and Pharm.Bull.(Japan), 14, 67 (1966).
66. M.Tomita, H.Furukawa, T.H.Yang, and T.J.Lin, Chem.and Pharm.Bull.(Japan), **13**, 39 (1965).
67. M.Tomita, H.Furukawa, T.H.Yang, and T.J.Lin, Tetrahedron Letters, 2637 (1964).
68. T.Kametani, S.Takano, and K.Satoh, J.Heterocyclic Chem., **3**, 546 (1966).
69. T.Kametani, S.Takano, H.Iida, and M.Shinbo, J.Chem.Soc.C, 298 (1969).
70. L.V.Volkova, V.E.Kosmacheva, V.G.Voronin, O.N.Tolkachev, and N.A.Preobrazhenskii, Khim.Geterotsikl. Soed., 522 (1967).
71. T.Kametani, H.Nemoto, T.Kobari, and S.Takano, J.Heterocyclic Chem., **7**, 181 (1970).
72. T.Kametani, H.Iida, S.Kano, S.Takano, K.Fukumoto, S.Shibuya, and H.Yagi, J.Heterocyclic Chem., **4**, 85 (1967).
73. T.Kametani, S.Takano, R.Yanase, C.Kibayashi, H.Iida, S.Kano, and K.Sakurai, Chem.and Pharm.Bull.(Japan), **14**, 73 (1966).
74. T.Kametani, K.Wakisaka, and K.Kigasawa, J.Heterocyclic Chem., **7**, 509 (1970).
75. H.Kondo, H.Kataoka, and K.Kigasawa, Ann.Report ITSUU Lab., **6**, 13 (1955).
76. H.Kondo, H.Kataoka, and K.Kigasawa, Ann.Report ITSUU Lab., **6**, 46 (1955).
77. H.Kataoka, Ann.Report ITSUU Lab., **8**, 1 (1957).
78. H.Kondo, Y.Hayashi, and T.Uchibori, Ann.Report ITSUU Lab., **9**, 1 (1958).
79. W.M.Whaley, W.L.Dean, and L.N.Starker, J.Org.Chem., **19**, 1020 (1954).
80. W.M.Whaley, L.N.Starker, and M.Meadow, J.Org.Chem., **18**, 83 (1953).
81. H.Kondo, H.Kataoka, and Y.Baba, Ann.Report ITSUU Lab., **5**, 59 (1954).
82. W.M.Whaley, L.N.Starker, and W.L.Dean, J.Org.Chem., **19**, 1018 (1954).
83. H.Kataoka, Ann.Report ITSUU Lab., **8**, 35 (1957).
84. D.H.R.Barton, G.W.Kirby, and A.Wiechers, J.Chem. Soc.C, 2313 (1966).
85. T.Kametani, O.Kusama, and K.Fukumoto, J.Chem.Soc. C, 1798 (1968).
86. T.Kametani, O.Kusama, and K.Fukumoto, Chem.Comm., 1212 (1967).
87. M.Tomita, K.Fujitani, and T.Kishimoto, Yakugaku Zasshi, **82**, 1148 (1962).
88. Y.Inubushi, Y.Masaki, S.Matsumoto, and F.Takami, Tetrahedron Letters, 3399 (1968).
89. Y.Inubushi, Y.Masaki, S.Matsumoto, and F.Takami, J.Chem.Soc.C, 1547 (1969).
90. S.M.Kupchan, N.Yokoyama, and B.S.Thyagarijan, J.Pharm.Sci., **50**, 164 (1961).
91. E.Fujita, A.Sumi, and Y.Yoshimura, Chem.and Pharm. Bull.(Japan), **20**, 368 (1972).
92. M.Tomita, Y.Inubushi, and Y.Masaki, Jap.P.71, 21 396 (1971).
93. W.M.Whaley and C.N.Robinson, J.Org.Chem., **19**, 1029 (1954).
94. H.Kondo, H.Kataoka, and Y.Baba, Ann.Report ITSUU Lab., **4**, 20 (1953).
95. H.Kondo, H.Kataoka, and Y.Baba, Ann.Report ITSUU Lab., **5**, 55 (1954).
96. H.Kondo, H.Kataoka, and Y.Baba, Ann.Report ITSUU Lab., **6**, 41 (1955).
97. M.Tomita, K.Fujitani, and Y.Aoyagi, Tetrahedron Letters, 1201 (1967).
98. M.Tomita, K.Fujitani, Y.Aoyagi, and K.Kajita, Chem. and Pharm.Bull.(Japan), **16**, 217 (1968).
99. M.Tomita, K.Fujitani, and Y.Aoyagi, Jap.P.70, 26 280 (1970); Chem.Abs., **74**, 3761 (1971).
100. M.Tomita and Y.Aoyagi, Yakugaku Zasshi, **87**, 1425 (1967).
101. M.Tomita, Y.Masaki, K.Fujitani, and Y.Sakatani, Chem.and Pharm.Bull.(Japan), **16**, 688 (1968).
102. Y.Inubushi, Y.Aoyagi, and M.Matsuo, Tetrahedron Letters, 2363 (1969).
103. B.Franck, G.Blaschke, and G.Schlingloff, Angew. Chem., **74**, 497 (1962).
104. BRD P.1 203 784 (1966).
105. BRD P.1 207 932 (1966).
106. S.Kimoto and S.Honjo, Yakugaku Zasshi, **64**, 258 (1944); Chem.Abs., **45**, 5137 (1951).
107. X.A.Dominguez, B.Gomez, E.Homberg, and J.Slim, J.Amer.Chem.Soc., **77**, 1288 (1955).
108. E.N.Tsvetkov, I.N.Gorbacheva, and N.A.Preobrazhenskii, Zhur.Obshch.Khim., **27**, 3370 (1957).
109. Yu.S.Tsizin, O.N.Tolkachev, L.V.Volkova, and N.A.Preobrazhenskii, Zhur.Obshch.Khim., **29**, 1631 (1959).
110. L.V.Volkova, O.N.Tolkachev, and N.A.Preobrazhenskii, Dokl.Akad.Nauk SSSR, **102**, 521 (1955).
111. O.N.Tolkachev, A.A.Cherkasova, and N.A.Preobrazhenskii, Zhur.Obshch.Khim., **29**, 1627 (1959).
112. K.Fujitani, T.Kishimoto, and S.Niimura, Yakugaku Zasshi, **83**, 412 (1963).
113. K.Fujitani, T.Kishimoto, and S.Niimura, Chem.and Pharm.Bull.(Japan), **15**, 1996 (1967).
114. M.Tomita, K.Fujitani, and Y.Aoyagi, Tetrahedron Letters, 4243 (1966).
115. M.Tomita, K.Fujitani, and Y.Aoyagi, Chem.and Pharm. Bull.(Japan), **16**, 62 (1968).
116. M.Tomita, K.Fujitani, and Y.Aoyagi, Jap.P.31 667 (1967).
117. M.Tomita, Y.Aoyagi, Y.Sakatani, and K.Fujitani, Chem.and Pharm.Bull.(Japan), **16**, 56 (1968).
118. J.P.Sheth and O.N.Tolkachev, Tetrahedron Letters, 1161 (1967).
119. O.P.Belichenko and O.N.Tolkachev, Khim.Prirod.Soed., 125 (1976).
120. M.D.Mashkovskii, Priroda, No.10, 104 (1953).
121. D.A.Kharkevich, "Farmakologiya Kurarepodobnykh Sredstv" (Pharmacology of Curare-like Agents), Meditsina, Moscow, 1969.
122. T.Kametani, H.Iida, and K.Sakurai, J.Chem.Soc.C, 1024 (1971).

123. H.Kondo, H.Kataoka, and K.Kigasawa, Ann.Report ITSUU Lab., **7**, 37 (1956).
124. H.Kataoka, Ann.Report ITSUU Lab., **8**, 39 (1957).
125. R.Pummerer, D.Melamed, and H.Puttfarcken, Ber., **55**, 3116 (1922).
126. M.F.Grundon and H.J.H.Perry, J.Chem.Soc., 3531 (1954).
127. Yu.S.Tsizin, Candidate's Thesis, Moscow Institute of Fine Chemical Technology, 1961.
128. Yu.S.Tsizin and N.A.Preobrazhenskii, Zhur.Obshch. Khim., **20**, 47 (1960).
129. J.R.Crowder, M.F.Grundon, and J.R.Lewis, J.Chem. Soc., 2142 (1958).
130. J.R.Crowder, E.E.Glover, M.F.Grundon, and H.X.Kaempfen, J.Chem.Soc., 4578 (1963).
131. M.F.Grundon, J.Chem.Soc., 3010 (1959).
132. V.G.Voronin, O.N.Tolkachev, and N.A.Preobrazhenskii, Dokl.Akad.Nauk SSSR, **121**, 455 (1958).
133. V.G.Voronin, O.N.Tolkachev, and N.A.Preobrazhenskii, Dokl.Akad.Nauk SSSR, **122**, 77 (1958).
134. O.N.Tolkachev, V.G.Voronin, and N.A.Preobrazhenskii, Zhur.Obshch.Khim., **29**, 1192 (1959).
135. V.G.Voronin, O.N.Tolkachev, A.B.Prokhorov, V.P.Chernova, and N.A.Preobrazhenskii, Khim. Geterotsikl.Soed., 606 (1969).
136. O.N.Tolkachev, in "Tezisy Dokladov Sovetsko-indiiskogo Simpoziuma po Khimii Prirodnykh Soedinenii"] (Abstracts of Papers at a Soviet–Indian Symposium on the Chemistry of Natural Compounds), Tashkent, 1968, p.68.
137. V.G.Voronin, O.N.Tolkachev, and N.A.Preobrazhenskii, Izv.Vys.Ucheb.Zabed., Khim.i Khim.Tekhnol., 451 (1962).
138. O.N.Tolkachev, A.B.Prokhorov, V.G.Voronin, L.N.Krivko, A.I.Lyutik, and N.A.Preobrazhenskii, Zhur.Obshch.Khim., **31**, 1540 (1961).
139. O.N.Tolkachev, L.V.Volkova, G.S.Vasil'ev, A.B.Prokhorov, N.S.Kulachkina, and N.A.Preobrazhenskii, Khim.Geterotsikl.Soed., 831 (1969).
140. O.N.Tolkachev, L.P.Kvashnina, and N.A.Preobrazhenskii, Zhur.Obshch.Khim., **36**, 1764 (1966).
141. L.V.Volkova, V.E.Kosmacheva, V.G.Voronin, O.N.Tolkachev, and N.A.Preobrazhenskii, Khim. Geterotsikl.Soed., 522 (1967).
142. E.Hultin, Acta Chem.Scand., 17, 753 (1963).
143. E.Hultin, Acta Chem.Scand., **16**, 559 (1962).
144. M.Tomita, S.Ueda, and A.Teraoka, Tetrahedron Letters, 635 (1962).
145. S.Ueda, Yakugaku Zasshi, **82**, 714 (1962).
146. H.Kondo and S.Uyeo, Yakugaku Zasshi, **53**, 557 (1933).
147. M.Tomita, S.Ueda, and A.Teraoka, Yakugaku Zasshi, **83**, 87 (1963).
148. B.Anjaneyulu, T.R.Govindachari, and N.Viswanathan, Tetrahedron, **27**, 439 (1971).
149. M.Tomita and H.Furukawa, Yakugaku Zasshi, **83**, 676 (1963).
150. Y.Inubushi and M.Kozuba, Chem.and Pharm.Bull. (Japan), **2**, 215 (1954).
151. M.Tomita and H.Furukawa, Yakugaku Zasshi, **84**, 1027 (1964).
152. Y.Inubushi, Chem.and Pharm.Bull.(Japan), 2, 1 (1954).
153. M.Tomita and H.Furukawa, Yakugaku Zasshi, **83**, 760 (1963).

Lomonosov Moscow Institute
of Fine Chemical Technology

All-Union Scientific Research
Institute for Medicinal Plants

Translated from *Uspekhi Khimii*, **49**, 1651-1670 (1980) U.D.C. 547'13

Organometallic Compounds with Heteroatomic Chains

M.N.Bochkarev

Studies on the synthesis and chemical properties of organometallic compounds containing a chain of σ-linked atoms of heteroelements are surveyed and problems of the stability of such compounds are examined.
The bibliography includes 176 references.

CONTENTS

I.	Introduction	800
II.	Homoelemental compounds	800
III.	Two-element compounds	801
IV.	Three-element compounds	804
V.	Four-element compounds	806
VI.	The stability of polymetallic groups	806

I. INTRODUCTION

In classifying the chemistry of organometallic compounds from the standpoint of composition, it is easy to identify the field in which compounds whose molecules contain a metal–metal group are studied. Such products are referred to as organobimetallic, organotrimetallic, etc. or the terminology adopted from inorganic chemistry is more frequently used nowadays, terms such as di-, tri-, ... poly-nuclear derivatives, in accordance with the number of heteroatoms in the molecule, being employed. The first representatives of this class were obtained in the 1920s but vigorous research has developed only in the last two decades. This took place in two main directions: (1) the search for and investigation of the properties of new combinations of heteroelements M–M′ in di- and tri-nuclear derivatives and (2) the synthesis and study of polynuclear compounds. The latter include typical clusters, i.e. substances whose molecules contain a three-dimensional or planar lattice of heteroatoms, as well as a variety of such compounds comprising substances with chains of σ-linked non-organogenic atoms, which can have a linear, branched, or cyclic form. It is noteworthy that, despite the significant difference between the kinds of M–M′ bonds in typical clusters and in σ-linked chains, these two types of substances are so close in their nature and structure that in some instances the assignment of a given compound to one class or the other is arbitrary.

The amount of literature information is by no means distributed uniformly between the above two fields of study. Whereas numerous original articles and reviews (see, for example, Vyazankin et al.[1] and Vahrenkamp[2]) have been devoted to the first area of the above studies, i.e. the investigation of di- and tri-nuclear compounds, data on polynuclear systems, particularly linear and cyclic compounds, are widely scattered and are incomplete; there is particularly little information about their reactivity. This can evidently be explained by serious technical difficulties of the synthesis of substances of this kind, their isolation in a pure state, and purification. At the same time, sufficient data exist on polynuclear compounds to make it necessary to survey them and arrange them systematically.

In the present review the first attempt is made to survey the available data on the synthesis and properties of organometallic compounds containing chains of four and more σ-linked atoms of heteroelements. The latter include all metals and metalloids with the exception of C, H, N, O and the halogens†. Sulphur-containing derivatives of the type $R_2\overset{\frown}{Sn}-S-SnR_2-\overset{\frown}{S}$, etc. are considered together with their scandium and tellurium analogues, despite the fact that sulphur belongs to organogenic elements. This approach is dictated by the similarity of the properties of all chalcogeno-derivatives and by the important role which organoelemental sulphides play in the chemistry of polynuclear compounds by virtue of the high stability of M–S compounds, their relative availability, and their likely practical usefulness.

In each section the data are arranged in accordance with the position of the heteroelements in Mendeleev's table. Initially data are presented on derivatives of non-transition elements in Groups ranging from I to VI, next mixed compounds are considered, i.e. compounds containing a non-transition element and a transition metal, and in the concluding part of the given section derivatives of transition metals are discussed.

For a more complete treatment of data on polynuclear linear and cyclic compounds, certain transition metal carbonyls and carbonyl halides are considered together with organometallic derivatives.

II. HOMOELEMENTAL COMPOUNDS

Organometallic oligomers containing chains of atoms of a single element were investigated before polyelemental compounds. This group of substances is related to inorganic crystalline polymers of the type $[K_2Pt(CN)_4Br_{0.3}.3H_2O]_x^3$ and $[Ir(CO)_3Cl]_x^4$, but they differ from them fundamentally by the absence of a crystalline columnar structure and also by the constant valence of the heteroatoms in the chain.

When diorganohalogenosilanes interact with alkali metals, cyclic polysilanes, $(R_2Si)_n$ are formed[5,6]. Together with low-molecular-weight products with $n \cong 6$, unstable polymers with $n \cong 55$ are obtained. The analogous reaction of diorganohalogenogermanes also leads to cyclic polygermanes but with a smaller number of heteroatoms in the chain ($n \leqslant 6$).[7,8] In the case of tin derivatives the first stage of the reaction of

† The terms "organoelements", "polyelemental", and similar ones imply that the atoms of any element other than those enumerated are present in the given compound.

R_2SnCl_2 with active metals (Li, Na) involves the formation of bivalent tin compounds R_2Sn. They polymerise in the course of several hours yielding 8–10-membered rings $(R_2Sn)_n$.[9–11] The formation of bivalent intermediates R_2M undoubtedly occurs also in the first two instances:

$$n\,R_2MX_2 + 2nM' \rightarrow 2n\,M'X + n\,[R_2M] \rightarrow (R_2M)_n\ ;$$
M=Si, Ge or Sn; M'=Li or Na; X=halogen .

In the reviews of Satge et al., devoted to germylenes[12], and Neumann[13], devoted to stannylenes, it was shown that polymerisation reactions and reactions involving insertion in metal–metal, metal–hydrogen, and metal–halogen bonds with formation of linear and cyclic oligomers and polymers are extremely characteristic of these highly reactive species.

The reactions of the monohalides R_3MX with alkali metals give rise to linear dimers. Thus the tetrasilane $R_3SiSiR_2SiR_2$. $.SiR_3$ was obtained from R_2SiSiR_2Cl.[14,15] Cyclic stannanes $(R_2Sn)_n$ containing between 4 and 9 tin atoms in the ring are formed when diorganotin dihydrides are heated in the presence of amines[16]. In order to obtain homonuclear linear oligomers, Neumann and coworkers used the ring opening reaction of iodine[17,18]:

$$\begin{array}{l} Ph_2Ge{-}GePh_2 \\ \quad|\quad\ |\ \\ Ph_2Ge{-}GePh_2 \end{array} + I_2 \rightarrow I{-}GePh_2{-}[GePh_2]_2{-}GePh_2{-}I \xrightarrow{PhLi} Ph_3Ge{-}[GePh_2]_2{-}GePh_3$$

$$(Et_2Sn)_9 + I_2 \rightarrow I{-}SnEt_2{-}[SnEt_2]_7{-}SnEt_2{-}I\ .$$

A convenient method whereby one can sythesise Sn–Sn polymers as well as oligomers with a specified number of tin atoms has been developed[19,20]. The method consists in the hydrogenolysis of Sn–N bonds in amino- and amido-stannanes by organotin hydrides. This simple and convenient procedure for the formation of the metal–metal bond has come to be widely used also in the synthesis of two-element oligomers, examples of which are given in the next section.

An interesting Sn–Sn oligomer containing a cyclopentadienyltricarbonyltungsten substituent $\{Sn^{IV}[W(CO)_3Cp]_2\}_n$ have been obtained[21] by the reaction of $(CH_3C_5H_4)_2Sn^{II}$ with $HW(CO)_3Cp$. Unfortunately the value of n was not given for this compound, although it is apparently low:

$$(CH_3C_5H_4)_2\,Sn^{II} + 2HW(CO)_3\,Cp \xrightarrow{-CH_4C_5H_5}$$
$$\rightarrow \{Sn^{II}[W(CO)_3\,Cp]_2\} \rightarrow 1/n\,\{Sn^{IV}[W(CO)_3\,Cp]_2\}_n\ .$$

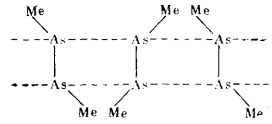
Silicon, germanium, and tin oligomers are viscous liquids, or, in rare cases, amorphous solids sparingly soluble in organic solvents. The solubility decreases with increase of molecular weight and the substances acquire a colour ranging from yellow to dark-red. Their thermal stability decreases on passing from silicon to germanium and tin and their reactivities increase in the same sequence.

Apart from Group IVB elements, homonuclear polymers are formed by phosphorus, arsenic, and antimony. Cyclic tetra-, penta-, and poly-phosphines are synthesised by the reaction of primary phosphines RPH_2 with dichlorophosphines[22,23]. The reaction of methylphosphine and methylarsine with dibenzylmercury results in the formation of the five-membered rings $(MeE)_5$ only[24]:

$$5MeEH_2 + 5\,(PhCH_2)_2Hg \rightarrow (MeE)_5 + 10PhMe + 5Hg$$
E = P or As.

The opening of rings of this type with the aid of RX leads to the formation of linear oligomers with the corresponding number of atoms of the heteroelement in the chain[25].

Penta- and hexa-nuclear formations are most typical for cyclic polyarsines, while in the linear oligomers the number of arsenic atoms can reach 50.[26,27] An X-ray diffraction study of the polymer $(MeAs)_n$, obtained by the reaction of $MeAsH_2$ with halogenoarsines or by the catalytic rearrangement of the cyclic pentomer $(MeAs)_5$, led to the conclusion that this compound has an unusual "ladder" structure[26]:



It was established that the length of the longitudinal As–As bonds (2.9 Å) appreciably exceeds the length of the transverse As–As bonds (2.4 Å) and the sum of the covalent radii (2.42 Å). On this basis, the authors[28] suggested that the aresenic atoms are linked to one another along the chain by "incomplete" bonds. In the determination of their physical properties it was found that the polymer is a semiconductor with a very low conductivity of 4.8×10^{13} cm Ω^{-1} (at 300 K).[28]

An analogous structure has been postulated for polymethylstibine $(MeSb)_n$, formed as a dark-red solid by the reaction of $MeSbH_2$ with dibenzylmercury[24]. The silylated polystibine $(Et_3SiSb)_n$ has been obtained together with ethylene and bromotriethylsilane by the reaction of $(Et_3Si)_3Sb$ with 1,2-dibromoethane[29].

III. TWO-ELEMENT COMPOUNDS

In the case of polynuclear compounds under consideration, the commonest are those whose molecules contain chains of atoms of two heteroelements. In the vast majority of cases the heteroatoms include those of silicon, germanium, or tin. The longest of the polynuclear derivatives whose existence has been demonstrated at the present time includes 11 heteroatoms: $Ph_3SiS{-}S_7{-}SSiPh_3$.[30] However, this nonasulphide should really be included among monoelemental compounds, since virtually the entire chain consists of sulphur atoms alone. The octanuclear cyclic cadmium ferrate $[-Fe(CO)_4-Cd-]_4$ should therefore be regarded as the two-element oligomer with the longest chain[31]. Several polymers are known whose molecular weights have not been determined owing to their poor solubility or low thermal stability, for example $[-Zr(SnPh_3)_2{-}SnPh_2-]_n$,[20] $[-Ge(C_6F_5)_2{-}Ge(C_6F_5)_2-Hg-]_n$,[32] and $(EtAlSe)_n$.[33,34] However, bearing in mind the considerable tendency of heteroatomic oligomers towards cyclisation, it is difficult to expect that n in these compounds exceeds 3–4. Furthermore, a more complex structure can be ruled out for the Zr–Sn polymer.

Derivatives of alkali metals with $M{-}(Si)_n{-}M$ chains (M = Li or Na; n = 4 or 5) have been obtained by the reaction of lithium or sodium and cyclic tetrasilane or pentasilane[35]. The products readily interact with organometallic halides[36,37] and are therefore suitable for the synthesis of other polynuclear compounds:

$$\begin{array}{l} Ph_2Si{-}SiPh_2 \\ \quad|\quad\ |\ \\ Ph_2Si{-}SiPh_2 \end{array} + M \xrightarrow{THF} M{-}SiPh_2SiPh_2SiPh_2SiPh_2{-}M\ ;$$

$$\xrightarrow[Cl_2BNMe_2]{Ph_2SnCl_2}$$

$$\begin{array}{ll} Ph_2Si{-}SiPh_2 & Ph_2Si{-}SiPh_2 \\ \quad|\quad\ |\ & \quad|\quad\ |\ \\ Ph_2Si\quad SiPh_2 & Ph_2Si\quad SiPh_2 \\ \quad\diagdown\quad\diagup & \quad\diagdown\quad\diagup \\ \quad\ SnPh_2 & \quad\ BNMe_2 \end{array}$$

M = Li or Na.

By allowing Ph_2GeH_2 to react with diethylmercury, Neumann and coworkers obtained the polymer $[-GePh_2-Hg-]_n$ in the form of a viscous yellowish resin[38,39]. However, this polymer cannot be regarded as an individaul compound, because its synthesis is accompanied by the liberation of metallic mercury and hence the formation of side products. It is impossible to

separate them from the polymer in view of the lability of the –Ge–Hg–Ge–Hg– chain. On heating or ultraviolet irradiation, the compound is readily demercurated with formation of polygermanes $[Ph_2Ge]_n$. The analogous silicon oligomer $[-SiMe_2-Hg-]_n$ has been synthesised by the reaction of dibromodimethylsilane with sodium amalgam[40].

The germylmercury chain becomes stable when the mercury atoms are in the γ-positions relative to one another. Thus the hexanuclear oligomer and the polymer have been obtained by the hydride method using 1,2-dihydro[tetrakis-(pentafluorophenyl)]digermane[32]:

$$(C_6F_5)_2Ge(H)-Ge(H)(C_6F_5)_2 \xrightarrow[-EtH]{EtHgGe(C_6F_5)_3} (C_6F_5)_5GeHgGe(C_6F_5)_2Ge(C_6F_5)_2HgGe(C_6F_5)_3$$

$$(C_6F_5)_2Ge(H)-Ge(H)(C_6F_5)_2 \xrightarrow[-(Me_3Si)_2NH]{[(Me_3Si)_2N]_2Hg} [-Ge(C_6F_5)_2-Ge(C_6F_5)_2-Hg-]_n .$$

Both products are thermally and hydrolytically stable and are not oxidised in air. In terms of its chemical properties and solubility, the former compound resembles $[(C_6F_5)_3Ge]_2Hg$.[41] The polymer $[-Ge(C_6F_5)_2Ge(C_6F_5)_2Hg^-]_n$ is virtually insoluble, as a result of which it exhibits a lower reactivity (for example, in oxidative addition reactions) than the above hexanuclear compound of bis[tris(pentafluorophenyl)germyl]-mercury.

Polynuclear substances having the general formula $[RMX]_n$, where M = Al, Ga, or In and X is a chalcogen, are formed in reactions of sulphur or hydrogen sulphide with R_3M [42,43] and also in the thermal decomposition of the unstable products of the interaction of hydrogen chalcogenides of the type Et_3GeSeH with triethylaluminium, triethylgallium, or triethylindium[33,34]. It has been suggested that the association of the M–X units in these substances,

$$(Et_3MX)_2M'Et \xrightarrow{\Delta} (Et_3M)_2E + 1/n\,(EtM'E)_n ;$$
M=Si or Ge; E=S, Se or Te; M'=Al, Ga or In

takes place via coordinate and not covalent bonds[34]. However, this hypothesis is based solely on a qualitative estimate of their solubility and requires additional confirmation. Analogous boron compounds (borasulphols) are known to exist as σ-heterocycles BR–S–RR–S–Br–S.[44]

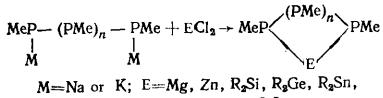
The method involving the hydrogenolysis of the Sn–N and Ge–N bonds by tin and germanium hydrides is extremely convenient for the formation of tin–germanium chains[19,20,45]:

$$2R_3GeNR'_2 + 2R_2SnH_2 \rightarrow 2R_3Ge-SnR_2H \xrightarrow[R'_2NH]{\Delta} R_3Ge-SnR_2-SnR_2-GeR_3 + H_2 ;$$

$$n\,R_2Sn(NR'_2)_2 + n\,R_2GeH_2 \rightarrow [-SnR_2-GeR_2-]_n + 2n\,R'_2NH$$
R = alkyl, aryl .

Compounds with the linear groups $Ge-(Sn)_3-Ge$, $Ge-(Sn)_4-Ge$, and GeSnGeSnGe have also been obtained by this method. In terms of their physical properties, they differ little from polygermanes and polystannanes, while in terms of their reactivity, they occupy an intermediate position.

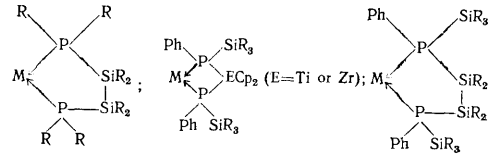
Group VB elements form a large series of polynuclear compounds. When phosphorus-containing rings $[RP]_n$ (n = 4 or 5) are opened under the influence of alkali metals, the products are linear polyphosphines containing Li, Na, and K atoms as the end-groups[46]. Their interaction with metal halides and organometallic halides yields penta- and hexanuclear heterocyclic products[46,47]:

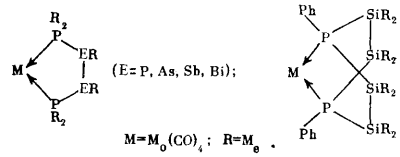


M=Na or K; E=Mg, Zn, R_2Si, R_2Ge, R_2Sn, S or Cp_2Ti; n=2.3 .

In certain cases the reactions under consideration are accompanied by the formation of polymers.

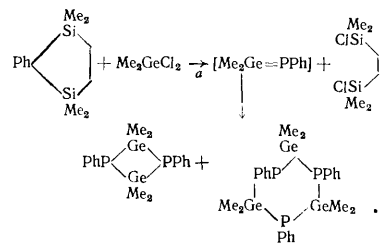
The high reactivity of alkali metal organophosphides is also used to synthesise linear silylpolyphosphines $R_3Si-(PR)_4-SiR_3$,[47] $Me_3Si-PPh-PPh-SiMe_3$,[48] $(Me_3Si)_2P-P(SiMe_3)_2$,[49,50] and $(Me_3Si)_2P-SiMe_2-P(SiMe_3)_2$.[51] The phosphorus atoms in these compounds, like those in the usual organophosphines, are capable of forming a coordinate bond with transition metal atoms. This made it possible to synthesise a series of unusual molybdenum complexes with phosphorus-containing heteroelemental polynuclear ligands[51–53]:





M=$M_0(CO)_4$; R=M_e .

The cyclic trimers $[-SiPh_2-PPh-]_3$ and $[-GePh_2-PPH-]_3$ have been obtained by the reaction of $PhPK_2$ with dichlorodiphenylsilane and $PhP(GeClPh_2)_2$ respectively[54]. Dimers and trimers with Ge–P units are also formed in reactions of dichlorodimethylgermane with phenylphosphine[55] and 2,5-disilaphospholan[56]. It has been shown[56] that in the latter case extremely active germaphosphimines $[R_2GePR']$, containing the Ge=P double bond, are formed at an intermediate stage:

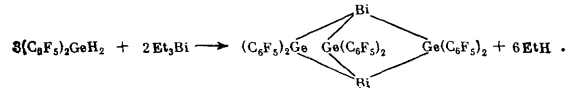


This reaction (stage *b*) is extremely characteristic of organometallic monomers. Resembling outwardly the polymerisation of olefins, it differs from the latter by the fact that it yields tetra-hexa-nuclear rings and not long linear chains.

The stannylphosphines $[-SnPh_2PPh-]_3$ and $[-SnPh_2-P(SnPh_3)-]_3$ are obtained by the reactions of triphenylstannyl-lithium with dichlorophenylphosphine[57].

Silyl-, germyl-, and particularly stannyl-phosphorus oligomers are readily hydrolysed and oxidised. In contrast to their phenyl analogues, the thermal stability of alkylstannylphosphines is low and they cannot be obtained by the above methods.

A surprisingly stable germylbismuth compound has been obtained recently by the reaction of $(C_6F_5)_2GeH_2$ with triethylbismuth[58]. An X-ray diffraction study failed to confirm the structure proposed initially for this product. It was established that its heteroelemental framework is made up of three germanium atoms and two bismuth atoms and has the form of a trigonal bipyramid[59]:

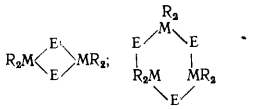


In contrast to $(C_6F_5)_3GeBiEt_2$ and $[(C_6F_5)_3.Ge]_2BiEt$, this product is not oxidised in air either in the crystalline state or in

solution. At the same time, it exhibits a higher reactivity with respect to compounds such as, for example, $Pt(PPh_3)_3$.

The interaction of the silyl sulphide $(Me_2SiS)_3$ with dichlorophenylphosphine[60] and dichlorophenylarsine[61] leads to pentanuclear cyclic oligomers $(PhMS)_3$, where M = P or As. The reaction of $(PhPS)_3$ with $(PhP)_5$ gives rise to cyclotetraphosphine sulphide PPh–PPh–S–PPh–PPh. A further twelve methods of synthesis of this substance have been published[62].

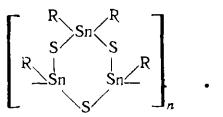
A cyclic structure is also most characteristic of oligomers with chains made up of atoms of Group IVB and VIB elements:



R = alkyl or aryl; E = S or Se; M = Si[63,64] or Ge[65–70]; Sn[71–76] or Pb[68].

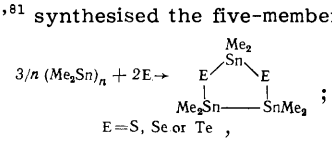
These compounds are usually obtained by the reaction of the dihalides R_2MHal_2 with a sodium chalcogenide or hydrogen sulphides in the presence of an amine. When sulphur or selenium is heated with tetra-alkyl(aryl)germanes and the corresponding stannanes, the dihydride $(C_6F_5)_2GeH_2$, or bis-(triphenylstannyl) sulphide to 100–150 °C, the same products are formed. In the majority of the reactions quoted compounds of the type of the germathione $[R_2Ge{=}S]$, whose polymerisation gives rise to tetra- or hexa-nuclear heterocycles, are apparently formed. This process has been established fairly reliably in relation to diethylgermathione in equilibrium with the cyclic trimer $(Et_2GeS)_3$.[77] The insertion of the stannathiones R_2SnS in the Sn–X bond in $R_{4-n}.SnX_n$ (X = Cl, Br, SCN, or OMe) yields a linear Sn–S oligomer[78].

The formation of linear intermediates of the type $R_3M-(Se)_n-SeR$ has been postulated in reactions of S or Se with R_4M.[68,72] In the presence of an excess of the chalcogen and for M = Sn this process leads to a product having the composition $R_4Sn_3S_4$, for which the authors postulate the polymeric cyclolinear structure[79]



One should also note the formation of cyclic and linear germyl and stannyl chalcogenides by the reaction of the sulphide $Ph_2Ge(SNa)_2$ [65] or the selenides $R_3SnSeLi$ [74] with halogeno-derivatives of the type Ph_2GeBr_2. The formation of the polymer $ClR_2Ge-(Se-GeR_2)_n-Se-GeR_2Cl$ together with the cyclic trimer has been noted in the reaction of Me_2GeCl_2 with Na_2Se,[66] but the number of Se–Ge units in the chain was not determined.

Mathiasch[80,81] synthesised the five-membered heterocycles



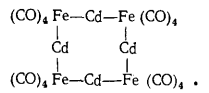
E = S, Se or Te,

by the oxidation of polymeric dimethyltin with chalcogens. Their stability decreases appreciably in the sequence S > Se > Te.

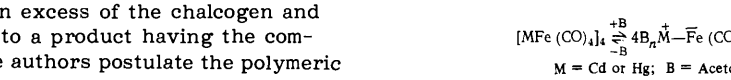
Chains having the composition Ge–S–S–Ge and $Si-S_n-Si$ (n = 5, 7, 9) are known. The former have been obtained by the interaction of triphenylgermanethiol or sodium triphenylgermyl sulphide with iodine[65,82] and the latter have been synthesised by the reaction of sodium triphenylsilyl sulphide with the dichloropolysulphides S_mCl_2 (m = 3, 5, 7).[30]

All compounds with chains consisting of Si(Ge, Sn) and sulphur atoms are colourless liquids (with R = alkyl) or crystalline solids (with R = aryl), which are stable in air. Selenium derivatives are less stable, decomposing rapidly in moist air with liberation of selenium. Both sulphur and selenium derivatives with a linear structure as a rule disproportionate on heating to 150–200 °C, forming four-membered hexanuclear heterocyles $(-MR_2-X-)_n$. X-Ray diffraction studies showed that the latter have the boat configuration and can exist in two crystalline modifications—tetragonal and monoclinic[83–85].

Compounds with chains comprising transition and non-transition metal atoms have been synthesised as some of the first polynuclear compounds. Thus cadmium and mercury carbonylferrates $[MFe(CO)_4]_4$ (M = Cd or Hg) have been obtained by the reactions of $Fe(CO)_5$ with cadmium and mercury salts[86,87]. An interesting method for the reversible degradation of such compounds under the influence of Lewis bases, which has been proposed recently, made it possible to obtain $[CdFe(CO)_4]_n$ in a crystalline form and to determine its structure[31]. It was found that the compound is a planar virtually square eight-membered heterocycle:



The reversible degradation method (involving the homolysis of M–M bonds) is important, because it makes it possible to solve one of the most difficult problems in the chemistry of polynuclear compounds—the purification of sparingly soluble and involatile substances with a high molecular weight. The crude polymer is depolymerised by simple dissolution in a basic organic solvent. The resulting solution of monomeric units solvated by solvent molecules, $[MFe(CO)_4].B_n$, is purified by the usual procedures and repolymerised by the gradual elimination of the solvent *in vacuo*[31,88,89].

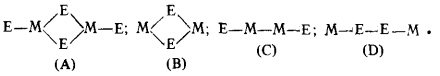


M = Cd or Hg; B = Acetone, THF, amine, etc.

We may note that in the given case polymerisation leads to cyclic oligomers and not linear macromolecules.

Compounds with chains comprising aluminium (gallium, indium) and transition metal atoms have apparently not been obtained hitherto#. However, the extremely stable Ir–Tl bond in the complexes $[(RCO_2)_2Tl-Ir(O_2CR)ClPPh_3]$ (R = alkyl)[91] showed that such oligomers can be entirely stable.

Group IVB elements form linear, cyclic, and mixed linear-cyclic polynuclear compounds with Mn, Fe, Ru, Os, Co, and Pt. The (A),[92–98] (B),[89,99–115] (C),[116–124] and (D)[125–132] structures are commonest (E is a Group IVB element and M is a transition metal):



(A) (B) (C) (D)

Six-membered Co–Sn and Fe–Ge heterocycles[133] and the linear nonanuclear compound $[(Ph_3Sn)_3Zr]_2SnPh_2$ [20] are also known. X-Ray diffraction data and measurements of the magnetic susceptibility showed that in certain compounds with structures (A) and (B) there is a direct M–M bond[93–95]. It has been suggested that deformations of rings (B) can lead to the cleavage of the M–E bonds and the formation of linear structures of the type $R_2E \rightarrow M-M \leftarrow ER_2$.[134] However, this has not been confirmed[115].

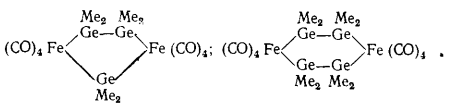
The gallium (indium)–manganese carbonyl complexes, described by Preut and Haupt[90] belong to the series of typical clusters and are therefore outside the scope of this review.

The principal methods for the synthesis of oligomers (A) and (B) include the reactions of metal carbonyls with organogermanium and organotin hydrides and halides. There is an interesting reaction of dicyclopentadienyltin with $Fe_2(CO)_9$ leading to the formation of the ring $[Cp_2SnFe(CO)_4]_2$ containing the Cp–Sn σ-bond, while the initial stannane has a "sandwich" structure[89]. The interaction of the hydrides R_3EH (E = Si or Ge) with the carbonyls $M_3(CO)_{12}$ leads to linear compounds (B). One or several carbonyl groups in the latter can be substituted by other ligands, for example, cyclopentadiene[119-121]. Chains with structure (D) are formed on alkylation with a Grignard reagent of halogeno-derivatives of the type $Cp(CO)_2Fe–GeCl_3$ when dicyclopentadienyltin interacts with metal carbonyls and in reactions of the dihalides R_2GeBr_2 with an anion of the type $(CO)_5Mn^-$.

The reaction involving the insertion of the zero-valent triphenylphosphine complex of platinum in the Ge–H bond of 1,2-dihydrodigermane has been proposed for the synthesis of a germylplatinum chain[132]:

$$\begin{matrix}(C_6F_5)_2Ge—H\\ |\\ (C_6F_5)_2Ge—H\end{matrix} + Pt(PPh_3)_3 \rightarrow \begin{matrix}(C_6F_5)_2Ge—Pt(PPh_3)_2—H\\ |\\ (C_6F_5)_2Ge—Pt(PPh_3)_2—H\end{matrix} + 2PPh_3 .$$

The reaction of 1,2-dichlorogermane with disodium iron tetracarbonyl leads to penta- and hexa-nuclear heterocycles[135]:



It has been suggested[136] that the interaction of tin tetrachloride with $Ru_3(CO)_{12}$ leads to the formation of a compound with the $Cl–Ru(CO)_4–Ru(CO)_4–Ru(CO)_4–SnCl_3$ chain. In contrast to fairly stable compounds having the structures (A), (B), (C), and (D), this oligomer is rapidly converted into the dinuclear complex $(CO)_4Ru(Cl)SnCl_3$ on heating. $Os_3(CO)_{12}$ reacts analogously[137].

On interaction with NH_4S_5, dicyclopentadienyltitanium dichloride forms compounds containing a heterocycle made up of five sulphur atoms and a titanium atom: $Cp_2\overline{TiSSSSS}$.[138] The conformational transformations of this product have been investigated[139].

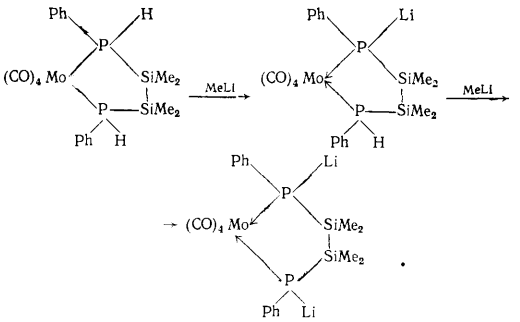
The complexes $[CpM(CO)_3M']_n$, where M = Mo or W and M′ = Cu or Ag, are examples of two-element polynuclear compounds whose skeleton is made up only of transition metal atoms[140]. They are obtained by the reaction of cyclopentadienyltricarbonyl-molybdenum or -tungsten anions with copper(I) and silver salts respectively. The complexes $[Co(CO)_4Ag]_n$, $[Co(CO)_4Cu(NH_3)_4]_n$, and $[(PhO)_3PFe(CO)_2.NOAg]_n$ have been synthesised similarly. On the basis of the stretching vibration frequencies of the CO groups in the infrared spectra, the authors postulate the presence of covalent M–M′ bonds in these compounds. The determination of n for the complex $[(Bu_3P)Co(CO)_3Ag]_n$ in various solvents showed that the degree of its polymerisation varies with the basicity of the solvent. Thus $n = 4$ in benzene and $n = 3$ in chloroform. Pyridine and other strong Lewis bases decompose these cyclic oligomers to monomeric units of the type $Co(CO)_4Ag.L$ (L is a solvent molecule). All the complexes decompose in the light and are oxidised in air.

The formation of an unstable intermediate with the linear Os–Os–Os–Au chain in the reaction of $Os_3(CO)_{12}$ with $ClAuPPh_3$ has been suggested[141].

IV. THREE-ELEMENT COMPOUNDS

The number of known compounds whose chains are made up of atoms of three different heteroelements is much smaller than that of two-element systems.

The only compound of this type, containing alkali metal atoms, has apparently been obtained by Johannsen and Stelzer[53], who metallated a bidentate phosphine ligand in a molybdenum complex:



A mercury derivative, with the Ge–Si–Hg–Si–Ge chain has been synthesised by the hydride method using the germylsilane $Et_3GeSiEt_2H$ as the starting material[142].

A large series of chalcogen-containing pentanuclear compounds have been obtained on the basis of the organoelemental hydride chalcogenides R_3MEH (M = Si, Ge, or Sn; E = S, Se, or Te). Their interaction with metals[143], metal alkyls[33,34,144,145], and organodielemental derivatives[146,147] proceeds readily and yields the required products with high yields as a rule

$$2(RO)_3SiSH + M \rightarrow (RO)_3SiSMSSi(OR)_3 + H_2 ;$$
$$M = Ca, Sr \text{ or } Ba$$
$$2Et_3SiSeH + Et_2M \rightarrow Et_3SiSeMSeSiEt_3 + 2EtH ;$$
$$M = Zn \text{ or } Cd$$
$$2Et_3SiSH + Et_3M \rightarrow (Et_3SiS)_2MEt + 2EtH ;$$
$$M = Al, Ga \text{ or } In$$
$$2Et_3SiTeH + (Et_3Ge)_2Hg \rightarrow Et_3SiTeHgTeSiEt_3 + 2Et_3GeH .$$

Zinc, cadmium, and mercury derivatives are stable under normal conditions and consist of colourless or pale-brown crystalline substances. The low solubilities and high melting points (decomposition temperatures) of the zinc and cadmium compounds apparently indicate their association. Chains based on Group IIIB metals have a very low thermal stability. In all cases, with the exception of $(Et_3SiS)_3AlEt$, they decompose fully in the course of the reaction. The reactions of triethylaluminium, triethylgallium, and triethylindium with an excess of the hydride chalcogenide lead to compounds of the $(Et_3SiTeAlTe)_n$ series[34], for which there is a possibility of both σ-linked Te–Al chains and associated coordination compounds with Te → Al bonds. These substances are evidently the products of the decomposition of unstable intermediates of the type $(Et_3GeSe)_3Al$. However, one should note that thermal decomposition of the analogous boron derivative $(Me_3SiS)_3B$ leads to products of another composition[148].

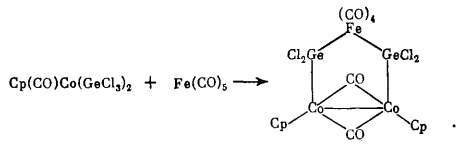
The tetranuclear organoelemental cadmium and mercury sulphides and selenides, for example, $(C_6F_5)_3GeSHgGe(C_6F_5)_3$, are obtained by the insertion of elemental chalcogens in the Ge–Hg, Ge–Cd, or Si–Hg bonds[70,149-151]:

$$(R_3Ge)_2Hg + 1/8\,E_8 \rightarrow R_3Ge—E—Hg—GeR_3 ;$$
$$E = S \text{ or } Se .$$

The insertion of a second chalcogen atom with formation of a pentanuclear chain of the type Ge–S–Hg–S–Ge is uncharacteristic of these reactions and is observed only on interaction of germylcadmium with sulphur. In contrast to the symmetrical pentanuclear compounds described above, all the tetranuclear chalcogen-containing substances decompose rapidly at room temperature (with the exception of the stable C_6F_5 derivative).

The condensation of $Cp_2Ti(SH)_2$ with dichlorodimethylsilane and similar compounds in the presence of an amine and also with dimethylsiloxane leads to cyclic products with the SiSTiSSi groups[152]. Ring closure takes place via the oxygen atom or siloxane groups.

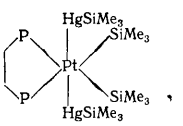
A stable heterocyclic compound incorporating the atoms of two transition metals has been synthesised via the reaction[133]



Metal carbonyl anions are frequently used in the synthesis of three-element oligomers. For example, the reaction of the anion $Me_3SiOs(CO)_4^-$ with $Me_3SiRu(CO)I$ gives rise to a compound with the SiOsRuSi group[153]. An unexpected pentanuclear linear complex $[Me_3GeRu(CO)_4]_2Hg$ has been isolated in the reaction of $Me_3GeRu(CO)_4^-$ with the iodide $CpFe(CO)_2I$.[96] The authors explain the formation of the mercury derivative by the fact that sodium amalgam was used to synthesise the anion.

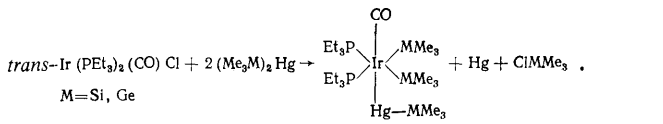
Frequent attempts have been made to employ carbonyl anions and dianions as well as carbonyl hydrides in polycondensation reactions with organometallic halides, for example, R_2SnCl_2, in order to form linear polymeric structures[118,154]. However, in most cases the reactions terminated by the formation of four-membered heterocycles. Collman and coworkers, who were the first to undertake an extensive search for methods of synthesis of organometallic polymers, were able to synthesise two linear pentanuclear complexes[154, 155]. The first of these $(CO)_5Re-SnBu_2-Os(CO)_4-SnBu_2-Re(CO)_5$, was obtained by the reaction of *trans*-$(ClBu_2Sn)_2.Os(CO)_4$ with rhenium pentacarbonyl hydride. The second, $(CO)_5Mn-GePh_2-Fe(CO)_4-GePh_2-Mn(CO)_5$ were synthesised by treating $Fe_2(CO)_9$ with two moles of $(CO)_5MnGePh_2H$. The iron derivative has the *trans*-configuration, which the authors believe gives grounds for the hope of obtaining longer chains.

Several methods, frequently used to synthesise three-element compounds, are based on the use of a series of compounds $(R_3M)_2Hg$, where M = Si, Ge or Sn, as the initial organoelemental mercury derivatives for the synthesis of three-element compounds. These methods include exchange reactions with halogen-containing transition metal complexes, oxidative addition reactions with zero-valent transition metal complexes, and a combination of these reactions. Thus the photochemical reactions of $Fe(CO)_5$ and $Fe_2(CO)_9$ with $(Me_3Si)_2Hg$, which lead to the pentanuclear compound $[cis\text{-}Fe(CO)_4SiMe_3]_2Hg$, are regarded as oxidative addition of the $Fe(CO)_4$ species to the Si–Hg bond[156]. By allowing bis(trimethylsilyl)mercury to react with $Cl_2Pt(Ph_2PCH_2)_2$, Glockling and Pollock[157] obtained a pale-red substance to which they attributed the following structure on the basis of spectroscopic data:



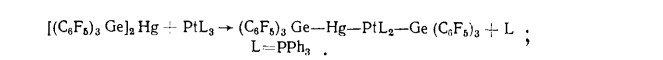
However, elemental analysis of this product was not carried out and, bearing in mind the very low stability of the analogous germanium groups $R_3Ge-Hg-Pt-GeR_3$, where R = alkyl[158], the proposed structure appears doubtful.

A similar combination of the exchange method and the method involving oxidative addition to a metal in a low-valence state obtains also in the reaction[159]



It is of interest to note that the Hg–Ir bond is chemically the most inert in the Si(Ge)–Hg–Ir–Si(Ge) chain formed.

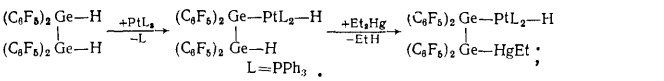
It was observed in 1976 that the triphenylphosphine complexes of zero-valent platinum and palladium are readily inserted in the M–M′ bond in compounds of the type $R_3Ge-Hg-GeR_3$.[160] The tetranuclear products formed proved to be entirely thermally stable in the case of $R = C_6F_5$:



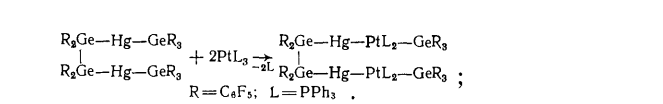
This made it possible to obtain a series of compounds with a wide variety of chains: GeHgPdGe, SnHgPtSn, GeCdPtGe, and GeZnPtGe.[158,160] The reaction involving $Ni(PPh_3)_4$ apparently leads to the analogous nickel derivatives, but they could not be isolated in a pure state.

X-Ray diffraction and ^{31}P NMR data have shown that the Pt–Hg complexes have a square planar *cis*-structure probably with a small admixture of the *trans*-isomer. In the palladium analogue both isomers are present in approximately equal proportions. Qualitative comparison established that their thermal and chemical stabilities decrease in the sequences Hg > Cd > Zn, Pt > Pd > Ni, and Ge > Sn. When $(C_6F_5)_3Ge.HgPtL_2Ge(C_6F_3)_3$ reacts with reagents such as Br_2 and hydrogen chloride, the Ge–Hg and Hg–Pt bonds are the first to be cleaved. The complexes are colourless or pale-yellow crystalline substances readily soluble in benzene, acetone, and tetrahydrofuran (THF).

The complex $(Ph_3Ge)_2CdPd(PPh_3)_2$, which the authors also believe to contain the metal chain GeCdPdGe, has been obtained similarly[161]. It has been established that a second PtL_2 species is not inserted in the remaining Ge–Hg bond in chains of the type GeHgPtGe, which can be explained both by steric hindrance and by changes in the nature of the Ge–Hg bond after the addition of platinum to the Hg atom. 1,2-Dihydro-1,1,2,2-tetrakis(pentafluorophenyl)digermane and a mercury derivative based on it have therefore been used to synthesise compounds with a longer chain. The product of the insertion of PtL_2 in one of the Ge–H bonds in $HGe(C_6H_5)_2-Ge(C_6F_5)_2H$ was made to react with Et_2Hg. Despite the excess of hydride, this results in the evolution of only one equivalent of ethane and a tetranuclear compound is formed[132]:

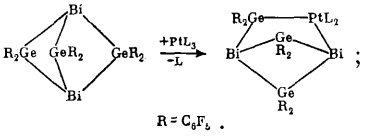


In the oligomer $(C_6F_5)_3GeHgGe(C_6F_5)_2Ge(C_6F_5)_2HgGe(C_6F_5)_3$ the atoms are separated by the Ge–Ge group and the reaction of this compound with a platinum complex leads to the addition of two equivalents of $Pt(PPh_3)_2$, as was to be expected[162]:



The resulting diplatinum octanuclear compound is entirely stable. Its reactivity, solubility, and infrared and ultraviolet spectra are similar to those of the tetranuclear complex $(C_6F_5)_3GeHgPtL_2Ge(C_6F_5)_3$. The great length of the polymetallic chain is manifested only by the appearance of broadened low-intensity bands in the long-wavelength part of the electronic absorption spectrum. It is easy to show by calculation that not less than nine steric (*cis*-, *trans*-) and structural isomeric forms can exist for this product (PtL_2 is not inserted in the Ge–Ge bond under the conditions adopted)[158]. This finding clearly demonstrates the feature characteristic of all the polyelemental oligomers, which consist in the fact that the difficulties associated with the identification and study of the reactivities of these compounds increase sharply after even a slight increase of the length of the heteroelement chain.

The triphenylphosphine complexes of zero-valent platinum are also inserted in the Ge–Bi bond of the tricyclic compound $R_2GeBiGeR_2BiGeR_2$:[59]



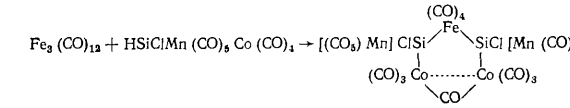
$R = C_6F_5$.

It is of interest that the second equivalent of PtL_2 is not inserted despite the presence of several Ge–Bi bonds remote from the platinum involved in the addition process. The structure of the product isolated from benzene in the form of dark cherry-red crystals was established by X-ray diffraction. The molecule of the complex contains the non-planar heterocycle PtGeBiGeBi with the $(C_6F_5)_2Ge$ bridging group.

The Ge–S(Se) and Hg–Fe groups proved to be inactive with respect to $Pt(PPh_3)_3$. In reactions with $(C_6F_5)_3GeXH$ (X = S or Se) platinum adds to the X–H bond with the simultaneous formation of a small amount of the pentanuclear compounds $[(C_6F_5)_3GeX]_2Pt(PPh_3)_2$ as side products[132]. In the interaction of $(ClHg)_2Fe(C_5H_5N)$ with PtL_3 the Hg–Cl bond is attacked. The platinum derivatives formed in the intermediate stages are unstable and are rapidly demercurated[163].

V. FOUR-ELEMENT COMPOUNDS

So far as we are aware, only five compounds whose chains contain the atoms of four heteroelements of different kinds have been synthesised at the present time. The first of these was obtained in the form of dark-green crystals by the reaction[164]



The labile compounds $Et_3SiXHgGeEt_3$ (X = S, Se, or Te) were synthesised by the protodegermylation of bis(triethylgermyl)mercury by the chalcogenide hydrides Et_3SiXH.[147]

In the interaction of tris(triphenylphosphine)platinum with $(C_6F_5)_3GeHgSn(C_6F_5)_3$ the PtL_2 species is evidently inserted in both Ge–Hg and Hg–Sn bonds with formation of the isomers GeHgPtSn and GePtHgSn, which cannot be separated[158]. There are virtually no data on the reactivities of these compounds.

Five-element chains have apparently not been obtained hitherto.

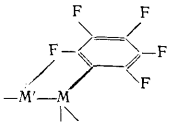
VI. THE STABILITY OF POLYMETALLIC GROUPS

One of the main conditions for the successful synthesis of organometallic compounds with chains comprising atoms of heteroelements is the stability of the resulting M–M bonds. The stability of the products is determined, like that of the usual mononuclear organometallic compounds[165], by quantum-chemical, thermodynamic, and kinetic factors. The first of these is manifested by the distinct dependence of the stability of polynuclear compounds on the positions in the Periodic Table of the heteroelements making up the chain. The stability of the oligomers incorporating atoms of *d* elements as a rule increases in each subgroup with increase of the atomic weight of the metal. The opposite variation of the stability of the M–M bond with the atomic weight of the element can be seen for *p* elements; the IIIB subgroup is intermediate in this respect.

The thermodynamic aspect is understood as the fulfilment of the condition $G_1 - G_2 > 0$ for stable compounds, where G_2 is the free energy of the oligomer system and G_1 the free energy of the system formed after the dissociation (spontaneous or under the influence of the attacking reagent) of the weakest or most reactive M–M bond. Presumably, in polymerisation and polycondensation reactions of organometallic compounds, the thermodynamic factor determines primarily the formation of small rings and not long linear molecules as in the case of *C*-derivatives. The possibility of the formation of conjugated groups as well as resonance effects lead to an appreciable energy gain for heterocycles compared with macrochains of the same elements.

The kinetic parameters constitute a no less important factor governing the stability of organopolymetallic compounds. The high activation energy for the initial decomposition reaction can lead to the stabilisation of thermodynamically unstable compounds or compounds with a low stability. Organic substituents at the heteroatoms play an important role in this respect. It is known that the presence of groups such as neopentyl-, t-butyl, trimethylsilylmethyl, etc. increases sharply the stability of the polymetallic compound[166-168]. For mononuclear compounds, the same effect has been explained[165] by the steric shielding of the metal atoms by bulky substituents from direct attack in collisions and also by the decrease of the efficiency of energy transfer to the M–C bond (which determines the stability of these compounds) in consequence of the distribution of energy among the vibrational levels of the substituents themselves. All these factors are equally applicable to compounds containing heteroelement chains§.

Evidently another cause leads to the stabilisation of pentafluorophenyl derivatives[158,169,170], because the bulk of the C_6F_5 ring is only slightly greater than that of the phenyl group. It has been suggested[59] that the stability of the compounds is achieved in this case by virtue of the intramolecular coordination of the unshared electron pairs of the *ortho*-fluorine atoms to the vacant orbitals of the heteroatom M′ in the β-position relative to the C_6F_5 substituent.



§ However, one cannot agree with the view[165] that polychloromethyl and the lower perfluoroalkyl groups are sterically hindered.

The spatial disposition of the o-F and M′ atoms favours such coordination[158,171]. We may note that, for this reason, i.e. by virtue of the molecular geometry, the coordination of o-F to the α-M atom, postulated for certain compounds $(C_6F_5)_n$ M (see. for example, Razuvaev et al.[172]), appears less probable. Evidently the coordination involving the β-heteroatom is impossible for compounds where M′ has no suitable vacant orbitals, for example, S, Se, Te, and Bi. In such cases the introduction of C_6F_5 substituents does not stabilise the polyelement groups[59,173]. On the other hand, if M′ is strongly electrophilic, then a rapid redistribution of bonds with liberation of the metal fluoride takes place in the five-membered coordination ring formed. Nor can one exclude the possibility of the dissociation of such compounds at the M–M′ bond with formation of highly reactive nucleophilic species of the type of $(C_6F_5)_3Ge^-$, which vigorously attack the C_6F_5 rings of the neighbouring molecules. For this reason, in the series of compounds with active M′ (Li, Pr, Nd) [174,175] the pentafluorophenyl derivatives are less stable than their H-analogues. On the other hand, in compounds with less active M′ (Zn, Cd, Hg, Pt) [158,169,170,176] intramolecular coordination increases the stability of the oligomer, formally increasing the energy of the M–M′ bonds in the M′–M–C_6F_5 fragments.

The chemistry of polynuclear organometallic compounds with linear and cyclic structures clearly exhibits the characteristic features of both the chemistry of the usual organometallic compounds and of carbochain polymers. At the same time oligomers and polymers with heteroelement chains have a number of specific properties, which require the development of fundamentally new methods of synthesis of such compounds and method for their investigation. These difficulties greatly inhibit studies on the field under consideration. However, virtually unlimited potential possibilities of varying the properties of organopolymetallic compounds (by selecting a wide variety of combinations of heteroatoms in the chains and their ligand environment) make substances of this class extremely attractive as convenient models for the solution of a number of theoretical problems in chemistry and physics. For the same reasons, the above compounds are extremely promising in the context of applied problems (high-temperature superconductivity, ferromagnetism, catalysis, etc.). There is no doubt that studies on organometallic polymers will develop vigorously in the immediate future.

REFERENCES

1. N.S.Vyazankin, G.A.Razuvaev, and O.A.Kruglaya, Organometal.Chem.Rev., A, **3**, 323 (1968).
2. H.Vahrenkamp, Angew.Chem., **90**, 403 (1978).
3. J.F.Shchegolev, Phys.Stat.Sol., A, **12**, 9 (1972).
4. A.H.Reis, V.S.Hagley, and S.W.Peterson, J.Amer. Chem.Soc., **99**, 4186 (1977).
5. C.A.Burkhard, J.Amer.Chem.Soc., **71**, 963 (1949).
6. H.Gilman, D.J.Peterson, A.W.Jarvie, and H.J.S.Winkler, J.Amer.Chem.Soc., **82**, 2076 (1960).
7. W.P.Neumann and K.Kuhlein, Tetrahedron Letters, 1541 (1963).
8. W.P.Neuman and K.Kuhlein, Ann.Chem., **702**, 13 (1967).
9. W.P.Neumann, Angew.Chem., **74**, 122 (1962); **75**, 225 (1963).
10. N.N.Zemlyanskii, E.M.Popov, and K.A.Koshechkov, Dokl.Akad.Nauk SSSR, **146**, 1335 (1962).
11. H.Gilmann, W.H.Atwell, and F.K.Cartledge, Adv. Organometal.Chem., **4**, 1 (1966).
12. J.Satge, M.Massol, and P.Riviere, J.Organometal. Chem., **56**, 1 (1973).
13. W.P.Neumann, "IInd International Conference on the Organometallic and Coordination Chemistry of Ge, Sn and Pb, Nottingham, U.K., 1977", Plenary lecture.
14. H.Gilman, T.C.Wu, H.A.Hartzfeld, G.A.Guter, A.G.Smith, J.J.Goodman, and H.E.Scott, J.Amer. Chem.Soc., **74**, 561 (1952).
15. G.R.Wilson and A.G.Smith, J.Org.Chem., **26**, 557 (1961).
16. W.P.Neumann and K.Konig, Angew.Chem., **74**, 215 (1962); **76**, 892 (1964).
17. W.P.Neumann and K.Kuhlein, Ann.Chem., **683**, 1 (1965).
18. W.P.Neumann and J.Redain, Ann.Chem., **672**, 32 (1964).
19. H.M.J.C.Creemers, J.G.Noltes, and G.J.M.Van der Kerk, Rec.trav.chim., **83**, 1284 (1964).
20. H.M.J.C.Creemers, "Hydrostannolysis, A General Method for Establishing Tin–Metal Bonds", Schotanus and Jens, Utrecht, 1967.
21. P.G.Harrison and S.R.Stobart, J.Chem.Soc., Dalton Trans., 940 (1973).
22. P.C.Crofts, Quart.Rev., **12**, 341 (1958).
23. W.A.Henderson, M.Epstein, and F.S.Seichter, J.Amer. Chem.Soc., **85**, 2462 (1963).
24. A.L.Rheingold and P.Choudhury, J.Organometal Chem., **128**, 155 (1977).
25. H.Hoffmann and R.Grunewald, Chem.Ber., **94**, 186 (1961).
26. M.Ya.Kraft, G.M.Borodina, I.N.Strel'tsova, and Yu.T.Struchkov, Dokl.Akad.Nauk SSSR, **131**, 1074 (1960).
27. M.Ya.Kraft, Dokl.Akad.Nauk SSSR, **131**, 1342 (1960).
28. A.L.Rheingold, J.E.Lewis, and J.M.Belloma, Inorg. Chem., **12**, 2845 (1973).
29. N.S.Vyazankin, O.A.Kruglaya, G.A.Razuvaev, and G.S.Semchikova, Dokl.Akad.Nauk SSSR, **166**, 99 (1966).
30. F.Feher and H.Goller, Z.Naturforsch., **22b**, 1224 (1967).
31. R.D.Ernst, T.J.Marks, and J.A.Ibers, J.Amer.Chem. Soc., **99**, 2090 (1977).
32. M.N.Bochkarev, L.P.Maiorova, and G.A.Razuvaev, "Tezisy Dokladov I Vsesoyuznoi Konferentsii po Metalloorganicheskoi Khimii, Moskva, 1979" (Abstracts of Reports at the Ist All-Union Conference on Organometallic Chemistry, Moscow, 1979), p.126.
33. M.N.Bochkarev, A.I.Charov, and N.S.Vyazankin, Izv. Akad.Nauk SSSR, Ser.Khim., 1995 (1977).
34. N.S.Vyazankin, M.N.Bochkarev, and A.I.Charov, J.Organometal.Chem., 27, 175 (1971).
35. H.Gilman, F.W.G.Fearon, and R.L.Harrell, J.Organometal.Chem., **5**, 592 (1966).
36. E.Hengge and U.Brychcy, Monatsh.Chem., **97**, 1309 (1966).
37. E.Hengge and D.Wolfer, Angew.Chem., **85**, 304 (1973).
38. W.P.Neumann, Angew.Chem., **75**, 679 (1963).
39. W.P.Neumann and K.Kuhlein, Ann.Chem., **683**, 1 (1965).
40. E.Wiberg, O.Stecher, H.J.Andraschek, L.Kreurbicher, and E.Staude, Angew.Chem., **75**, 516 (1963).
41. M.N.Bochkarev, L.P.Maiorova, and N.S.Vyazankin, J.Oganometal.Chem., **55**, 89 (1973).
42. L.I.Zakharkin and V.V.Gavrilenko, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 1391 (1960).
43. K.Geiersberger and H.Galster, Z.anorg.Chem., **274**, 289 (1953).
44. E.Wiberg and W.Z.Sturm, Z.Naturforsch., **10b**, 113 (1955).
45. H.M.J.C.Creemers and J.G.Noltes, J.Organometal. Chem., 7, 237 (1967).
46. K.Issleib, C.Rockstroch, J.Duchek, and E.Fluck, Z.anorg.Chem., **360**, 77 (1968).
47. K.Issleib, Fr.Krech, and E.Lapp, Syn.React,Inorg. Metal-Org.Chem., 7, 253 (1977).

48. M.Baudler, H.Hallob, A.Zarkadas, and E.Tolls, Chem.Ber., **106**, 3962 (1973).
49. H.Schumann and R.Fischer, J.Organometal.Chem., **88**, C 13 (1975).
50. G.Fritz and W.Nolderch, Z.anorg.Chem., **431**, 76 (1977).
51. O.Stelzer and E.Unger, Chem.Ber., **108**, 2232 (1975).
52. O.Stelzer, E.Unger, and V.Wray, Chem.Ber., **110**, 3430 (1977).
53. G.Johannsen and O.Stelzer, Chem.Ber., 110, 3438 (1977).
54. H.Schumann and H.Benda, Chem.Ber., **104**, 333 (1971).
55. H.Schumann and M.Schmidt, Angew.Chem., **23**, 1049 (1965).
56. C.Couret, J.Satge, J.D.Andriamizaka, and J.Escudie, J.Organometal.Chem., **157**, C **35** (1978).
57. H.Schumann, H.Kopf, and M.Schmidt, Chem.Ber., **93**, 3295 (1964).
58. M.N.Bochkarev, N.I.Gur'ev, and G.A.Razuvaev, J.Organometal.Chem., **162**, 289 (1978).
59. Yu.T.Struchkov, "Abstracts of the IXth International Conference on Organometallic Chemistry, Dijon, France, 1979", p.15.
60. E.W.Abel, D.A.Armitage, and R.P.Bush, J.Chem. Soc., 5584 (1964).
61. E.W.Abel and D.A.Armitage, J.Organometal.Chem., **5**, 326 (1966).
62. M.Baudler, Th.Vakratsas, D.Koch, and K.Kipker, Z.anorg.Chem., **408**, 225 (1974).
63. M.Schmidt and H.Ruf, Z.anorg.Chem., **321**, 270 (1963).
64. M.N.Bochkarev, L.P.Sanina, and N.S.Vyazankin, Zhur.Obshch.Khim., **39**, 135 (1969).
65. M.C.Henry and W.E.Davidson, Canad.J.Chem., **41**, 1276 (1963).
66. I.Ruidish and M.Schmidt, J.Organometal.Chem., **1**, 160 (1963).
67. M.Schmidt and H.Ruf, J.Inorg.Nuclear Chem., **25**, 557 (1963).
68. M.Schmidt and H.Schumann, Z.anorg.Chem., **325**, 130 (1963).
69. S.Mathur, G.Chandra, A.K.Rai, and R.C.Mehrotra, J.Organometal.Chem., **4**, 294 (1965).
70. M.N.Bochkarev, L.P.Maiorova, N.S.Vyazankin, and G.A.Razuvaev, J.Organometal.Chem., **82**, 65 (1974).
71. M.Schmidt and H.Ruf, Chem.Ber., **96**, 784 (1963).
72. M.Schmidt and H.Schumann, Chem.Ber., **96**, 780 (1963).
73. M.Schmidt, H.J.Dersin, and H.Schumann, Chem.Ber., 1428 (1962).
74. H.Schumann, K.F.Thom, and M.Schmidt, J.Organometal.Chem., **2**, 361 (1964).
75. W.T.Schwartz, Jr. and H.W.Post, J.Organometal. Chem., **2**, 425 (1964).
76. E.J.Kupchik and P.J.Calabretta, Inorg.Chem., **4**, 973 (1965).
77. H.Lavayssiere, G.Dousse, J.Barrau, J.Satge, and M.Bouchaut, J.Organometal.Chem., **161**, C 59 (1978).
78. A.G.Davies and P.G.Harrison, J.Chem.Soc.C, 2035 (1970).
79. M.Schmidt and H.Schumann, Chem.Ber., **96**, 462 (1963).
80. B.Mathiasch, J.Organometal.Chem., **122**, 345 (1976).
81. B.Mathiasch, Z.anorg.Chem., **432**, 269 (1977).
82. L.Birkofer, A.Ritter, and H.Goller, Chem.Ber., **96**, 3289 (1963).
83. B.Menzebach and P.Bleckmann, J.Organometal.Chem., **91**, 291 (1975).
84. H.J.Jacobsen and B.Krebs, J.Organometal.Chem., **136**, 333 (1977).
85. M.Dräger, A.Blecher, H.-J.Jacobson, and B.Krebs, J.Organometal.Chem., **161**, 319 (1978).
86. H.Hock and H.Stuhlmann, Chem.Ber., **61**, 2097 (1928).
87. F.Feigl and P.Krumholz, Z.anorg.Chem., **215**, 242 (1933).
88. T.J.Marks and A.R.Neumann, J.Amer.Chem.Soc., 95, 769 (1973).
89. A.B.Cornwell, P.G.Harrison, and J.A.Richards, J.Organometal.Chem., **108**, 47 (1976).
90. H.Preut and H.-J.Haupt, Chem.Ber., **107**, 2860 (1971).
91. P.I.Van Vlien and K.Vrieze, J.Organometal.Chem., **139**, 337 (1977).
92. S.A.R.Knox, B.A.Sosinsky, and F.G.A.Stone, J.Chem.Soc., Dalton Trans., 1647 (1975).
93. K.Triplet and M.D.Curtis, Inorg.Chem., **15**, 431 (1976).
94. M.M.Crozat and S.F.Watkins, J.Chem.Soc., Dalton Trans., 2512 (1972).
95. H.Preut and H.-J.Haupt, Z.anorg.Chem., **422**, 47 (1976).
96. S.A.R.Knox and F.G.A.Stone, J.Chem.Soc.A, 2874 (1971).
97. J.D.Cotton, S.A.R.Knox, and F.G.A.Stone, J.Chem. Soc.A, 2758 (1968).
98. S.F.Watkins, J.Chem.Soc.A, 1552 (1969).
99. O.Kahn and M.Bigorgne, J.Organometal.Chem., **10**, 137 (1967).
100. A.B.Cornwell and P.G.Harrison, J.Chem.Soc., Dalton Trans., 2017 (1975).
101. C.J.Gilmore and P.Woodward, J.Chem.Soc., Dalton Trans., 1387 (1972).
102. S.D.Ibekwe and M.J.Newlands, J.Chem.Soc.A, 1783 (1967).
103. J.D.Cotton, S.A.Knox, J.Paul, and F.G.A.Stone, J.Chem.Soc.A, 264 (1967).
104. T.J.Marks and G.W.Grunkewich, J.Organometal.Chem., **91**, C 9 (1975).
105. E.H.Brooks, M.Elder, W.A.G.Graham, and D.Hall, J.Amer.Chem.Soc., **90**, 3587 (1968).
106. C.J.Fritchie, R.M.Sweet, and R.Schunn, Inorg. Chem., **6**, 749 (1967).
107. C.J.Gilmore and P.Woodward, J.Chem.Soc., Dalton Trans., 1387 (1972).
108. F.Hein and E.Henser, Z.anorg.Chem., **225**, 125 (1947).
109. F.Hein, P.Kleinert, and W.Jehn, Naturwiss., **44**, 34 (1957).
110. W.Hieber and R.Breu, Chem.Ber., **90**, 1270 (1957).
111. M.T.Jones, Inorg.Chem., **6**, 1249 (1967).
112. R.Kummer and W.A.G.Graham, Inorg.Chem., 7, 1208 (1968).
113. R.M.Sweet, C.J.Fritchie, and R.A.Schumann, Inorg. Chem., 6, 749 (1967).
114. R.D.Adams and F.A.Cotton, J.Amer.Chem.Soc., **92**, 5003 (1970).
115. R.D.Adams, F.A.Cotton, W.R.Cullen, D.L.Hunter, and L.Mithichuk, Inorg.Chem., **14**, 1395 (1975).
116. S.A.R.Knox, C.M.Mitchell, and F.G.A.Stone, J.Organometal.Chem., 16, P 67 (1969).
117. J.D.Cotton, S.A.R.Knox, and F.G.A.Stone, Chem. Comm., 965 (1967).
118. S.A.R.Knox and F.G.A.Stone, J.Chem.Soc.A, 2559 (1969).
119. A.Brookes, J.Howard, S.A.R.Knox, F.Gordon, A.Stone, and P.Woodward, Chem.Comm., 587 (1973).
120. J.D.Edwards, J.A.K.Howard, S.A.R.Knox, V.Riere, and F.G.A.Stone, J.Chem.Soc., Dalton Trans., 75 (1976).
121. S.A.R.Knox, R.P.Phillips, and F.G.A.Stone, J.Chem. Soc., Dalton Trans., 658 (1974).

122. R.A.Sosinsky, S.A.R.Knox, and F.G.A.Stone, J.Chem.Soc., Dalton Trans., 1633 (1975).
123. B.J.Aylett, Inorg.Nuclear Chem.Letters, **4**, 79 (1968).
124. B.F.G.Johnson, R.D.Johnston, P.L.Josty, J.Lewis, and I.G.Williams, Nature, **213**, 901 (1967).
125. I.A.Thomson and W.A.G.Graham, Inorg.Chem., **6**, 1875 (1967).
126. A.N.Nesmeyanov, K.N.Anisimov, N.E.Kolobova, and S.S.Denisov, Izv.Akad.Nauk SSSR, Ser.Khim., 2287 (1971).
127. A.N.Nesmeyanov, K.N.Anisimov, N.E.Kolobova, and A.V.Antonov, Izv.Akad.Nauk SSSR, Ser.Khim., 160 (1966).
128. A.N.Nesmeyanov, K.N.Anisimov, N.E.Kolobova, and A.V.Antonov, Dokl.Akad.Nauk SSSR, **176**, 844 (1967).
129. K.D.Bos, E.J.Bulten, and J.G.Noltes, J.Organometal. Chem., **71**, C 52 (1974).
130. A.L.Spek, K.D.Bos, E.J.Bulten, and J.G.Noltes, Inorg.Chem., **15**, 339 (1976).
131. K.D.Bos, E.J.Bulten, J.G.Noltes, and A.L.Spek, J.Organometal.Chem., **92**, 33 (1975).
132. M.N.Bochkarev, G.A.Razuvaev, and L.P.Maiorova, "Abstracts of the IInd International Conference on Organometallic and Coordination Chemistry of Ge, Sn, and Pb, Nottingham, U.K., 1977", A 22.
133. M.J.Bennet, W.Brooks, M.Elder, W.A.G.Graham, D.Hall, and R.Kummer, J.Amer.Chem.Soc., **92**, 208 (1970).
134. T.J.Marks and G.W.Grunkewich, J.Organometal.Chem., **91**, C 9 (1975).
135. K.Triplett and M.D.Curtis, J.Organometal.Chem., **107**, 23 (1976).
136. R.K.Pomeroy, M.Elder, D.Hall, and W.A.G.Graham, Chem.Comm., 381 (1969).
137. J.R.Moss and W.A.G.Graham, J.Organometal.Chem., **18**, P24 (1969).
138. H.Köpf, B.Block, and M.Schmidt, Chem.Ber., **101**, 272 (1968).
139. E.W.Abel, M.Booth, and K.G.Orrell, J.Organometal. Chem., **160**, 75 (1978).
140. P.Hackett and A.R.Manning, J.Chem.Soc., Dalton Trans., 1606 (1975).
141. C.W.Bradford, W.van Bronswijk, R.J.H.Clark, and R.S.Nyholm, J.Chem.Soc.A, 2889 (1970).
142. E.N.Gladyshev, N.S.Vyazankin, E.A.Arkhangel'skaya, G.A.Razuvaev, and S.P.Korneva, Dokl.Akad.Nauk SSSR, **183**, 338 (1968).
143. M.Wojnowska and W.Wojnowski, Z.anorg.Chem., **403**, 179 (1974).
144. M.N.Bochkarev, A.I.Charov, and N.S.Vyazankin, Izv. Akad.Nauk SSSR, Ser.Khim., 2320 (1969).
145. A.I.Charov, M.N.Bochkarov, and N.S.Vyazankin, Izv.Akad.Nauk SSSR, 2825 (1971).
146. M.N.Bochkarev, L.P.Maiorova, A.I.Charov, and N.S.Vyazankin, Zhur.Obshch.Khim., **41**, 1408 (1971).
147. M.N.Bochkarev, L.P.Maiorova, A.I.Charov, and N.S.Vyazankin, Dokl.Akad.Nauk SSSR, Ser.Khim., 1375 (1972).
148. E.W.Abel, D.A.Armitage, and R.P.Bush, J.Chem.Soc., 3045 (1965).
149. E.N.Gladyshev, N.S.Vyazankin, V.S.Andreevichev, A.A.Klimov, and G.A.Razuvaev, J.Organometal. Chem., **28**, C 42 (1971).
150. E.N.Gladyshev, V.S.Andreevichev, A.A.Klimov, N.S.Vyazankin, and G.A.Razuvaev, Zhur.Obshch. Khim., **42**, 1077 (1972).
151. V.T.Bychkov and N.S.Vyazankin, Dokl.Akad.Nauk SSSR, 2614 (1970).
152. C.Ungurenasu and I.Haiduc, Rev.Roumaine Chim., **13**, 957 (1968).
153. S.A.R.Knox and F.G.A.Stone, J.Chem.Soc.A, 3147 (1970).
154. J.P.Collman, D.W.Murphy, E.B.Fleischer, and D.Swift, Inorg.Chem., **13**, 1 (1974).
155. J.P.Collman, J.K.Hoyano, and D.W.Murphy, J.Amer. Chem.Soc., **95**, 3424 (1973).
156. W.Jetz and W.A.G.Graham, J.Organometal.Chem., **69**, 383 (1974).
157. F.Glockling and R.J.I.Pollock, J.Chem.Soc., Dalton Trans., 2259 (1974).
158. M.N.Bochkarev, G.A.Razuvaev, L.P.Maiorova, N.P.Makarenko, V.J.Sokolov, V.V.Bashilov, and O.A.Reutov, J.Organometal.Chem., **131**, 399 (1977).
159. K.A.Hooton, J.Chem.Soc.A, 1251 (1971).
160. V.I.Sokolov, V.V.Bashilov, O.A.Reutov, M.N.Bochkarev, L.P.Maiorova, and G.A.Razuvaev, J.Organometal. Chem., **112**, C 47 (1976).
161. V.T.Bychkov, S.N.Titova, and I.V.Lomakova, Zhur. Obshch.Khim., **46**, 2629 (1976).
162. M.N.Bochkarev, L.P.Maiorova, and G.A.Razuvaev, Zhur.Obshch.Khim., **50**, 903 (1980).
163. V.I.Sokolov and G.Z.Suleimanov, Inorg.Chem.Acta, **25**, L 149 (1977).
164. K.M.Abraham and G.Urry, Inorg.Chem., 12, 2850 (1973).
165. G.A.Domrachev, "Tezisy Dokladov, II Vsesoyuznoe Soveshchanie po Metalloorganicheskim Soedineniyam dlya Polucheniya Metallicheskikh i Okisnykh Pokrytii, Gor'kii, 1977" (Abstracts of Reports. The IInd All-Union Conference on Organometallic Compounds for the Preparation of Metallic and Oxide Coatings, Gorky, 1977), p.102.
166. U.Blaukat and W.P.Neumann, J.Organometal.Chem., **63**, 27 (1973).
167. B.V.Fedot'ev, O.A.Kruglaya, and N.S.Vyazankin, Dokl.Akad.Nauk SSSR, 713 (1974).
168. O.A.Kruglaya, G.S.Kalinina, B.I.Petrov, and N.S.Vyazankin, J.Organometal.Chem., **46**, 51 (1972).
169. M.N.Bochkarev, L.P.Maiorova, and N.S.Vyazankin, J.Organometal.Chem., **55**, 89 (1973).
170. M.N.Bochkarev, S.P.Korneva, L.P.Maiorova, V.A.Kuznetsov, and N.S.Vyazankin, Zhur.Obshch. Khim., **44**, 308 (1974).
171. A.Karipides, C.Forman, R.H.P.Thomas, and A.T.Reed, Inorg.Chem., **13**, 811 (1974).
172. G.A.Razuvaev, V.N.Latyaeva, G.A.Kilyakova, and G.Ya.Mal'kova, Dokl.Akad.Nauk SSSR, **191**, 629 (1970).
173. M.N.Bochkarev, G.A.Razuvaev, and N.S.Vyazankin, Izv.Akad.Nauk SSSR, Ser.Khim., 1820 (1975).
174. M.N.Bochkarev, N.S.Vyazankin, L.N.Bochkarev, and G.A.Razuvaev, J.Organometal.Chem., **110**, 149 (1976).
175. G.S.Kalinina, L.N.Bochkarev, G.A.Razuvaev, and M.N.Bochkarev, "Abstracts of the XIXth International Conference on Coordination Chemistry, Prague, Czechoslovakia, 1978", p.65.
176. M.N.Bochkarev, L.P.Maiorova, S.P.Korneva, L.N.Bochkarev, and N.S.Vyazankin, J.Organometal. Chem., **73**, 229 (1974).

Institute of Chemistry,
USSR Academy of Sciences,
Gorky

Translated from *Uspekhi Khimii*, **49**, 1671-1686 (1980) U.D.C. 621.793.1:547,1'13

The Formation of Inorganic Coatings in the Decomposition of Organometallic Compounds

G.A.Domrachev and O.N.Suvorova

The present status of the methods for producing inorganic coatings from the vapour phase by the decomposition of organometallic compounds (OMC) is considered critically and systematically. The methods are classified in terms of physicochemical features and the physical procedures involved. The efficiencies of various methods for the preparation of coatings from the vapour phase in the thermal decomposition of OMC and the possibilities of their employment for a specific alteration of the properties of the coatings obtained are compared. Patent data on various procedures and devices used in the formation of inorganic coatings from the vapour phase in the decomposition of OMC are widely used.
The bibliography includes 96 references.

CONTENTS

I. Introduction 810
II. Chemical features of the use of organometallic compounds for the preparation of coatings from the vapour phase 810
III. The use of the physicochemical characteristics of the decomposition of organometallic compounds for the deposition of coatings 811
IV. Physical characteristics of the methods for the deposition of coatings from the vapour phase 816

I. INTRODUCTION

There exist numerous patents and other publications on the deposition of inorganic coatings from the vapour phase in the thermal decomposition of organometallic compounds (OMC) and metal carbonyls. In the USSR a group of investigators and technologists led by Academician G.A.Razuvaev is concerned with systematic studies and technological development of these processes.[1] Razuvaev showed an interest in the isolation of metals from organometallic compounds in thermal reactions as early as the 1920s.[2] These studies subsequently served as a basis for research by Razuvaev and his students into the thermal decomposition and photodecomposition of OMC in solution and then in the vapour phase; these studies have been surveyed in a monograph[1].

However, the literature contains no systematic review of the existing methods for the deposition of inorganic coatings from the vapour phase on decomposition of OMC; in the present review an attempt is made at such a systematic account.

II. CHEMICAL FEATURES OF THE USE OF ORGANOMETALLIC COMPOUNDS FOR THE PREPARATION OF COATINGS FROM THE VAPOUR PHASE

The use of OMC for processes where their intermediate formation transfers a metal to the substrate makes it possible to carry out the deposition at low temperatures and to increase the concentration of the working compound as a result of the lower decomposition temperature of the OMC and their higher vapour pressure at low temperatures[1]. The fundamental mechanism of the deposition of films from the vapour phase in the thermal decomposition of OMC can be formulated as follows:

$$R_nM\ (\text{solid or liq.}) \xrightarrow{t^\circ} R_nM\ (\text{gas}),$$
$$R_nM\ (\text{gas}) \xrightarrow[\text{support}]{t^\circ} R_nM\ (\text{ads.}),$$
$$R_nM\ (\text{ads.}) \xrightarrow{t^\circ} M\ (\text{solid})/\text{support} + nR\ (\text{ads.}),$$
$$nR\ (\text{ads.}) \xrightarrow{t^\circ} nR\ (\text{gas}).$$

These stages of the process determine its chemical nature and constitute the basis for the development of methods of deposition of coatings. In order to select the deposition procedure and to carry out the latter in a specific technological scheme, it is necessary to analyse in detail each stage of the process.

In the preparation of a multicomponent coating, for example a binary coating, a mixture of the necessary number of OMC of different metals, for example two, or a mixture of the OMC of one metal and the hydride of another element, is used[3-7]:

$$MR_n + M'R'_m \rightarrow M{-}M' + nR + mR',$$
$$Me_3Ga + AsH_3 \rightarrow GaAs + 3CH_4,$$
$$Me_4Pb + Me_2Te \rightarrow PbTe + x\,C_nH_m,$$
$$Me_3Ga + AsMe_3 \rightarrow GaAs + x\,C_nH_m.$$

It has been established that the intermediates in the joint decomposition of two OMC are, as in the case of Me_3Ga and Me_3As, oligomeric and polymeric fragments containing the $(R{-}Ga{-}As)_x$ group[6]; these fragments cannot catalyse the subsequent decomposition of the OMC mixture.

Hence it follows that, for the decomposition of binary compounds and OMC, one can employ the thermal decomposition of molecular complexes of OMC of the type $Me_3Ga.AsMe_3$ or organobimetallic compounds containing covalent M–M or M–E bonds[8]:

$$R_nM{-}M'R_m\ (\text{solid or liq.}) \xrightarrow{t^\circ} R_nM{-}M'R_m\ (\text{gas}) \xrightarrow[t^\circ]{\text{support}} \rightarrow (n+m)R\ (\text{gas}) + M{-}M'\ (\text{solid})/\text{support} + mR\ (\text{gas}).$$

Adsorption and desorption processes can also be involved in this scheme. In the general case the formation of a two-component system on the surface requires that the reaction between the metals liberated or the decomposition reaction must proceed via the formation of intermediate compounds containing the M–M′ bond[7].

Bearing in mind the high efficiency of the metal transfer to the support with the aid of OMC, one can also employ the metal transport reaction with the aid of organic radicals or ligands. The best known classical example of a transport

reaction with participation of free radicals is provided by the method of Paneth mirrors[9]:

$$R_nM\ (gas) \xrightarrow{t^\circ} M(solid) + n\,R\ (gas) \xrightarrow{+M'_l(solid)} R_mM\ (gas) \rightarrow \xrightarrow[t^\circ]{support} \rightarrow M'_l(solid)/support + m\,R\ (gas).$$

Free radicals, generated by the thermolysis of readily available OMC, for example Me_2Hg, behave as transporting agents for the transfer of solid metal through the gas phase to the region of higher temperatures; the support on which the metal film is formed by the thermal dissociation of the OMC formed is placed in this region. Such processes include the transport of nickel by carbon monoxide as a result of the reversibility of the reaction[10,11]:

$$Ni(solid) + 4CO \rightleftarrows Ni(CO)_4 \rightleftarrows Ni(solid)/support + 4CO.$$

Here carbon monoxide functions as the metal-transporting ligand. A metallic alloy, for example MM', can be transported similarly[12]:

$$MM'(solid) + (n + m)\,R\ (gas) \rightleftarrows \begin{cases} \rightarrow R_nM{-}M'R_m\ (gas) \\ \rightarrow R_nM\ (gas) + R_mM'\ (gas) \end{cases} \xrightarrow{t^\circ} MM'(solid) + (n+m)R\ (gas).$$

Combinations of these methods for the transport of metal are also possible.

However, a common feature of all these procedures is a high volatility of the OMC, a low decomposition temperature of the OMC with liberation of the metal, the obligatory presence of organic OMC decomposition products and sometimes their strong influence on the process, the possibility of the adsorption and secondary reactions of the OMC decomposition products, and a comparatively high vapour pressure of the organic OMC decomposition products at the deposition temperatures.

Although the first two factors are favourable from the standpoint of the use of OMC for the formation of coatings, the negative influence of the decomposition products can sometimes abolish altogether the positive effect. For the successful realisation of the OMC thermal decomposition processes, it is therefore necessary to employ special procedures for the deposition of coatings from the vapour phase in which the harmful effects of the decomposition products are diminished or eliminated with the aid of mass and heat transfer phenomena and mechanical and chemical methods.

The chemical features of the procedures for the deposition of coatings are determined by the composition and structure of the OMC and by the addition of various chemical reagents. In terms of the composition of the gas–vapour phase for the coating, the methods can be classified as follows:

(1) methods using an individual OMC;

(2) methods using a mixture of individual OMC;

(3) methods using an individual OMC mixed with the hydrides of other elements or with readily decomposed inorganic metal compounds;

(4) methods using individual OMC or their mixture in an atmosphere of a reactive gas [reducing to the metals (H_2),[13,14] oxidising (O_2),[13] etc.], which improves the elemental and phase compositions of the coatings;

(5) methods using OMC in mixtures with additives which serve as energy transferring agents or with "quenching agents" for the excited states (for example, iodine[15,16], amines[17–19], ammonia[15,20], diolefins[21,22], ferrocene[23], and other OMC[24–27]);

(6) methods using OMC in mixtures with added decomposition catalysts (halogen derivatives[28], sulphur derivatives[29] for the decomposition of bisarenechromium, transition metals for aluminium hydride complexes[30], and transition metal salts for metallocenes[31,32]);

(7) methods using OMC in a mixture with added active hydrogen atom donors in radical reactions (glycols for the decomposition of copper acetylacetonate[33,34], hydrogenated aromatic compounds of the type of dihydrobiphenyl, tetralin, cyclohexadiene, and cyclohexene[1], amines[35], etc.);

(8) methods using OMC in a mixture with added surfactants, which are adsorbed more strongly than the decomposition products, but less so than the OMC themselves and are displaced by the latter from the surface—for example, ferrocene in the decomposition of tri-isobutylaluminium[36];

(9) methods using OMC in the presence of added reactive gases (H_2S, H_2Te, NH_3, CO_2, etc.) and vapours (H_2O), which modify the elemental and phase compositions of the coating[1].

The above methods make it possible to obtain a wide variety of coatings whose composition corresponds to both pure metals, binary alloys, or semiconductor compounds and to pure oxides, carbides, nitrides, sulphides, etc. Furthermore it is possible to obtain mixed coatings of the type of carboxides[37], carbonitrides[38], etc.

The content of impurities in the phase composition of coatings can be regulated both by the chemical procedures enumerated above and by physicochemical and purely physical methods.

III. THE USE OF THE PHYSICOCHEMICAL CHARACTERISTICS OF THE DECOMPOSITION OF ORGANOMETALLIC COMPOUNDS FOR THE DEPOSITION OF COATINGS

There are many ways of depositing films and coatings from the vapour phase of OMC in their thermal decomposition; numerous devices and different types of apparatus have been developed, embodying various methods for deposition from the vapour phase.

The methods of deposition of coatings from the vapour phase can be classified in terms of the principal process parameters. The methods can differ in terms of (1) the procedure used to generate the vapour phase, (2) the pressure of the reaction mixture in the decomposition zone, (3) the state of the article being coated in the reactor, (4) the method used to heat the article being coated, and (5) the state of the principal units of the reactor.

1. Methods for the Generation of the Vapour Phase of the OMC

The methods for the deposition of coatings from the vapour phase in the decomposition of OMC differ in the procedure used to generate the vapour phase, which can be significantly non-equilibrium, or can be in equilibrium with the condensed OMC phase. Depending on this factor, when different procedures are used to generate the vapour phase, it is possible to attain markedly different maximum rates of deposition, which depend on the degree of supersaturation of the vapour phase by the metal, which is determined in its turn by the concentration of the OMC in the vapour.

Deposition from a non-equilibrium vapour phase can be carried out under both static and dynamic conditions. In the former case the process is usually performed with a deficiency

of OMC in a closed volume where the OMC vaporises completely and forms an unsaturated vapour, which is not in equilibrium with the condensed phase (since the latter is absent). The decomposition of the OMC under such conditions proceeds as a rule at low temperatures in the kinetic region, the aim being to obtain coatings with controllable physical properties (for example, the preparation of films for measuring devices).[39]

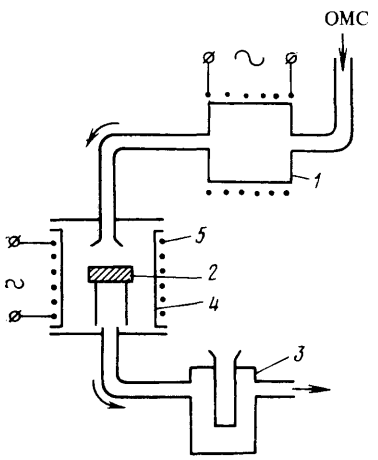


Figure 1. Deposition of coatings from a non-equilibrium vapour phase under dynamic conditions established in an autonomous evaporator: 1) evaporator; 2) support; 3) trap; 4) reactor; 5) heater.

The deposition of coatings from a non-equilibrium vapour phase under dynamic conditions is most frequently used. The equilibrium vapour phase generated by the evaporation of the condensed (liquid or solid) OMC phase is transported via pipes to the heated article to be coated, which is located in the reaction chamber. In the absence of a condensed phase in the pipes and under the conditions of high temperatures near the article to be coated and its dilution by the vapours of the decomposition products, the initially saturated OMC equilibrium vapour phase becomes unsaturated with respect to the OMC and is no longer in equilibrium with the OMC condensed phase. The state of this vapour phase, i.e. the degree of its deviation from the state of saturation with respect to the OMC and its state of equilibrium, is difficult to estimate and control. As a result of the decomposition of the OMC, the state of the vapour phase changes still further due to constant dilution by the decomposition products. For the practical employment of such a non-equilibrium vapour phase, one therefore creates dynamic conditions and uniform fluxes of the vapour phase near the surface of the article to be coated. Under such conditions, it is possible to attain reproducible rates of deposition of the coating.

However, owing to the unsaturation and the non-equilibrium nature of the OMC vapour phase, it is impossible to achieve high rates of deposition of coatings. The devices most frequently employed in this case are provided with autonomous evaporators located outside the limits of the reaction chamber used for the deposition[10,40-43] (Fig.1). The principles of the operation of the evaporator can be extremely varied, but usually one employs closed or flow compartments ("stills") and bubbling devices[44].

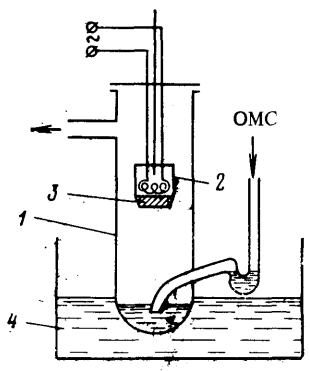


Figure 2. Deposition of coatings from an equilibrium vapour phase generated under static conditions: 1) reactor; 2) heater; 3) support; 4) thermostat.

The deposition of coatings from the vapour phase in equilibrium with the condensed (solid or liquid) OMC phase is a more effective process. Here it is possible to establish higher concentrations of the OMC in the vapour phase; since the vapour phase is in a state of dynamic equilibrium with the condensed phase, the vapour is enriched in the organometallic component when the latter is consumed in the deposition process. The process can be carried out under static or dynamic conditions such that the condensed (usually liquid) OMC phase in equilibrium with the vapour phase can exist. Under static conditions, the equilibrium OMC vapour phase is generated by the evaporation of the solid or liquid OMC within the reaction chamber. The location of the OMC condensed phase being evaporated can be below the article to be coated[45,46] or above it[47] (Figs.2 and 3). Furthermore, it has been suggested[46] that the condensed (solid) phase be placed around the article to be coated (Fig.4).

Under conditions where the condensed phase is located below the article to be coated, the deposition process takes place under least favourable conditions. This is because, in the course of the formation of the OMC decomposition products and the increase of their pressure, the partial pressure of the OMC diminishes and conditions for the supersaturation of the OMC vapour are frequently created, which is accompanied by the formation of aerosol particles of the condensed phase ("dew point"). These particles of the condensed OMC phase precipitate and the overall OMC concentration in the vapour phase diminishes. The additional vaporisation of this part of the OMC as a result of the heat radiated from the superheated (relative to the vapour temperature) support cannot occur owing to the negative temperature gradient in the direction of the fall of the particles. When this method is used, one usually observes a "peak" rate of deposition of the coating[48,49] at the initial instant of the coating process. In other words, the rate of formation of the coating initially increases to a maximum and then falls approximately by two orders of magnitude in consequence of

the decrease of the effective concentration of the OMC in the vapour phase[49].

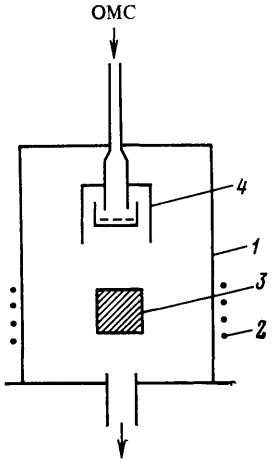


Figure 3. Deposition of coatings from a vapour phase in equilibrium with a static liquid OMC phase located below the article: 1) reactor; 2) heater; 3) support; 4) evaporator.

If the condensed OMC phase in equilibrium with the vapour phase is located on the particle to be coated and the outlet for the removal of the decomposition products ("evacuation") is placed below, then more favourable conditions are created for increasing the OMC concentration in the vapour phase[47]. Even under the "dew point" conditions, where part of the OMC condenses on increasing the pressure of the decomposition products and is precipitated in the form of liquid and solid particles, the OMC concentration in the vapour phase increases as a result of the re-evaporation of these particles as they fall freely downwards under the conditions of a positive temperature gradient towards the article to be coated, which is placed below the vaporisation zone.

We may note that the case under consideration, where the condensed OMC phase in equilibrium with the vapour phase is located above the article to be coated, cannot be classified as purely static: although the main bulk of the condensed phase is in a static state, the condensed OMC particles are in a state of dynamic equilibrium with the vapour. The use of a vertical temperature gradient (the temperature above the article is higher than under it) makes it possible to set up a pressure gradient which gives rise to a flux of particles and vapour along the surface of the article to be coated and this converts the procedure from one involving a static condensed phase in equilibrium with the vapour into a method with dynamic vapour and condensed phases in a flux[47]. Such conditions ensure higher rates of deposition of coatings than under static and dynamic conditions from a non-equilibrium vapour and under conditions of a static condensed phase located below the article to be coated and involved in equilibrium with the vapour phase.

The methods in which the condensed phase is placed around the article to be coated are a logical conclusion of the development of procedures for deposition from an equilibrium vapour phase in the presence of a static condensed OMC phase[46].

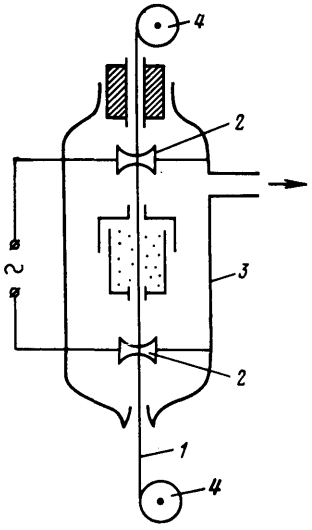


Figure 4. Deposition of coatings from an equilibrium vapour phase with a translational movement of the article: 1) filament (wire) to be coated; 2) electrical terminals; 3) reactor; 4) drums for rewinding the wire.

This method is usually applied when an article of small area is to be coated (for example, when a heated filament is drawn through a channel in a compressed substance undergoing decomposition[46]). The vaporisation of the substance being decomposed takes place as a result of its being heated by the heat emitted from the filament being coated. This method[46] makes it possible to generate a vapour phase in equilibrium with the static condensed phase.

However, in the presence of a quasi-closed reaction space bounded by the condensed OMC phase and when the area to be coated is large, the atmosphere may be supersaturated by the decomposition products, which leads to the appearance of stagnant zones, a decrease of the rate of deposition of the coating, and its contamination as a result of increased adsorption of secondary reaction products (carbon, oxides, carbides, resins, etc.). The method is then actually converted into a procedure in which coatings are deposited from a vapour phase in equilibrium with a static condensed phase under static (or quasi-static) conditions relative to the dynamics of the vapour phase. The first two instances ensure, in contrast to the last, the dynamics of the vapour phase in equilibrium with the condensed phase, although the mass fluxes established in the first case decrease the concentration of the OMC in the vapour near the substrate, while in the second the OMC concentration is actually increased in the descending vapour streams.

The use of methods involving the generation of a vapour phase in equilibrium with the condensed phase directly in the reactor for the deposition of coatings, in contrast to the procedures described above in which a non-equilibrium vapour phase is used, makes it possible to prepare coatings using involatile OMC with low vapour pressures and low decomposition temperatures. The introduction of the condensed OMC phase directly into the reactor creates conditions for the molecular distillation of involatile OMC[50] and significantly extends the scope of the deposition method under consideration compared with the previous procedures using a non-equilibrium vapour, the transport of which is relatively ineffective for involatile substances.

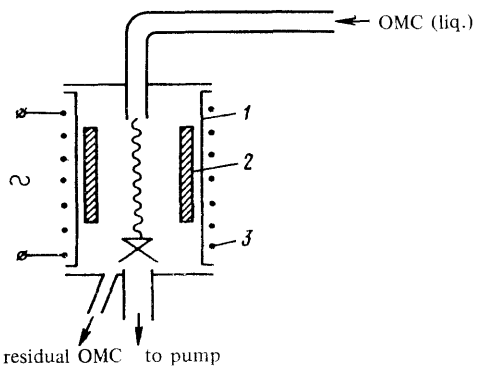


Figure 5. Deposition of coatings from an equilibrium vapour phase generated under dynamic conditions: 1) reactor; 2) support; 3) heater.

By analogy with this situation, which is observed in distillation processes, methods for the generation of a dynamic vapour phase in equilibrium with a moving liquid phase, are the most effective and have the greatest range of applications. One of the effective methods for the generation of the vapour phase in the deposition process which have been suggested[51–57] involves the use of a falling film of liquid OMC, its solution, or its suspension in a suitable solvent (Fig.5). The method permits a continuous and effective generation of the vapour phase in equilibrium with a moving spontaneous stream of the liquid phase (by analogy with all the advantages of film distillation—see Krel[50], p.301). The most important advantages of film vaporisation are that there is no need to heat thick layers of liquid for effective vaporisation[58], as happens in vaporisation from a still. This provides considerable possibilities for the employment of a wide range of involatile and readily decomposed OMC for the deposition of coatings.

The deposition of coatings by this procedure[51–57] on the surface of the heated article takes place with a continuous flow of liquid containing the OMC (liquid compound, solution, or suspension taken separately or in an appropriate combination) along the treated surface under the influence of gravitational force. As a result of the vaporisation of the liquid under the influence of the heat emitted from the article, the concentration of the vapour of the working OMC in equilibrium with its condensed phase is ensured. As the liquid moves along the surface of the article being coated, it is heated to higher temperatures, which promotes a more vigorous vaporisation of the substance being decomposed and leads to an increase of its concentration in the vapour phase and hence to an increase in the rate of deposition of the coating. An increased concentration of the vapour of the OMC being decomposed is also promoted by the fact that the particles of the condensed phase formed as a result of the condensation of the vapour, as the pressure of the decomposition products increases, migrate under the influence of gravitational force along the surface of the article being coated and are heated and revaporised as when deposition occurs from a static equilibrium vapour phase and the condensed OMC phase is located above the article to be coated.

Thus, over the entire pathway traversed by the liquid being decomposed, the saturated OMC vapour is in equilibrium with it. This leads to an appreciable increase of the steady-state OMC concentration in the vapour phase during the deposition of the coating and ensures high rates of formation of the latter; furthermore, this ensures the formation of more homogeneous coatings, with respect to thickness and chemical composition, owing to the smaller changes in the relative concentrations in the OMC vapour.

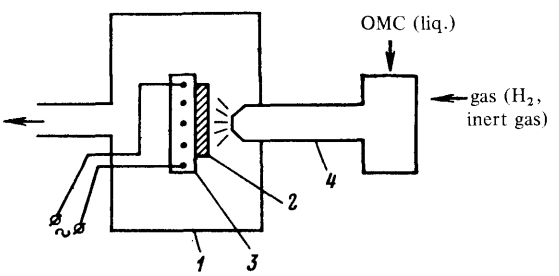


Figure 6. Deposition of coatings from an equilibrium vapour phase under dynamic atomisation conditions: 1) reactor; 2) support; 3) heater; 4) atomiser nozzle.

In this way it is possible to achieve rates of deposition of coatings of approximately 1–2 mm h^{-1} (or >10–20 μm min^{-1}), which is 10–100 times greater than the usual rates of deposition from the vapour phase by the methods already described. This procedure is most effective in the following cases: for the formation of thick coatings, particularly for the internal surfaces of hollow articles; when it is necessary to achieve a continuous process; when the rate of deposition of the coating is the rate-limiting stage of the process (when the process is automated). The method proposed in a number of patents[51–57] can be applied both for a freely falling liquid film (this is desirable for long articles and surfaces) and when the working liquid containing the OMC flows via the guiding surface under the influence of gravitational force and then along the surface to be coated starting from its upper section. The distance between the guiding surface and the

surface to be coated must ensure the heating and vaporisation of the moving liquid as a result of the thermal emission from the heated article. If heating (thermostatting) of the guiding surface is used to ensure uniform vaporisation of the liquid, then the minimum distance between the guiding and coated surfaces is determined by the distance over which there is no premature "ebullition" of the falling liquid film (before the attainment of the lower end of the article) due to heating of the liquid by the heat emitted from the article regardless of the thermostatting. The rate of vaporisation can be regulated either by altering the distance between the surfaces or by altering the rate of the free fall of the liquid along the guiding surface by changing the inclination, roughness, and relief of the latter.

The list of the available methods for the deposition of coatings from a vapour phase in equilibrium with a dynamic condensed phase is logically completed by the method involving the enforced movement of the condensed phase at the required rates. It consists in the atomisation or sputtering of the liquid phase onto the surface to be coated with thermal conditions in the heated article such that vaporisation of the condensed dispersed particles near the surface to be coated is ensured[59-61] (Fig.6). When nickel carbonyl is used, this method makes it possible to obtain coatings having a smooth surface with a thickness of several hundredths of a centimetre in the course of several seconds[59].

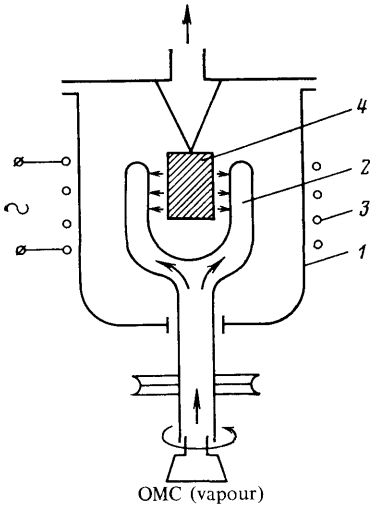


Figure 7. Deposition of coatings from a non-equilibrium vapour phase by the rotation of the vapour inlet: 1) reactor; 2) vapour inlet; 3) induction heating; 4) article.

However, despite the considerable gain in the rate of deposition of coatings compared with other methods, the atomisation procedure is relatively inapplicable to the preparation of coatings from the vapour phase using compounds having low vapour pressures. For such substances, it reduces to the preparation of coatings from the liquid phase and in many instances suffers from all the disadvantages of this procedure (contamination of the surface and bulk of the coating, difficulties when it is necessary to obtain crystalline coatings, and inhomogeneity of the coating with respect to thickness on articles of complex shape).

An interesting version of the method employing a non-equilibrium vapour phase transported along the surface of the article to be coated and gradually enriched in the decomposition products has been proposed in a patent[62]; in this method an increased rate of deposition from a vapour depleted in the working substance is achieved by establishing a temperature gradient throughout the entire extent of the article, which increases toward the end of the latter. However, this method is effective only in the kinetic region and for very large fluxes and is recommended for epitaxial processes.

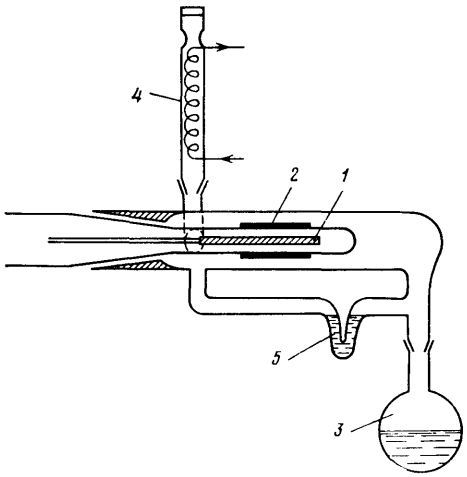


Figure 8. Method of deposition of coatings from the vapour phase in solvent vapour[1,44]: 1) support; 2) heater; 3) evaporator; 4) reflux condenser; 5) hydraulic seal.

One of the modifications of the method of deposition from a non-equilibrium vapour phase, which ensures the formation of a homogeneous coating, involves the establishment of a dynamic non-equilibrium vapour phase, proposed in a patent[63], around the article by mechanical means—by rotating a multichannel inlet supplying the vapour (Fig.7).

2. The Influence of Pressure on the Characteristics of the Deposition Process

It is possible to distinguish methods in which coatings are obtained (1) at atmospheric or elevated pressures of the test substance without a gaseous diluent, (2) at atmospheric or elevated overall pressures in the presence of a gaseous diluent, a carrier gas (usually nitrogen, inert gases, etc.), or the vapour of an inert solvent[64-66] (Fig.8), (3) at a

reduced pressure in the absence of a carrier gas, (4) at a reduced pressure in the presence of a carrier gas, a gaseous diluent, or the vapour of an inert solvent, and (5) in a high vacuum under molecular beam conditions in the absence of a gaseous diluent.

The methods used at atmospheric or elevated pressures have advantages over the remaining procedures in the sense that they make it possible to generate large mass fluxes of the test substance in the vicinity of the support to be coated, which leads to an increase in the diffusional limit to the rate of deposition of the coating and an expansion of the temperature range of the kinetic region.

However, together with this positive effect, a marked adsorption of the OMC decomposition product on the surface of the coating is observed at elevated and atmospheric pressures. For reactive coatings and decomposition products, such adsorption can promote secondary reactions leading to the formation of carbides, oxides, and similar compounds, which are in many instances undesirable. Furthermore, since the vapour pressure of the majority of OMC reaches 1 atm above their decomposition temperatures, the low thermal stability of the OMC restricts the upper limit of the OMC concentration in the gas phase and hence the rate of deposition of coatings at elevated and atmospheric pressures. On the other hand, high flow rates of the carrier gas in many cases preclude the formation of sufficiently homogeneous coatings (this is an advantage of the method of deposition of coatings from the vapour phase), leading to the appearance of a "shadow effect" due to the geometrical factors of the reactor and the support. The limiting case of this process is sputtering from an atomiser[67].

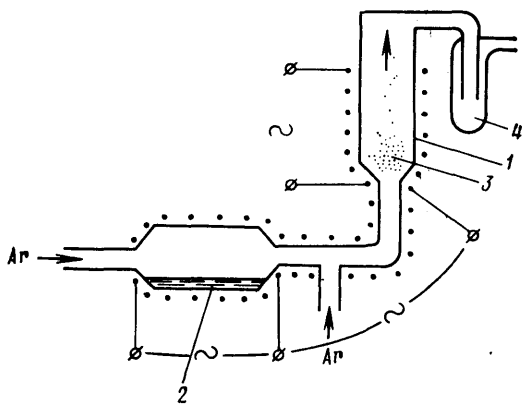


Figure 9. Deposition of coatings from a non-equilibrium vapour phase with an outside evaporator under the conditions of a fluidised bed consisting of the powdered specimen to be coated; 1) reactor; 2) evaporator; 3) specimen; 4) trap.

The use of reduced pressures makes it possible to obtain coatings with purer compositions owing to the decreased influence of adsorption by the products of decomposition and secondary reactions. However, the rates of deposition decrease owing to the decrease of the OMC concentration in the gas phase. In principle, similar rates of deposition can be attained in a stream of carrier gas at atmospheric pressure and in the absence of carrier gas at a reduced pressure. The difference between the rates of desorption of the decomposition products *in vacuo* and in an atmosphere of the carrier gas at elevated pressure may be altered. This sometimes leads to a significant difference between the impurity contents in the coatings (for example, 10% C in chromium deposited in a carrier gas and 2–3% C in chromium deposited *in vacuo* at the same temperatures[40]).

The homogeneity of the coatings obtained at reduced pressures is as a rule high. The deposition of coatings under molecular beam conditions[68] has the advantage that it makes it possible to increase the purity of the coating, but the rate of deposition is then reduced and a "shadow effect" appears when coatings are deposited onto articles of complex shape.

IV. PHYSICAL CHARACTERISTICS OF THE METHODS FOR THE DEPOSITION OF COATINGS FROM THE VAPOUR PHASE

1. Methods Differing in the State of the Article to be Coated in a Reactor

The state of the article to be coated can be determined both by its material and shape as well as its movement. The surface to be coated can be the outer or inner surface of the article or part of it, and the article can consist of a compact or porous solid body. For articles of small size, coatings can be obtained on a large number of the latter in a single cycle or with each article subjected consecutively to a single cycle. The formation of coatings on powders and friable materials requires specific deposition procedures.

Depending on the material of the substrate (the surface of the article), the methods of deposition of coatings differ mainly as regards the method and rates of heating of the surface and the employment of various chemical systems.

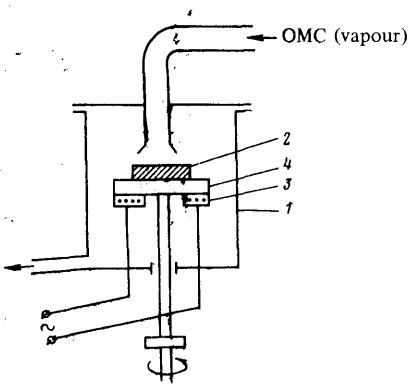


Figure 10. Deposition of coatings from a non-equilibrium vapour phase with rotation of the article: 1) reactor; 2) support; 3) heater; 4) rotating table.

A number of procedures for the deposition of coatings from the vapour phase differ by the type of movement of the article being coated in the reactor. The article to be coated may be stationary or have a wide variety of different types of movement: oscillatory movement—vibration or ultrasonic oscillations[69], a fluidised bed[10,44,70–72] (Fig.9) for the coating of powders, rotation of the article[73,74] (Fig.10), and translational movement of the article or a programmed movement[46,75–78]. A combination of different types of movement is frequently employed.

2. Methods of Heating of the Article to be Coated

The methods for the deposition of coatings from the vapour phase using OMC can differ by the method whereby energy is supplied to the article being coated. It has been suggested that different forms of energetic influences be used: thermal, light (ultraviolet and infrared irradiation[1]), laser beam[75,79-81], electron and ion impacts[82-85], and different forms of electric discharges and plasmas[84,86-88].

In methods with thermal heating of the articles to be coated, both direct heating (by an electric current[48], by a high frequency current[48], and by an electric heater built into the article[48]) and indirect heating (by the infrared irradiation of an external resistive heater[1] and by the absorption of visible and infrared radiation by the support[48]) are used.

There exist methods for the preliminary heating of the support and for carrying out the deposition process on a cooled support[89,90]. The latter is used to prepare thin films on articles with a low thermal conductivity. Despite the fact that the deposition takes place at a continuously decreasing temperature, these processes are used both in laboratory practice and in industry[77,91,92]. The possibility of employing such conditions arises partly from the fact that the process takes place at high temperatures in the diffusion region, where it depends only slightly on temperature. The coating process is highly technological and can be fully automated[92]; this being particularly suitable for the coating of dielectrics.

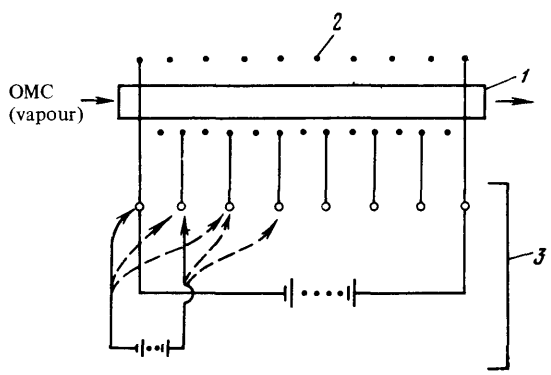


Figure 11. Zone coating of the inner surfaces of tubes from a non-equilibrium vapour phase: 1) reactor (tube); 2) electric heater; 3) switch for the maintenance of the temperature of the tube above the vaporisation temperature of the OMC and for the maintenance of the temperature of a narrow mobile zone equal to the deposition temperature of the coating.

The use of a laser beam for the local heating of the surface of the support[93,94] gives rise to extensive technological possibilities for the preparation of shaped coatings from the vapour phase[75,80,81]. The deposition process with local heating of the support by laser radiation is determined by a number of fundamental factors: the optical properties of the material of the support (high absorption coefficient and low reflection coefficient for the radiation at the wavelength of the laser emission); the thermophysical properties of the material of the support (low thermal conductivity and high melting point); the energy density of the laser beam and the duration of its action on a single site on the support (low energy density and short duration of pulses with a high repetition frequency); the rate of the chemical reaction and of mass transfer, which determine the rate of deposition.

For high local energy densities of the laser beam, a high thermal conductivity of the material of the support, a long duration of the local action, and an autocatalytic mechanism of the thermal decomposition of the OMC, the limits of the deposition of the coating undergo "temperature-dependent spreading". For high absorption coefficients of the radiation in the material of the support, there is a possibility of local fusion of parts of the support. The minimum "temperature-dependent spreading" of the limits of the coating will occur on supports with a low thermal conductivity and with a maximum absorption coefficient for the radiation. In this case the thinnest possible surface layer of the material of the support is heated and, owing to the low thermal conductivity, the energy relaxation along the surface is also minimal. The energy of the laser beam used for the local deposition of coatings from the vapour phase must therefore be optimal to avoid the breakdown of the surface of the support and to reduce the "temperature-dependent spreading" of the limits of the coating. To ensure the maximum possible rate of deposition, it is useful to employ the maximum possible concentration of the saturated OMC vapour by adjusting the temperature of the working chamber and the rate of evacuation. The temperature of the working chamber can be raised to values lower by 50–100 °C than the temperature of the coating deposition process to avoid the autocatalytic deposition of the coating over the entire surface of the support after the onset of deposition.

With a favourable combination of all four factors enumerated above, the local shaped coatings obtained possess the most satisfactory qualities.

3. Methods Differing by the State of the Fundamental Units of the Reactor

In order to obtain high-quality homogeneous coatings on articles made of different materials and of different complexity of shape and on long articles, particularly at sites which are relatively inaccessible (internal surfaces, cavities, etc.), and for the protection of friable, fibrous, and other materials, the technological features of the method and the device must be analysed.

Procedures have been developed for the deposition of coatings using different states of the fundamental units of the reactor (the evaporator, the heating of the decomposition zone, and the guiding devices for the supply of the given substance). It is possible to distinguish methods with a stationary arrangement of the units of the reactor[44], methods involving the rotation of the guiding devices for the introduction of the working substance[51-57,59,73] and the rotation of the heater together with the decomposition zone, and methods employing a translational movement of the heater or the heating zone[73,95] (Fig.11).

Depending on the purpose of the coating, a particular method of deposition and method of transferring the metal to the support (chemical transfer or a combination of several methods) are used. By virtue of the wide range of possibilities for the deposition of coatings from the vapour phase and the highly technological nature of the deposition process, coatings are extremely promising as regards their industrial applications. This is particularly important when it is possible to set up a waste-free manufacture of coatings where decomposition products such as aromatic hydrocarbons formed in the decomposition of bisarene derivatives of transition metals can be reused for the direct synthesis of OMC from

atomised metals by cocondensation[96]. This combination of "synthesis–decomposition" processes constitutes a virtually closed manufacturing cycle, which requires only the expenditure of energy and the metal and makes it possible to apply the given metal to articles of complex shape ("transfer" of the metal).

REFERENCES

1. G.A.Razuvaev, B.G.Gribov, G.A.Domrachev, and B.A.Salamatin, "Metalloorganicheskie Soedineniya v Elektronike" (Organometallic Compounds in Electronics), Izd.Nauka, Moscow, 1972.
2. V.N.Ipat'ev, G.A.Razuvaev, and I.F.Bogdanov, Zhur.Russ.Fiz.-Khim.Obshch., **61**, 1971 (1929).
3. H.M.Manasevit, J.Electrochem.Soc., **118**, 647 (1971).
4. US P.3 244 554 (1966); Chem.Abs., **64**, 17213 (1966).
5. L.S.Garba, N.I.Dychkova, and L.A.Ivanyutin, Electronnaya Tekhnika, Ser.6, 66 (1974).
6. D.J.Schlyer and M.A.Ring, J.Organometal.Chem., **114**, 9 (1976).
7. H.M.Manasevit and W.J.Simpson, J.Electrochem. Soc., **122**, 444 (1975).
8. US P.4141778 (1979).
9. F.Paneth and W.Hofeditz, Ber., **62b**, 1335 (1929).
10. V.G.Syrkin, "Khimiya i Tekhnologiya Karbonil'nykh Materialov" (The Chemistry and Technology of Carbonyl Materials), Izd.Khimiya, Moscow, 1972.
11. A.L.Kipnis, N.V.Kul'kova, and N.F.Mikhailova, Kinetika i Kataliz, **17**, 472 (1976).
12. "The Physics and Chemistry of II–VI Compounds" (Translation from English Edited by S.A.Medvedev), Izd.Mir, Moscow, 1970, p.83.
13. C.F.Powell, L.E.Campbell, and B.W.Gonsen, "Vapor-Plating", John Wiley, New York, 1955.
14. US P.3356527 (1967).
15. B.V.Zhuk, G.A.Domrachev, and A.M.Ob'edkov, Symposium, "Khimiya Elementoorganicheskikh Soedinenii" (The Chemistry of Organoelemental Compounds), Gorky, 1977, No.5, p.64.
16. W.K.Duerksen and M.Tamres, J.Amer.Chem.Soc., **90**, 1379 (1968).
17. R.H.Young, D.Brewer, R.Kayser, R.Martin, D.Feriozi, and R.A.Keller, Canad.J.Chem., **52**, 2889 (1974).
18. R.H.Young and R.L.Martin, J.Amer.Chem.Soc., **94**, 5183 (1973).
19. N.Nakashima and N.Mataga, Int.J.Chem.Kinet., **5**, 833 (1973).
20. B.V.Zhuk, G.A.Domrachev, and A.M.Ob'edkov, Izv.Akad.Nauk SSSR, Ser.Khim., 1201 (1977).
21. L.M.Stephenson, D.G.Written, G.F.Vesley, and G.S.Hammond, J.Amer.Chem.Soc., **88**, 3665 (1966).
22. A.N.Terenin, "Fotonika Molekul Krasitelei i Rodstvennykh Soedinenii" (Photonics of the Molecules of Dyes and Related Compounds), Izd.Nauka, Leningrad, 1967.
23. R.G.Brown and D.Phillips, J.Amer.Chem. Soc., **96**, 4784 (1974).
24. A.Farmilo and F.Wilkinson, Chem.Phys.Letters, **34**, 575 (1975).
25. D.Husain and J.G.F.Littler, Int.J.Chem.Kinet., 6, 61 (1974).
26. M.Bigwood and S.Boul, Chem.Comm., 529 (1974).
27. J.Grotwold and E.A.Lissy, Chem.Comm., 1367 (1961).
28. C.R.Bock and E.A.Koerner Von Gustorfin, "Advances in Photochemistry", Vol.10 (Edited by J.N.Pitts, Jr., V.S.Hammond, and K.Vollnick), John Wiley, New York, 1977, p.221.
29. US P.3203827 (1965).
30. US P.3372055 (1968); Chem.Abs., **68**, 98220 (1968).
31. Yu.A.Kaplin, L.S.Chernyshova, G.V.Belysheva, and I.F.Solov'ev, Izv.Vys.Ucheb.Zaved., Khim.i Khim.Tekhnol., **20**, 944 (1977).
32. Yu.A.Kaplin, G.V.Belysheva, T.V.Guseva, L.S.Chernysheva, and I.F.Solov'ev, Izv.Vys.Ucheb. Zaved., Khim.i Khim.Tekhnol., **20**, 771 (1977).
33. Yu.A.Kaplin, G.A.Domrachev, T.P.Starostin, G.V.Belysheva, V.S.Khabarova, and N.P.Merkulova, USSR P.496605 (1974); Byul.Izobret., No.47 (1976).
34. Yu.A.Ryukhin, G.A.Fokin, V.I.Nosach, and L.G.Molokanova, "Tezisy Dokladov II Vsesoyuznogo Soveshchaniya po MOS dlya Polucheniya Metallicheskikh i Okisnykh Pokrytii (Gor'kii)" [Abstracts of Reports at the IInd All-Union Conference on Organometallic Compounds for the Preparation of Metallic and Oxide Coatings (Gorky)], Izd.Nauka, Moscow, 1977, p.44.
35. K.G.Kochetikhina, G.A.Domrachev, and G.A.Razuvaev, Zhur.Org.Khim., **40**, 327 (1970).
36. B.V.Zhuk, V.K.Khamylov, B.A.Nesterov, G.A.Domrachev, and N.K.Zaglumonina, Dokl.Akad. Nauk SSSR, **223**, 862 (1977).
37. B.V.Zhuk, G.A.Domrachev, and N.M.Semenov, "V Vsesoyuznoe Soveshchanie 'Fizicheskie i Matematicheskie Metody v Koordinatsionnoi Khimii', Kishinev, 1974" (The Vth All-Union Conference 'Physical and Mathematical Methods in Coordination Chemistry', Kishinev, 1974), p.160.
38. G.A.Domrachev, V.A.Varyukhin, V.V.Kutyreva, O.N.Suvorova, and B.A.Nesterov, Izv.Akad.Nauk SSSR, Neorg.Materialy, **15**, 1692 (1979).
39. G.V.Almazov and V.A.Varyukhin, "Tezisy Dokladov II Vsesoyuznogo Soveshchaniya po MOS dlya Polucheniya Metallicheskikh i Okisnykh Pokrytii (Gor'kii)" [Abstracts of Reports at the IInd All-Union Conference on Organometallic Compounds for the Preparation of Metallic and Oxide Coatings (Gorky)], Izd.Nauka, Moscow, 1977, p.92.
40. G.G.Devyatykh, S.M.Vlasov, and S.M.Mazavim, Izv.Akad.Nauk SSSR, Ser.Metally, 2, 87 (1974).
41. A.G.Tumanov and K.I.Portnoi (Editors), "Tugoplavkie Metally v Mashinostroenii" (Refractory Metals in Machine Construction), Izd.Mashinostroenie, Moscow, 1967.
42. V.E.Ivanov, E.P.Nechiporenko, V.M.Krivoruchko, and V.V.Sagalovich, "Kristallizatsiya Tugoplavkikh Metallov iz Gazovoi Fazy" (Crystallisation of Refractory Metals from the Gas Phase), Atomizdat, Moscow, 1974.
43. G.G.Petukhov, A.S.Luzin, and I.N.Skuridina, Zashchita Metallov, 6, 722 (1973).
44. C.F.Powell, J.H.Oxley, and J.M.Blocher (Editors), "Vapor Deposition" (Translated into Russian), Atomizdat, Moscow, 1970.
45. I.I.Artuyushenko and G.V.Zemskov, Fizika i Khimiya Obrabotki Materialov, **3**, 34 (1971).
46. BRD P.533644 (1931).
47. V.A.Kostenkov, G.A.Domrachev, B.V.Zhuk, and V.N.Krasheninnikov, USSR P.598964 (1978); Byul. Izobret., No.11 (1978).
48. J.E.Knap, B.Pesetsky, and F.Hill, Plating, **53**, 772 (1966).
49. G.A.Domrachev, G.A.Razuvaev, V.V.Mel'nikov, and K.K.Fukin, Dokl.Akad.Nauk SSSR, **184**, 395 (1969).

50. E.Krell, "Handbuch der Laboratoruims–Destillation" (Translated into Russian), Inostr.Lit., Moscow, 1960, p.306.
51. US P.3729335 (1973).
52. B.P.1306784 (1973).
53. Canadian P.935336 (1973).
54. Swedish P.359322 (1973).
55. French P.2090384 (1976).
56. BRD P.2124400 (1975).
57. Japanese P.804958 (1975).
58. C.J.Heckmann, E.Krell, and H.Stage, Chem.Techn., 2, 252 (1950).
59. Canadian P.519674 (1955).
60. US P.3702780 (1972).
61. B.P.1325564 (1970).
62. B.P.2700365 (1955).
63. B.P.1073524 (1967).
64. French P.1406882 (1974).
65. US P.3316121 (1967); Chem.Abs., **67**, 37172 (1967).
66. BRD P.1521105.
67. E.V.Antoshin, "Gazotermicheskoe Napylenie Pokrytii (Gas-Thermal Sputtering of Coatings), Izd. Mashinostroenie, Moscow, 1974.
68. O.A.Kuznetsov, T.N.Sergievskaya, and V.A.Tolomasov, Tezisy Dokladov II Vsesoyuznogo Soveshchaniya po MOS dlya Polucheniya Metallicheskikh i Okisnykh Pokrytii (Gor'kii)" [Abstracts of Reports at the IInd All-Union Conference on Organometallic Compounds for the Preparation of Metallic and Oxide Coatings (Gorky)], Izd.Nauka, Moscow, 1977, p.92.
69. V.G.Syrkin, A.A.Uel'skii et al., USSR P.301379 (1966); Byul.Izobret., No.14 (1972).
70. B.P.1010063 (1965).
71. US P.3253944 (1966).
72. US P.3247014 (1966).
73. US P.2763576 (1956).
74. DDR P.1072723 (1973).
75. US P.3364087 (1968); Chem.Abs., **68**, 63746 (1968).
76. BRD P.1196466 (1965); Chem.Abs., **63**, 12850 (1965).
77. K.I.Martyushov and Yu.V.Zaitsev, "Tekhnologiya Proizvodstva Rezistorov" (The Technology of the Manufacture of Resistors), Izd.Vysshaya Shkola, Moscow, 1972, p.107.
78. US P.3075858 (1963).
79. W.M.Shaub and S.H.Bauer, Int.J.Chem.Kinet., 7, 509 (1975).
80. French P.1536496 (1968).
81. French P.1468426 (1966).
82. B.A.Vishnyakov and K.A.Osipov, "Elektronnoluchevoi Metod Polucheniya Tonkikh Plenok iz Khimicheskikh Soedinenii" (The Electron Beam Method for the Preparation of Thin Films from Chemical Compounds), Izd.Nauka, Moscow, 1970.
83. V.V.Demin, Z.Yu.Gotra, and M.D.Matviikiv, "Progressivnye Metody Proizvodstva Mikroskhem" (Advanced Methods for the Manufacture of Microcircuits), Izd.Kamenyar, Lvov, 1973.
84. K.A.Osipov and G.E.Folmanis, "Osazhdenie Plenok iz Nizkotemperaturnoi Plazmy i Ionnykh Puchkov" (Deposition of Films from Low-Temperature Plasma and Ionic Beams), Izd.Nauka, Moscow, 1973.
85. G.A.Efremenko, Candidate's Thesis, Moscow State University, Moscow, 1975.
86. A.A.Babad-Zakhryapin and G.D.Kuznetsov, "Khimiko-Tekhnologicheskaya Obrabotka v Tleyushchem Razryade" (Chemical-Technological Treatment in a Glow Discharge), Atomizdat, Moscow, 1975.
87. L.S.Polak, A.A.Ovsyannikov, D.I.Slovetskii, and F.B.Vurzel', "Teoreticheskaya i Prikladnaya Plazmokhimiya" (Theoretical and Applied Plasma Chemistry), Izd.Nauka, Moscow, 1975, p.277.
88. US P.3243363 (1966); Chem.Abs., **64**, 18662 (1966).
89. BRD P.1196466 (1966).
90. US P.3240623 (1966).
91. K.I.Martyushov and Yu.V.Zaitsev, "Rezistory" (Resistors), Izd.Energiya, Moscow–Leningrad, 1966, p.66.
92. N.Ya.Pratusevich and I.F.Solov'ev, "Tezisy Dokladov II Vsesoyuznogo Soveshchaniya po MOS dlya Polucheniya Metallicheskikh i Okisnykh Pokrytii (Gor'kii)" [Abstracts of Reports at the IInd All-Union Conference on Organometallic Compounds for the Preparation of Metallic and Oxide Coatings (Gorky)], Izd.Nauka, Moscow, 1977, p.7.
93. J.P.Reiser [Tentative spelling (Ed. of Translation)] (Editor), "The Effect of Laser Radiation" (Translated into Russian), Izd.Mir, Moscow, 1978.
94. J.Rady [Tentative spelling (Ed. of Translation)] "The Effect of Intense Laser Radiation" (Translated into Russian), Izd.Mir, Moscow, 1974.
95. US P.3294575 (1966).
96. G.A.Domrachev and V.D.Zinov'ev, Uspekhi Khim., **47**, 679 (1978) [Russ.Chem.Rev., No.4 (1978)].

Institute of Chemistry,
USSR Academy of Sciences,
Gorky

Translated from *Uspekhi Khimii*, **49**, 1687-1710 (1980) U.D.C. 541.67 : 547.245 : 547.258.11

Spectroscopic Study of π-Acceptor Effects in Compounds of Silicon Subgroup Elements

A.N.Egorochkin and S.Ya.Khorshev

The general state of research into the π-acceptor properties of silicon subgroup elements (E) by spectroscopic methods is examined and the data obtained are surveyed. It is shown that the π-acceptor properties are weakened with increase of the atomic number of the element E, and the analogy between these properties and the conjugation effect in unsaturated carbon compounds is traced. The widespread interpretation of π-acceptor properties of these elements as a manifestation of the effect of the d_π-p_π interaction is justified.
The bibliography includes 167 references.

CONTENTS

I. Introduction 820
II. Characteristics of the manifestation of the π-acceptor effects 821
III. The nature of the π-acceptor effects in compounds of silicon subgroup elements 826

I. INTRODUCTION

The study of the nature of the chemical bond in compounds of silicon and the elements of its subgroup (E) is not only of great independent interest but is also of undoubted importance for the understanding of the characteristics of the chemical bond in organoelemental compounds of non-transition elements as a whole.

Despite the theoretical and practical importance of this problem (many of the compounds considered are used in the national economy), many of its aspects still remain controversial. These include primarily the problem of the mechanism of the π-acceptor effect of the atoms E, which is observed in M–X fragments, where X is an atom with unshared electron pairs (n-donor substituent) or an α,β-unsaturated hydrocarbon group (π-donor substituent) and is one of the causes of the sharp difference between the properties of compounds of carbon and the elements E.[1-6] The study of the intramolecular interaction between the E and X atoms not linked directly by chemical bonds has been studied vigorously in recent years[7]; it is evidently also a consequence of the manifestation of the acceptor properties of the atoms E.[8]

The traditional interpretation of the π-acceptor properties of the atoms E is based on the idea of the d_π–p_π interaction in E–X fragments caused by the presence of vacant nd orbitals in the atoms E.[9] The E–X bond then acquires a partial double bond character, the amount of double bond character depending on the ratio of the donor properties of X and the acceptor properties of E. The donor–acceptor properties depend on the nature of other substituents linked to the E and X atoms[3,6]. The hypothesis of vacant nd orbitals explains at least qualitatively all the properties of the compounds of silicon subgroup elements which significantly distinguish these derivatives from carbon compounds.

The possibility, in principle, of d_π–p_π binding has been demonstrated by a quantum-chemical method[10-12] and some of its aspects have been considered: the dependence of the overlap integrals of the p_π and d_π orbitals on the molecular geometry[3,11] and the enhancement of the double bond character with increase of the positive charge on the central element E.[11] The size of the d orbitals of the atom depends on the nature of the substituents linked to it[13]. For this reason, firstly, the atomic d orbitals can differ appreciably from molecular d orbitals[14] and, secondly, it is difficult to make an *a priori* estimate of the relative contribution of the d_π–p_π binding for compounds of different structure. At the same time critical analysis of the data obtained using various quantum-chemical computational methods showed that, in order to account for the nature of the bond in compounds of non-transition elements (particularly in silicon compounds), it is necessary to take into account the contribution of the 3d atomic orbitals of these elements[15]. We may note, however, that the opposite view has also been expressed[16].

The quantum-chemical data indicated above[10-16] and those quoted below in the present review should apparently be considered from two standpoints. On the one hand, the involvement of nd orbitals in the formation of bonds by the elements E is entirely possible. On the other hand, the actual degree of this involvement is in many cases so small that, although the effect produced by this can in fact be observed experimentally, their magnitude is comparable to the accuracy of the computational methods. For this reason, the application of modern quantum-chemical methods in many cases fails to yield an unambiguous result in the study of effects of this kind and, for reasons described above, the idea of the d_π–p_π interaction was partly in the nature of a working hypothesis from its very inception.

During the last decade other ideas have been invoked to account for the properties of compounds of silicon subgroup elements together with the nd-orbital hypothesis[17,18]. The more significant role of the hyperconjugation effects in organoelemental compounds compared with carbon derivatives, due to the greater polarisability of the bonds in the former compounds, has been known for a long time[19]. However, Pitt's attempt[17] to put forward the hyperconjugation effect as an alternative to the hypothesis of the decisive role of the d_π–p_π interaction in organosilicon compounds, maintained in some investigations (see, for example, Ponec and Chvalovsky[20,21]), was subsequently disproved by its author[22], who concluded that both effects are important: hyperconjugation and d_π–p_π interaction.

In 1969 Musher proposed the model of hypervalent bonds to account for the acceptor properties of Group V–VIII elements of the Periodic System in the highest valence states in compounds where the number of ligands is greater than four[18]; on the basis of this model, it was shown, in particular, that there is a transannular bond between the silicon and nitrogen atoms in silatranes[23]. With the exception of the study of Sidorkin et al.[23], there is no information about the applicability of this hypothesis to the study of compounds of silicon subgroup elements. This hypothesis cannot therefore be

recognised at present as an effective alternative to the idea of the d_{π}–p_{π} interaction[24,25].

Thus there are several points of view on the problem of the mechanism of the π-acceptor properties of the atoms E. While the possibility, in principle, of the involvement of the *d* orbitals of such atoms E in the formation of a bond is not to be denied, quantum-chemical methods do not yield unambiguous conclusions about the magnitude of the *d*-orbital contributions in specific compounds because of their approximate nature. At the same time, there are extensive literature data obtained in experimental studies of the π-acceptor effects of the E atoms by spectroscopic methods. A critical consideration of these data makes it possible to formulate the fundamental characteristics of the manifestation of these effects, which, as will be shown below, do not conflict with the hypothesis of the involvement of the *nd* orbitals of the E atoms in the formation of bonds of the d_{π}–p_{π} type. The present review deals only with those studies, among the large number described, in which the π-acceptor properties of the E atom have been studied by a correct method and which lead to generalisations and are of fundamental importance for the understanding of the subject of this review.

II. CHARACTERISTICS OF THE MANIFESTATION OF THE π-ACCEPTOR EFFECTS

We believe it to be most useful to arrange the literature data systematically on the basis of the type of E–X bonds. The π-acceptor effects of the elements of the silicon subgroup will be designated in the present review by the term d_{π}–p_{π} interaction (arguments justifying the legitimacy of this term are given in Section III).

1. The E-Group VII Element Bond

The E–X interatomic distances (X = halogen) in halogeno-derivatives of the E elements are in many cases shortened compared with the values calculated from the covalent radii of the E and X atoms after correction for their electronegativities. For example, the experimental[26] and calculated (given below in brackets) values are as follows for the compounds SiF_4, $SiCl_4$, $SiBr_4$, SiI_4, GeF_4, and SnF_4 respectively (in Å): 1.54 (1.69); 2.01 (2.05); 2.25 (2.22); 2.43 (2.44); 1.67 (1.75); 1.84 (1.94). These findings were used by Brockway and Wall[27] and also by Pauling[9] as a basis for the introduction of the concept of the d_{π}–p_{π} conjugation between the *d* orbitals of silicon and the unshared electron pairs of the halogens. A tendency has been observed towards a decrease of the discrepancy between the experimental and calculated E–X lengths in the series Si > Ge > Sn and F > Cl > Br > I; however, one should note that analysis of the discrepancies is complicated by the inadequate accuracy of the experimental E–X distances and some uncertainity in their calculated values.

The double bond character of the E–X fragments has been demonstrated more unambiguously by spectroscopic methods and by experiments designed to investigate the dipole moments. The occurrence of d_{π}–p_{π} binding between the E and X atoms is indicated by a whole series of facts.

1. The high valence force constants of the Si–X (X = halogen) indicating the partial double character of these linkages. A detailed examination of the dependence of the force constants on the electronic effects of the substituents led to the conclusion[2,28–32] that the force constants of the Si–X bonds cannot be described solely in terms of the inductive influence of X and other substituents.

2. The higher energies of the unshared electron pairs of the halogens in silicon compounds compared with the isostructural carbon compounds and the intermediate values of the germanium derivatives[33–36]. Thus the vertical ionisation potentials of the *np* orbitals of the halogens, determined by photoelectron spectroscopy, are 11.28, 11.61, and 11.34 eV for CH_3Cl, SiH_3Cl, and GeH_3Cl respectively and 10.70, 11.03, and 10.72 eV for CH_3Br, SiH_3Br, and GeH_3Br respectively[33]. It might have been expected that the replacement of a carbon atom by a less electronegative silicon or germanium atom would lead to an increase of the negative charge on the Cl and Br atoms and hence to a decrease of the ionisation potentials of the halogens. However, this is not observed experimentally owing to the manifestation of π-acceptor properties by the silicon atom (and to a lesser extent by the germanium atom).

3. The low-electron-donating capacity of chlorosilanes in the formation of a hydrogen bond[37]. In conformity with the ionisation potential data examined above, the compounds $(CH_3)_3MCl$ and $(CH_3)_2ECl_2$ (E = C, Si, Ge, or Sn), which are electron donors in the formation of a hydrogen bond with phenol, exhibit the lowest electron-donating capacity for E = Si. This also confirms the partial delocalisation of the unshared electron pairs of the chlorine atoms over the vacant 3*d* orbitals of the silicon atom.

4. The opposite signs of the conjugation contributions of the substituents R_i to the NQR frequencies of the halogens in the carbon derivatives $(R_i)_3CX$ and derivatives of the silicon subgroup elements $(R_i)_3EX$, where X = Cl or Br and E = Si, Ge, or Sn.[38] It has been observed that the NQR frequencies (characterising the state of the valence electrons and the type of chemical bond in which the halogens are involved) are correlated, within the limits of each of the above eight series of compounds, with the sums of the inductive Taft constant σ* of the substituents R_i. However, a more rigorous treatment leads to the conclusion that one must take into account not only the inductive but also the conjugation influence of R_i on the NQR frequency. Analysis of the correlation analysis data indicates an increased multiplicity of the E–X bonds and its dependence on the d_{π}–p_{π} interaction in the E–R_i fragments.

5. The reduced frequencies and increased intensities of the absorption bands associated with the stretching vibrations of the E–H bonds (E = Si or Ge) in the infrared spectra of halogenosilanes and halogenogermanes compared with the values expected on the hypothesis of a purely inductive influence of the halogens[39–42]. The transfer of electron density in the H–E–X fragment from the halogen atom to the E atom leads on the one hand, to a decrease of the acceptor properties of the halogen and a decrease of the force constant of the E–H bond and of its stretching vibration frequency and, on the other hand, it induces an increase of the negative charge on the hydrogen atom of the E–H bond and increases its polarity and the intensity of the E–H stretching vibration band in the infrared spectrum.

6. The increased shielding constants of the methyl and ethyl groups in the ^1H NMR spectra of alkylhalogeno-silanes and -germanes $R_{3-n}EX_n$ (R = CH_3 or C_2H_5; E = Si, or Ge; X = F, Cl, Br, or I).[43] Calculation taking into account the purely inductive influence of the substituents on the chemical shifts of the protons in the group R by the method of correlation analysis with corrections for magnetic anisotropy leads to a discrepancy between the calculated chemical shifts and their experimental values. The increased shielding of the groups R is a result of the weakening of the electron-accepting properties of the halogen atoms in consequence of the d_{π}–p_{π} interaction in the E–X fragments.

7. The smaller dipole moments of halogenosilanes compared with the corresponding halogenomethanes[3]. On the basis of

the lower electronegativity of silicon compared with that of carbon, a greater polarity of the Si–X bond compared with C–X might have been expected. However, experiment failed to confirm this. The example of the simplest silane derivatives shows that the polarity of the Si–X bonds[3] as well as the polarity of the E–X bonds in alkylhalogeno-derivatives of silicon, germanium, tin, and lead (see, for example, Sorriso et al.[44]) is reduced owing to the delocalisation of the unshared electron pairs of the halogen atoms over the *nd* orbitals of the E atoms.

2. The E–Group VI Element Bond

Among the compounds having this bond, the practically important derivatives containing the Si–O siloxane linkage and the Si–O–Si disiloxane linkages have been studied in greatest detail. Modern ideas about the nature of the siloxane linkage have been considered in a monograph[45]. The characteristic results of the manifestation of a strong d_π–p_π interaction in the Si–O bond are as follows[45]: the shorter length of the Si–O bond (~1.65 Å) compared with the sum of the covalent radii (1.83 Å) of the silicon and oxygen atoms; the greater Si–O–Si angle (105–180°); the high energy (100–120 kcal mol^{-1}) and high force constant[46] as well as the low polarity (dipole moment 1.2–1.6 D) of the Si–O bond; the weak-electron-donating properties of the oxygen atoms in alkoxysilanes, which are still further reduced in disiloxanes compared with the corresponding carbon analogues; the appreciably greater acidity of silanes compared with carbinols.

The strong d_π–p_π interaction in the Si–O bond is appreciably weakened on passing to the Ge–O fragment. The expected bond length in $(H_3Ge)_2O$ is therefore smaller by only 0.06 Å than the experimental value and the Ge–O–Ge angle (126°) is significantly smaller than the Si–O–Si angle in disilyl ether (144°).[47] The E–O–E angles in the $[(CH_3)_3Ge]_2O$ and $[(CH_3)_3Sn]_2O$ molecules, which are ~141°, indicate the important role of the effect of the d_π–p_π interaction also in the formation of the Sn–O bond[48].

Systematic studies of the dependence of the d_π–p_π interaction in the E–X fragment on the nature of the silicon sub-group elements E and the group VI elements X have been carreid out by infrared spectroscopy and ^{1}H NMR [40,43,46,49,50]. The use of correlation analysis methods showed that the frequency and intensity of the stretching vibrations of the E–H bond in the infrared spectra of compounds with the H–E–X (E = Si, or Ge; X = O, S, or Se) fragment are determined, apart from the inductive effect, also by the conjugation interactions in the E–X groups. The role of such interactions diminishes with increase of the atomic number of the elements E and X, i.e. in the sequences Si > Ge > Sn and O > S > Se > Te. The contribution of the d_π–p_π interaction to the Si–Te bond is extremely small if any.

A convincing confirmation of these conclusions was obtained by three independent methods: in the study of the relative electron-donating capacity of compounds with E–X–E groups in the formation of hydrogen bonds by them[51]; in the analysis of the chemical shifts in the ^{1}H NMR spectra of the protons of the CH_3E groups of the compounds $(CH_3)_3SiXCH_3$ (X = O or S) and $(CH_3)_3GeOCH_3$;[43] in the study of the variation of the stretching vibration frequency ν(E–C) as a function of the substituents X in organodielemental compounds of the type $[(C_2H_5)_3E]_nX$, where E = Si, Ge, or Sn and X is a Group I–VII element[52]. The following features of the spectroscopic parameters, which do not agree with the hypothesis of their dependence solely on the inductive influence of the various substituents, have been found using these three different methods: (1) the change in the electron-donating capacity of compounds with E–X–E groups, where E is a silicon subgroup element, as the Group VI elements X are varied is inconsistent with the sequence O > S > Se > Te known to hold[53] for carbon compounds. The differences diminish with increase of the atomic numbers of the elements E and X. The increase of the mobility of the hydrogen in the X–H group in structurally similar compounds with the E–X–H fragment corresponds to a decrease in the electron-donating capacity of the compounds with such a fragment[54,56]; (2) corrections for magnetic anisotropy and the inductive effect showed that the shielding constants of the protons of the CH_3E group in trimethylmethoxygermane and to an even greater extent in trimethylmethoxysilane are too high. The shielding constant of trimethylthiosilane has increased less than the constant of trimethylmethoxysilane[43]; (3) the points corresponding to compounds with E–Group VI element bonds deviate from the linear correlation between the ν(E–C) frequencies in the compounds $[(C_2H_5)_3E]_nX$ and the electronegativity of the elements X (where X is a Group I–III element); the deviations decrease in the sequence O > S > Se > Te.[52] However, they cease to be "anomalous" if one takes into account the effect of d_π–p_π interaction. In the E–X and E–X–E fragments this effect opposes the inductive effect of the atom X and therefore leads to the above deviations, which diminish with increase of the atomic numbers of the elements E and X

Specific aspects of the problem of the d_π–p_π interaction have been examined in a number of studies, in which details of the general relations discussed above were obtained. One of the most significant problems in this connection is competition between the effects of the d_π–p_π interaction and p,π conjugation in compounds containing groups of the type C_6H_5–X–Si< and R–C(=O)OE<. [49,57]. In $C_6H_5SiH_3$ both unshared electron pairs of the oxygen atom are involved in conjugation—one with the benzene ring and the other with the silicon atom[47][sic], [58]. In contrast to oxygen, the sulphur atom supplies only one electron pair for conjugation[59]. Therefore in $C_6H_5SSiH_3$ only the energetically more favourable conjugation with the benzene ring takes place, while there is no d_π–p_π interaction in phenylthiosilanes, in contrast to alkylthiosilanes[49]. The reduction of the electron density at the oxygen atom of the E–O–C fragment in benzoates and acetates in consequence of the R_3E–$\overset{\curvearrowright}{O}$–CR=$\overset{\curvearrowright}{O}$ conjugation is responsible for the small amount of the d_π–p_π character of the M–O bond in these compounds[57], compared with, for example, the alkoxy-derivatives of the elements E.

3. The E–Group V Element Bond

Fairly clear evidence in support of the operation of the effect of the d_π–p_π interaction in some of the E–Group V element bonds has been obtained in structural studies, selected results of which are presented in Table 1.

A classical example of the influence of the d_π–p_π interaction is the planar disposition of the heavy atoms in trisilylamine (with the Si_3N molecular skeleton), in contrast to the pyramidal structure of the C_3N fragment in trimethylamine. The delocalisation of the unshared electron pair of the nitrogen atom over the 3*d* orbitals of the silicon atoms leads to a sharp reduction of the basicity of trisilylamine compared with trimethylamine[3]. Solely on the basis of the smaller electronegativity of the silicon atom compared with the carbon atom, one would actually expect a greater basicity of trisilylamine compared with trimethylamine. The configuration of the bonds involving nitrogen atoms becomes nearly planar also in

the molecules of disilylmethylamine, silyldimethylamine, trigermylamine, and $Sn[N(CH_3)_2]_4$.[65] This shows that the effect of the d_π–p_π interaction contributes to the energy of not only the Si–N bond but also the Ge–N and Sn–N bonds. However, owing to the decrease of the contribution of the d_π–p_π interaction with increase of the atomic number of the elements E, the heavy atoms in trigermylamine are not entirely coplanar, unlike trisilylamine[63]. In contrast to derivatives with E–N bonds, the trisilylphosphine and trigermylphosphine molecules have a pyramidal configuration, while their E–P–E valence angles differ slightly from the C–P–C angle (~100°) in trimethylphosphine. The heavy atoms are also non-coplanar in trisilylarsine and trisilylstibine (Table 1).

Table 1. The bonds lengths and valence angles in derivatives of Group V elements.

Compound	E–X bond length, Å		E–X–E angle (°)	References
	experimental	calculated as the sum of covalent radii of E and X (Ref.60)		
$(H_3Si)_3N$	1.734	1.87	119.7	61
$(H_3Si)_2NCH_3$	1.726	1.87	125.4	61
$H_3SiN(CH_3)_2$	1.715	1.87	—	61
$(H_3Si)_3P$	2.246	2.27	96.8	62
$(H_3Si)_3As$	2.353	2.38	94.1	62
$(H_3Si)_3Sb$	2.555	2.58	89	62
$(H_3Ge)_3N$	—	1.92	116	63
H_3GeNCO	1.831	1.92	—	64
$(H_3Ge)_3P$	2.306	2.32	95.7	62
$(H_3C)_3N$	1.47	1.47	108	60
$(H_3C)_3P$	1.87	1.87	100	60
$(H_3C)_3As$	1.98	1.98	96	60

It follows from Table 1 that the Si–N and Ge–N interatomic distances deviate appreciably from the sum of the covalent radii of the E and N atoms. As in siloxanes, in silazanes the Si–N bond length is reduced (the bond length calculated from the covalent radii after introducing corrections for the amount of ionic character of the bond by the Schomaker–Stevenson method[66] is 1.80 Å) and the valence angles at the nitrogen atom are increased. These facts agree with the hypothesis of an increased order of the Si–N bond in silazanes due to the d_π–p_π interaction[67]. Thus structural data clearly indicate an increase of the E–N (E = Si, Ge, or Sn) bond orders. The amount of double bond character then decreases with increase of the atomic number of E.

On the other hand, the experimental E–X bond lengths (where E = Si or Ge and X = P, As, or Sb) virtually agree with the sum of the covalent radii of the E and X atoms. As stated above, compounds containing such bonds have a pyramidal structure like their carbon analogues (i.e. with E = C). Thus the structural data for derivatives containing elements of the phosphorus subgroup do not indicate an appreciable increase of the angles or a decrease of the interatomic distances which might be ascribed to the influence of the effect of the d_π–p_π interaction.

These facts, pointing to a significant weakening of the d_π–p_π interaction already on transiton from the E–N bond to the E–P bond were subsequently convincingly confirmed by infrared spectroscopy[68]. Analysis of the stretching vibration frequencies of the Si–H bond in the infrared spectra of compounds with the H–Si–N fragment showed that values of ν(Si–H) depend not only on the inductive influence of the three substituents at the silicon atom but are also determined by the influence of several mesomeric effects, the principal ones being those of the d_π–p_π interaction and the σ,p conjugation. In contrast to this, the frequencies ν(Si–H) in the infrared spectra of compounds containing the H–Si–P fragment depend solely on the inductive influence of the three substituents linked to the silicon atom[68].

The significant d_π–p_π character of the Si–N bond and the absence of double bond character in the Si–P group can be explained by assuming that the d_π–p_π interaction in the E–X bond has a profound analogy with conjugation effects in organic chemistry, for example, with the effect of ρ,π conjugation in the benzene derivatives C_6H_5–X (where X has the same substituents as in the organo-elemental compounds with the E–X bond). The possibility of drawing such an analogy is justified in detail in Section III of the present review.

The proposed approach makes it possible to regard d_π–p_π interaction as a process which depends on two factors: the electron-accepting properties of the atom E and the electron donating properties of the substituent X. It is well known[69] that, as a substituent in an aromatic ring, the dialkylamino-group exhibits an exceptionally high capacity for conjugation. This property of the dialkylamino-group is responsible for the considerable amount of the d_π–p_π character of the Si–N bond in fragments of the type $Si–N(CH_3)_2$.[68] The $P(CH_3)_2$ group has a low capacity for conjugation of the p,π type[70] due to the weak p character of the orbitals of the unshared electron pair of tervalent phosphorus[71]. This is the reason for the virtual absence of d_π–p_π character in the Si–P bond[68], which applies to an even greater extent, according to structural data, to other bonds of the type E–P and also to E–X bonds where X is a phosphorus subgroup element[52].

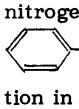
Important information about the π-acceptor properties of silicon subgroup elements E has been obtained in a systematic study of the electron-donating capacity of compounds containing E–N fragments[59,72–80]. The electron-donating capacity was estimated from the shift of the stretching vibration frequency of the C–D bond in deuterochloroform or the N–H bond of pyrrole in the infrared spectrum when the above compounds form a hydrogen bond with organoelemental compounds. The electron-donating capacity of organosilicon, organogermanium, and organotin amines depends significantly, like that of the usual organic amines, on the nature of the substituents linked to the Group IVb element; in the absence of appreciable steric hindrance, it decreases steadily with enhancement of the electron-accepting properties of the substituent. In isostructural series of compounds with a variable element E, the electron-donating capacity depends greatly on the nature of the atom E.[73–77,79].

In all cases, the electron-donating capacity of amines having one or several Si–N bonds is greatly reduced compared with that for the corresponding carbon compounds[59,72,75]. A typical example is provided by the extremely low electron-donating capacity of trisilylamine[3], while trimethylamine is a strong base. The electron-donating capacity of germanium-containing amines is also appreciably weakened compared with that of carbon compounds of analogous structure[75–77]. The relative electron-donating capacity of the nitrogen atoms in isostructural compounds is reduced to the sequence C–N–C > C–N–Ge > Ge–N–Ge > C–N–Si > Si–N–Si when the immediate environment of the nitrogen atom is altered[75]. This sequence is directly opposed to that expected on the basis of the electronegativities of the Group IV elements. The electronegativity varies in the sequence C > Ge > Si,[6] so that it might have been expected that carbon-based amines and silylamines would exhibit the minimum and maximum electron-donating capacities respectively. The experimentally observed opposite sequence of electron-donating capacities indicates the delocalisation of the unshared electron pairs of the nitrogen atoms over the vacant nd orbitals of the E atoms (i.e. d_π–p_π interaction occurs). This effect is enhanced on passing from germanium derivatives to silylamines and also with increase of the number of silicon atoms linked to the nitrogen atom[81].

The π-acceptor properties of the E atoms, which involve the transfer of electron density in the E–N fragments from the nitrogen atom to that of the silicon subgroup element, should lead to an increase of the mobility of the hydrogen atom in the E–N–H group compared with that expected on the basis of the inductive effect of the substituents linked to the nitrogen atom. The validity of this conclusion was demonstrated by comparing the relative acidities of amines and silylamines. It has been shown by infrared spectroscopy that, on formation of a hydrogen bond, silylamines exhibit much more pronounced electron-accepting properties than their carbon analogues in relation to electron donors to which they are linked by hydrogen bonds[74,75,82,83]. The effect of the d_π–p_π interaction in the Si–N bond leads to the appearance of electron-accepting properties in the R_3Si group, as a result of which the mobility of the hydrogen atom in compounds containing the R_3Si–N–H fragment increases sharply[83].

An extremely characteristic feature of compounds with an E–N fragment is the significant role of conjugation effects in the latter, which operate together with the d_π–p_π interaction. The specific features of the appearance of these effects are determined mainly by two factors: firstly, the exceptionally high capacity of the dialkylamino-group for conjugation, which has already been noted, and, secondly, the presence of only one electron pair at the nitrogen atom and the consequent possibility of competition between different conjugation effects involving this pair. If the conjugation effects are comparable in intensity, they do not appreciably weaken one another, acting independently. On the other hand, if one of the effects is energetically clearly preferable, its influence becomes dominant and that of the other effects is suppressed. The situation of the first type is characteristic of alkyl(dialkylamino)silanes and that of the second type is characteristic of *N*-trimethylsilyl, *N*-trimethylgermyl, and *N*-trimethylstannyl derivatives of aniline.

Analysis of the factors influencing the frequency and integral intensity of the stretching vibration of the Si–H bond in the infrared spectra of ethyl(diethylamino)silanes shows that, together with the d_π–p_π interaction, a second mesomeric effect—the σ, *p* conjugation $R_2\overset{\curvearrowright}{N}$–Si → H—plays a significant role in the Si–N bond in these compounds[84]. The manifestation of the σ, *p* conjugation is promoted by the small inductive effect ($\sigma_I \cong 0.1$) and the high capacity of conjugation ($\sigma_R = -0.8$) of the diethylamino-group. The introduction of second and third diethylamino-groups into the silane molecule is accompanied by the enhancement of the overall *-I* effect of the substituents, but the inductive effect is fully compensated by the electron-donating properties of the diethylamino-group via the d_π–p_π and σ, *p* conjugation mechanisms. Therefore, in contrast to any other silanes with functional groups, the frequencies ν(Si–H) decrease, and not increase, as the number of diethylamino-groups is increased. The dipole moment of the Si–H bond and the negative charge on the hydrogen atom in ethyl(diethylamino)silanes become greater than in trialkylsilanes as a result of the joint influence of the effects of the d_π–p_π interaction and the σ, *p* conjugation[84].

Typical systems in which the competition between the effects of the d_π–p_π interaction and the *p*, π conjugation induces a virtually complete suppression of the former effect are *N*-substituted anilines[85]. In the study of these compounds by infrared spectroscopic and NMR methods no stereochemical evidence for the occurrence of the d_π–p_π interaction in the E–N bonds was found. This is caused by the stronger *p*, π conjugation of the single unshared electron pair of the nitrogen atom with the aromatic ring in the fragment E–$\overset{\curvearrowright}{N}$–  (E = Si, Ge, or Sn) compared with the d_π–p_π interaction in the E–N bonds[68]. A similar phenomenon has been observed, as already mentioned above, in phenylthiosilanes[49] where the involvement of the sulphur atom in *p*, π conjugation with the aromatic ring Si–$\overset{\curvearrowright}{S}$i–  leads to the "switching off" of the d_π–p_π interaction between this atom and the 3*d* orbitals of silicon.

Thus, other conditions being equal, the d_π–p_π interaction is energetically less favourable than the *p*, π conjugation.

4. The E–Aromatic Ring Bond

The π-acceptor properties of silicon subgroup elements E in relation to an aromatic ring linked to them are indicated by numerous spectroscopic data. The principal data refer to the study of benzene derivatives; only a few have been concerned with aromatic heterocycles.

The electron-accepting properties of the E atoms linked to an aryl substituent are indicated by a series of data.

1. The higher energies of the first band in the photoelectron spectrum of phenylsilane compared with toluene, which indicate the stabilisation of the highest energy orbital in phenylsilane via d_π–p_π binding[86]. This has been confirmed by data for halogenotriphenyl derivatives of Group IV elements[87] and for the *p*-substituted derivatives of trimethylphenylsilane[88,89], which also indicate an appreciable transfer of electron density from the benzene ring to the silicon atom.

2. The enhanced electron-accepting properties of the substituents ER_3 compared with the corresponding carbon substituents (according to NMR data). ^1H NMR and particularly ^{19}F NMR of benzene derivatives constitute thoroughly developed methods for the estimation of the electronic effects of substituents linked to the benzene ring[90]. In particular, the secondary scale of Hammett constants is based on NMR data[90]. Derivatives of trimethylphenylsilanes containing different substituents in the *ortho*-, *meta*-, and *para*-positions have been studied by NMR [91]: compounds of the $(C_6H_5)_3EX$ series (E is a group IVB element and X are different substituents)[92]; the fluoro-derivatives *m*- and *p*-FC_6H_4E [93]; the pentafluorophenyl derivatives of Group IVB elements[94]; organotin compounds containing monofluorophenyl substituents[95–97]. The above investigations showed that, in the case of all the organoelemental substituents, including the organotin substituents, ideas based on the electronegativities of the silicon subgroup elements are insufficient for the description of the characteristic features of the variation of the chemical shifts and the spin–spin coupling constants. The electronic interactions between the organoelemental substituents and the aromatic ring proceed via a combined (inductive and resonance) mechanism (d_π–p_π interaction).

3. The increase, according to microwave spectroscopic data[98], of the potential barrier to the rotation of the silyl group in phenylsilane, compared with the analogous quantity for the methyl group in toluene, owing to the d_π–p_π binding between the silicon atom and the aromatic ring.

4. The smaller electron-donating capacity of silicon- and germanium-containing derivatives of benzene compared with their carbon analogues on formation by these compounds as π-donors of a hydrogen bond with electron acceptors[99,100]. This effect is caused by the reduced electron density in the benzene ring in organoelemental compounds in consequence of the d_π–p_π interaction in the E–C_6H_5 fragments.

5. The higher frequencies, ν_{CT}, of the charge-transfer bands in the electronic absorption spectra of charge-transfer complexes of phenylsilanes with tetracyanoethylene compared with their carbon analogues and the intermediate values of ν_{CT} in phenylgermane complexes[100–103]. Charge-transfer

complexes of the π,π type are formed between π-donors (aromatic compounds) and π-acceptors (for example, tetracyanoethylene). The absorption of a light quantum $h\nu_{CT}$ by such a complex causes the transition of the latter from the ground to an excited state. The energy $h\nu_{CT}$ is linearly related to the ionisation potential of the π-donor and the σ_n^+ constants of the substituents in the aromatic ring[100]. Analysis of the values of ν_{CT} in the spectra[100-103] and of the calculated Brown–Okamoto σ_n^+ constants shows unambiguously that the overall electronic effect of the substituents ER_3 in the ring (E is a silicon subgroup element) is the sum of two components—inductive and resonance (i.e. d_π–p_π interaction takes place). The d_π–p_π interaction is most pronounced in phenylsilanes.

6. The inadequacy of inductive ideas alone for the description of the nature of the changes in the frequencies and intensities of the stretching vibration bands of the E–H bond (E = Si or Ge) in the infrared spectra of silane and germane derivatives containing phenyl substituents[40-42,50,105]. This is caused by the effect of the d_π–p_π interaction in the E–C_6H_5 fragments. The dependence of the effectiveness of the d_π–p_π binding on the nature of the substituents in the aromatic ring will be specially considered in Section III of the present review in relation to arylsilanes[105].

7. Numerous data for the dipole moments of phenyl derivatives of Group IVB elements, which have been discussed in fair detail in a number of reviews[3,5,6] and surveys[106-110] have shown that the ER_3 fragments (E is a silicon subgroup element) manifest, together with a positive inductive effect, a negative mesomeric effect (d_π–p_π interaction), which diminishes on passing from organosilicon compounds to germanium and tin derivatives. The degree of d_π–p_π interaction depends on the nature of the substituents at the E atom and in the benzene ring. The presence of typically electron-donating substituents in the *para*-position in the ring leads to a direct polar conjugation effect in which the ER_3 fragment behaves as an acceptor centre.

As mentioned above, the d_π–p_π interaction between the E atoms and the aromatic ring has been studied mainly for benzene derivatives. However, it has been established in a number of studies[111-117] that significant π-binding is characteristic also of silylnaphthalenes.

Electronic spectroscopy of charge-transfer complexes has been used to investigate the π-acceptor effects of organoelemental substituents in thiophen[118] and furan[119] derivatives. Analysis of the frequencies of the charge-transfer bands in the spectra of charge-transfer complexes of these compounds (π-donors) with tetracyanoethylene (π-acceptor) and also comparison of these frequencies with proton chemical shifts in NMR spectra show convincingly that the electron-donating properties of the trimethylsilyl and trimethylgermyl groups are weaker than those of the t-butyl group owing to the d_π–p_π interaction. The decrease of the d_π–p_π character of the E–furyl bond as E is varied in the sequence Si > Ge > Sn [119] has been established in relation to furan derivatives and has been confirmed by NMR data[120].

Thus the sum total of the available spectroscopic data clearly indicates the d_π–p_π character of the E–aromatic ring bonds.

5. E–C = C and E–C ≡ C Systems

Numerous literature data have confirmed the involvement of the π electrons of an α,β-unsaturated hydrocarbon substituent linked to a silicon subgroup element (E) in d_π–p_π interaction with the vacant *nd* orbitals of the E atom. The most striking of these results are described below.

1. The smaller valence force constants of the C = C [112,121] and C ≡ C [122-124] bonds in organoelemental derivatives, compared with their carbon analogues, which is particularly pronounced for silicon derivatives. For example, the carbon–carbon bond orders in the compounds $H_3EC \equiv CH$ with E = C, Si, or Ge, are respectively 2.65, 2.47, and 2.53.[124] The maximum degree of delocalisation of the π electrons of the multiple bonds over the vacant *d* orbitals in the silicon compounds corresponds to the minimum order of the multiple bond in these compounds.

2. The lower electron-donating capacity of organoelemental compounds (as π-bases in the formation of hydrogen bonds with electron acceptors[122,125,126] and as π-donors in the formation of charge-transfer complexes of the π,π type[127,128]), linked indirectly to the lower force constant, as well as the greater mobility of the acetylenic hydrogen atom of the E–C = C–H fragment (E is a silicon subgroup element) compared with carbon analogues[129-132]. All these factors, caused by the π-acceptor properties of the E elements, are most strongly manifested in silicon compounds, while in lead derivatives they are virtually absent[129].

3. The inadequacy of inductive ideas alone for the description of the change in the frequency of the highly characteristic[133] out-of-plane deformation vibration of the $=CH_2$ group in the infrared spectra of ethylene derivatives $CH_2 = CH–ER_3$ containing organoelemental substituents ER_3 (E = Si, Ge, or Sn).[134] The frequency of this vibration is determined by the joint inductive and mesomeric (π,π and π,*p* conjugation as well as d_π–p_π interaction for organoelemental compounds) effects of the substituents.

4. The occurrence of a resonance interaction, together with the inductive effect, between the silicon atom and the C = C and C ≡ C fragments, which is manifested in the infrared spectra of silane derivatives containing such fragments[135]. The influence of the resonance effect (d_π–p_π interaction) is shown by the deviation of the stretching vibration frequencies of the Si–H bond from the values expected on the basis of allowance for the purely inductive effect of these fragments.

5. Analysis of the parameters of the NMR spectra[136-140] and the dipole moments[106,109,137] of organoelemental derivatives of ethylene and acetylene also demonstrate the necessity to take into account the π-acceptor properties of silicon subgroup elements in the interpretation of the experimental relations.

The experimental data considered in this section indicate unambiguously the presence of π-acceptor properties in silicon subgroup elements (E) with respect to the *n*- or *p*-donor type substituents linked to them (d_π–p_π interaction). In compounds having one E = X bond or one E–X–E fragment the capacity for d_π–p_π interaction is reduced with increase of the atomic numbers of the E and X atoms. The decrease of the capacity for d_π–p_π interaction with a constant E and a variable X is greater the smaller the number of the Group in the Periodic System to which X belongs. Other characteristics of the d_π–p_π interaction will be examined in Section III.

The results of the experimental study of the d_π–p_π interaction have been confirmed by quantum-chemical calculations by the molecular orbital method using various approximations. These calculations indicate an appreciable involvement of the vacant *d* orbitals in the formation Si–O,[141-143] Si–N,[144-146] Si–halogen[146-148], Si–aryl[143,149-155], Ge–C_6H_5,[152] and Si–C = C [155,156] bonds. However, as mentioned in the introduction, the conclusions reached in such calculations can depend on the accuracy of the method employed, which reduces sharply their value compared with experiment.

III. THE NATURE OF THE π-ACCEPTOR EFFECTS IN COMPOUNDS OF SILICON SUBGROUP ELEMENTS

Numerous literature data have shown that spectroscopic methods make it possible to investigate the fine details of the π-acceptor properties of silicon subgroup elements. Without going into the details of the mechanism of the π-effects, we adopted for these effects, following the majority of published studies, the terms d_π–p_π interaction (interaction between an E atom and a substituent X which is an *n*- or π-donor in the E–X fragment) and (p–d) σ-interaction (interaction through space between atoms E and X not linked by a valence bond). The use of these terms is absolutely correct only when it is demonstrated unambiguously that the *nd* orbitals of the E atoms are responsible for the manifestation of π-acceptor properties by the latter. There is no direct evidence for this at the present time, but there exist no firmly demonstrated alternative to the hypothesis of vacant *nd* orbitals.

At the same time extensive experimental data have been accumulated on the relations obeyed by the π-acceptor properties of silicon subgroup elements. Under these conditions, it is important to analyse the extent to which the conclusions reached on the basis of these experimental data are consistent with the postulates of the *nd*-orbital hypothesis. In the fundamental study by Jaffé [11] and in other investigations[3,10,12–15], it was shown that the d_π–p_π bonds in the E–X fragment are formed when the following three necessary and sufficient conditions are fulfilled: (1) the substituent X must possess *n*- or π-donor properties; the involvement of *d* orbitals should lead to effects similar to those arising on conjugation of π-bonds; (2) there should be a positive charge on the atom E, an increase of which should entail an enhancement of the d_π–p_π interaction; (3) the effect of the d_π–p_π interaction arises only in the presence of high overlap integrals of the p_π and d_π orbitals of the interacting X and E atoms.

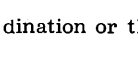
These conditions are inter-related. For example, the contraction of the *d* orbitals of the atom E and the decrease of the energy and electron affinity with increase of the positive charge on the E atom[13] create more favourable conditions for the interaction of the d_π orbitals of the E atom with the p_π orbitals of the X atoms, i.e. they increase the overlap integrals of the interacting orbitals of the E and X atoms[11]. Under these conditions, it is extremely significant that the molecular d_π orbitals are much less diffuse and have a much lower energy than the corresponding atomic orbitals[14] and their energy is therefore closer to that of the p_π orbitals of the X atom. In addition, the size of the molecular d_π orbitals, their energy, and the values of their overlap integrals with the p_π orbitals of the X atom depend also on the nature of the substituents at the E atom[13]. Electron-accepting substituents linked to E increase the positive charge of the latter and favour the d_π–p_π interaction[11]. Conditions (2) and (3) quoted above are therefore closely related.

At the same time condition (3) is of independent importance, particularly when not one but several X atoms involved in d_π–p_π interaction with tetrahedral E atoms are linked to the latter. Under these conditions, owing to the difference between the valence angles (~109.5°) and between the angles between the maximum intensity vectors of the d_π orbitals (90°), the interaction of E with several X proceeds when the orientation of the d_π orbitals is such that it does not lead to the maximum overlap integral in any of the E–X bonds[11]. In view of this, the overall effect of the d_π–p_π interaction in the molecule depends strongly and non-additively on the number of X atoms linked to E.[11,14].

The main task of the present section of the review is to examine to what extent the results of experimental studies of the d_π–p_π interaction are consistent with the above three conditions for the formation of d_π–p_π bonds and the conclusions arising therefrom.

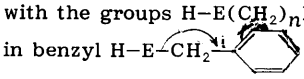
1. Analogy Between the π-Acceptor Effects of the Elements E and the Conjugation Effects in Carbon Compounds

Systematic studies of the π-acceptor properties of silicon subgroup elements E, carried out in relation to organosilicon and organogermanium compounds by infrared spectroscopy and ^{1}H NMR, [39,40,49,50,157,158], have shown unambiguously that the elements E exhibit π-acceptor properties only when they are linked by direct chemical bonds to the group X in the E–X fragment, where X can be an atom with unshared electron pairs (*n*-donor) or an α,β-unsaturated hydrocarbon radical (π-donor). On the other hand, if E and X are separated by a fragment of the type $(CH_2)_n$, then the carbofunctional substituent $(CH_2)_nX$ in the group $E(CH_2)_nX$ exhibits only an inductive effect.

Generally speaking, the claim that the mutual influence of the atoms E and X in the fragment $E(CH_2)_nX$ occurs solely via an inductive mechanism is not entirely rigorous. In reality, there can be interactions of at least two types between these atoms. The first involves intramolecular coordination or the so-called α-effect (for $n = 1$):  [7]

The results of a number of studies have shown[6,8,160] that this type of interaction takes place through space, but its mechanism continues to be the subject of a lively discussion[159].

A detailed examination of this type of interaction is of independent interest and is outside the scope of the present review. We shall only mention that the majority of the spectroscopic features of the manifestation of intramolecular coordination in the fragment $E(CH_2)_nX$ can be given a non-contradictory explanation if the following view on the mechanism of the effect is adopted[6]. Intramolecular coordination takes place between the atoms E and X. The X atom behaves as an *n*-donor by virtue of the presence of unshared electron pairs; the E atom then behaves as an acceptor by employing the vacant *nd* orbitals with the formation of a new weak bond of the (p–d) σ-type with the atom X. The principal difference between the bond thus formed and the σ-bond between E and D in compounds of the type EX_4D and EX_4D_2 is that the former has a much smaller energy. Thus the enthalpy of formation of the (p–d) σ-bond in dimethylchloromethylsilane is ~1 kcal mole^{-1}.[160] The low energy of bonds of the (p–d) σ-type is apparently largely caused by the impossibility of the mutual approach of the atoms E and X in the fragment ECH_2X to a distance close to the sum of the covalent radii. Such mutual approach would require a significant alteration of the geometry of the fragment ECH_2X, which involves a considerable expenditure of energy. Intramolecular coordination has almost no effect on the chemical shifts of the protons of the group R in the fragments R–E (C = CH_3 or C_2H_5; E = Si or Ge) in the NMR spectra of compounds with the groups $E(CH_2)_nX$,[48] and its influence on the frequency and intensity of the stretching vibration of the E–H bond in the infrared spectra of compounds with the fragment $H–E(CH_2)_nX$ is manifested distinctly only for $n = 1$ [160] and can be taken into account by correlation analysis[160].

The second type of resonance interaction in the groups $E(CH_2)_nX$ is the effect of the σ,π conjugation manifested for $n = 1$. A detailed study of the frequency and intensity of the ν(E–H) vibration in the infrared spectra of compounds with the groups $H–E(CH_2)_nX$ showed that the σ,π conjugation in benzyl  and allyl ($H–E–CH_2–CH=CH_2$)

derivatives has almost no influence on the above spectroscopic parameters[39-43,49,50,158], although this effect does influence the change in electron density in the aromatic ring and in the double bond[99,125,161,162]. This is probably caused by the comparatively small effect of the σ,π conjugation in the ground electronic state, which intensifies appreciably only in the presence of a positive charge in the benzene ring or in the double bond, which follows from theoretical considerations[163,164] and from the electronic spectra of the charge-transfer complexes of benzyl and allyl derivatives of silicon subgroup elements[100,128].

Taking into account the foregoing it is possible to formulate the requirements which must be met by the correct empirical method for the estimation of the π-acceptor properties of the silicon and germanium atoms (E) in the fragment E–X.[6] In the first place, it is necessary to have a sufficiently representative series of compounds whose spectroscopic parameters depend exclusively on the electronic effects of the substituents (inductive and conjugation effects) and are sufficiently sensitive to the influence of substituents. In addition, it is extremely important that the research method employed should make it possible to separate the overall influence of the electronic effects of substituents into components due to the influence of the inductive and conjugation effects. The inductive and conjugation effects can be separated by methods of correlation analysis, which have been thoroughly developed for the study of problems of this kind in unsaturated carbon compounds[90]. The application of this approach leads to the possibility of a quantitative study of the characteristics of the manifestation of the π-acceptor properties of the elements E.

All the requirements enumerated above are satisfied by silane and germane derivatives. Important information has been obtained in the analysis of the frequencies and integral intensities of the Si–H and Ge–H stretching vibration bands in the infrared spectra of these derivatives[39-43,49,50,157,158]. The stretching vibration of the E–H bond (E = Si or Ge) takes place virtually only along the bond. The mass of the substituents linked to the atom E does not affect these vibrations. The mechanical interactions of the vibration with other vibrations in the molecule are very weak, so that the stretching vibrations of the E–H bond are highly characteristic as regards mode. At the same time, when other substituents at the atom E are varied, the frequency and intensity of the ν(E–H) band vibrations vary over a wide range owing to the electronic effects of the substituents which alter the force constant and the polarity of the E–H bond.

The ν(Si–H) frequencies were first investigated in the infrared spectra of compounds containing the $Si(CH_2)_nX$ fragments where resonance interactions between the atoms Si and X are ruled out[39,43,49,132]; the substituents in these compounds exhibit only an inductive effect. The ν(Si–H) frequencies in the infrared spectra of the above compounds are therefore linearly related to the sums of the inductive Taft constants $\sum \sigma^*$. For tri-, di-, and mono-derivatives of silane, individual correlation straight lines parallel to one another are observed+:

$$\nu_{ind} = 23 \sum \sigma^* + 2112 \ (R_3SiH), \quad (1)$$

$$\nu_{ind} = 23 \sum \sigma^* + 2121 \ (R_2SiH_2), \quad (2)$$

$$\nu_{ind} = 23 \sum \sigma^* + 2132 \ (RSiH_3). \quad (3)$$

The existence of three correlation straight lines has been explained by the hyperconjugation effect (σ,σ conjugation).[132] If the molecule contains even one *n*- or π-donor atom or a fragment X linked to a silicon atom, then the experimental stretching vibration frequency of the Si–H bond (ν_{exp}) in the infrared spectrum of such a compound becomes smaller than the value calculated from the corresponding equation in system (1)–(3). The differences $\Delta\nu = \nu_{ind} - \nu_{exp}$ are in all cases positive[39,43,49]. The difference Δν is caused by the manifestation of π-acceptor properties by the silicon atom. The inductive -*I* effect of the substituent X and the π-acceptor effect of the silicon atom in relation to the substituent X act in opposite directions. The resultant electronic effect can therefore be interpreted as a decrease of the inductive effect of the substituent X, which causes a decrease of the values of ν_{exp} relative to ν_{ind}.

The differences Δν depend strongly on the nature of the substituents X. Even a qualitative examination[157] shows that the series corresponding to increasing Δν is the same as the series based on the increase of the capacity of the substituents X for conjugation with the benzene ring when the latter is characterised by the quantity σ_R ($\sigma_R = \sigma_n - \sigma_I$, where σ_I is the inductive component of the Hammett constant σ_n of the *para*-substituent in the benzene ring). Next it was shown[157] that the quantities Δν and σ_R are linearly related:

$$\Delta\nu = -66 \sigma_R + 3. \quad (4)$$

The data examined above show, firstly, that the silicon atom exhibits an acceptor effect only when the substituent linked to it is an *n*- or π-donor and, secondly, that the π-acceptor effect of silicon exhibits the features which are observed in conjugation in unsaturated carbon compounds.

As mentioned at the beginning of this review, these features constitute one of the conditions whose fulfillment confirms that *nd* orbitals are responsible for the manifestation of acceptor properties by the atoms E. Taking into account data[134] for conjugation in ethylene derivatives, one may conclude that the mechanism of the d_π–p_π interaction is similar to that of conjugation with an aromatic ring and the vinyl group. Thus the well known[19] analogy in the behaviour of the π,π-, π,*p*-, π,σ-, and σ,σ-conjugated systems extends also to d_π–p_π interaction. When the molecule contains several groups X capable of involvement in resonance interaction with E, the degree of d_π–p_π interaction depends on the positive charge on the atom E and on the group overlap integral of the d_π and p_π orbitals of the atom E and the substituents X in the fragment EX. This will be examined in detail in the next section.

Features similar to those observed for silane derivatives are characteristic also of germane derivatives. Thus the following parallel correlation straight lines are observed for tri- and di-substituted germanes containing substituents which do not form d_π–p_π bonds with the germanium atom[40,158]:

$$\nu_{ind} = 23 \sum \sigma^* + 2015 \ (R_3GeH), \quad (5)$$

$$\nu_{ind} = 23 \sum \sigma^* + 2029 \ (R_2GeH). \quad (6)$$

The introduction into the molecule of a substituent capable of d_π–p_π interaction with the germanium atom leads, as for silane derivatives[39,43], to a decrease of the experimental stretching vibration frequency of the Ge–H bond (ν_{exp}) relative to the value calculated from the corresponding equation [(5) or (6)] on the basis of the inductive effect (ν_{ind}). The differences $\Delta\nu = \nu_{ind} - \nu_{exp}$, which constitute a quantitative

+ Here and henceforth in this review the frequencies ν, Δν, etc. are expressed in cm^{-1} and the intensities 10^{-4} *A* are expressed in $mole^{-1}\ cm^{-2}$.

measure of the effect of the d_π–p_π interaction for the compounds R_2XGeH and $RXGeH_2$, are linearly correlated with the constants σ_R of the substituents X [158]:

$$\Delta\nu = -53\,\sigma_R + 4. \quad (7)$$

Comparison of the parameters of the linear equations (4) and (7) demonstrates a smaller capacity of the germanium atom for d_π–p_π interaction compared with the silicon atom. The latter is not characteristic only of silane and germane derivatives, containing a single substituent in the molecule capable of d_π–p_π interaction with the silicon or germanium atom, but is a general property of organoelemental compounds of Group IVB elements. This problem will be examined in greater detail in the next Section; here we shall only mention that the values of $\Delta\nu$ in the infrared spectra of organosilicon and organogermanium compounds ($\Delta\nu_{Si}$ and $\Delta\nu_{Ge}$), incorporating from one to three substituents capable of d_π–p_π interaction, are linearly related[40]:

$$\Delta\nu_{Si} = 1.17\,\Delta\nu_{Ge} - 4. \quad (8)$$

It follows from Eqn.(8) that (a) the principal features of the d_π–p_π interaction in organosilicon and organogermanium compounds are identical and (b) the germanium atom exhibits a smaller capacity for d_π–p_π interaction than the silicon atom.

The results obtained in the analysis of the stretching vibration frequencies of the E–H bond in the infrared spectra of silane and germane derivatives have been confirmed by the intensities of these absorption bands (the intensity data are quoted below).

Thus the mechanism of the π-acceptor effect of the E atoms (E = Si or Ge) in compounds with the fragments E–X has a profound analogy with the effects of the conjugation of the substituent X with an aromatic ring or the vinyl group. In conformity with Jaffé's work[11], this conclusion constitutes the first argument in support of the involvement of the vacant *nd* orbitals of the atoms E in the manifestation of π-acceptor properties by these atoms.

Experimental data consistent with theoretical postulates (2) and (3) of the *nd* orbital hypothesis are examined below.

2. Dependence of the π-Acceptor Effects on the Charge on the Atoms E

As already mentioned at the beginning of this section, the strength of the d_π–p_π bonds E–X increases with increase of the positive charge on the central element E.[11] The increase of the positive charge on E (for example, as a result of the addition of electron-accepting substituents Y to the given E) while the substituent X in the molecule XEY_3 remains unchanged induces a decrease of the energy of the d_π orbitals of the atom E, since the energy of the latter approaches that of the p_π orbitals of the atom X.[13] This entails an increase of the overlap integrals of the p_π and d_π orbitals of the atoms X and E and an increase of the strength of the d_π–p_π bond E–X.

We shall consider how well these theoretical postulates [(2) and (3)] of the *nd*-orbital hypothesis are consistent with the results of the spectroscopic study and the characteristics of the π-acceptor effects of the silicon and germanium atoms in organoelemental compounds. Silane and germane derivatives are convenient objects for the investigation of the dependence of the π-acceptor properties of the element E (Si or Ge) on its charge. As shown above, the difference $\Delta\nu = \nu_{ind} - \nu_{exp}$ between the stretching vibration frequencies of the E–H bond (E = Si or Ge) in the infrared spectra calculated by Eqns.(1) to (3), (5), and (6), on the one hand, and the experimental values ν_{exp}, on the other, is a quantitative measure of the electron-accepting properties of the atoms E.

In the study of the dependence of the π-acceptor properties of the atoms E on their positive charge a number of difficulties are encountered. They are associated with the fact that an increase of the positive charge on E is usually achieved by the addition to E of substituents X having a negative inductive $-I$ effect. However, such substituents X are as a rule *n*- or π-donors and are involved in resonance interaction with the atom E, which increases the electron density on the latter. The magnitude and sign of the resultant charge on the atom E (particularly in the presence of several substituents X of the type under consideration) are therefore determined by the ratio of the electron-accepting and electron-donating properties of the substituents, i.e. depend on the relative roles of the inductive and mesomeric effects of these substituents[135].

For the reasons described, the dependence of the π-acceptor properties of the atoms E on their effective charge can be conveniently investigated by considering the values of $\Delta\nu$ for a series of compounds with an increasing number of substituents. Here the simplest case is provided by compounds with a single substituent X of the type R_2XEH or (more specifically) of the type $(C_2H_5)_2XEH$.[157] These compounds can be regarded as products of the substitution of one ethyl group in triethylsilane or triethylgermane by a substituent X. Since the silicon and germanium atoms in triethylsilane and triethylgermane have quite definite effective charges, the π-acceptor effects of these atoms are determined largely by the ability of the substituent X to transfer its unshared electron pairs to the atom E (d_π–p_π interaction). It is therefore natural to compare $\Delta\nu_1$, characterising the π-acceptor effect, with the parameter characterising the ability of unshared electron pairs of the substituent X to participate in conjugation phenomena. As shown above, such parameters are the constants σ_R. The linear correlation between $\Delta\nu_1$ and σ_R in compounds with a single substituent X [see Eqns.(4) and (7)] now becomes entirely understandable.

Consider a compound RX_2EH containing two substituents X.[135,158] The values of $\Delta\nu_2$ for these compounds, which represent the differences $\nu_{ind} - \nu_{exp}$ and are calculated by the method already examined, differ from the values of $\Delta\nu_{add}$, which are equal to twice the values of $\Delta\nu_1$ for the corresponding compounds R_2XEH (Table 2). The compounds RX_2EH can be regarded as products of the substitution of an alkyl group R in R_2XEH by the substituent X. The effective charge on the atom E in R_2XEH depends both on the inductive $-I$ effect of X and on the opposed π-acceptor effect of E in relation to X (or, in other words, the π-donor effect of X in relation to E). The magnitude and sign of this effect determine the strength of the second d_π–p_π bond between E and X and hence the overall π-acceptor effect of the atom E in X_2EH.[135,158]. This is the first cause of the discrepancy between $\Delta\nu_2$ and $\Delta\nu_{add}$ for RX_2EH (Table 2).

The charge on the atom E induced by the substituent X can be taken into account by the sum of two constants $\sigma_I + \sigma_R$, where σ_I characterises the inductive effect of X and σ_R characterises, as shown above, the π-donor effect of X in relation to E. The sum of the constants $\sigma_I + \sigma_R$ represents the Hammett σ_n constant of the substituent X. The Hammett constants are known[90] to be proportional to the charges induced by the substituent on the reaction centre. The σ_n constant of the substituent X is therefore the simplest parameter proportional to the effective charge on E. Following an enhancement of the electron-accepting properties of X, σ_n for the substituent X increases and so does the positive charge on the atom E.

According to theoretical ideas[11,12], the second cause of the discrepancy between $\Delta\nu_2$ and $\Delta\nu_{add}$ [i.e. the origin of the differences $\delta(\Delta\nu) = \Delta\nu_2 - \Delta\nu_{add}$; see Table 2] is a complex

but non-additive relation between the two- centre and group overlap integrals S. The group overlap integrals of EX_2 are related to two-centre integrals s of the E–X bonds by the expression $S = \sqrt{4/3}s$.[11] However, the values of $\Delta\nu_2$ for RX_2EH differ from the values of $\Delta\nu_{calc}$ calculated by the formula $\Delta\nu_{calc} = \sqrt{4/3}\Delta\nu_1$, where $\Delta\nu_1$ are the corresponding values for the compounds R_2XEH.

Table 2. The values of $\Delta\nu$ in the infrared spectra of the compounds $(C_2H_5)X_2SiH$.

X	$\Delta\nu_2$, cm^{-1}	ν_{add}, cm^{-1}	$\delta(\Delta\nu)$, cm^{-1}	$\Delta\nu_{calc}$, cm^{-1}	$\Delta(\Delta\nu)$, cm^{-1}	σ_n
C_6H_5	18	18	0	10	8	0.01
CH_2=CH	17	28	−11	16	1	−0.01
F	28	50	−22	29	−1	0.06
Cl	38	44	−6	25	13	0.22
Br	42	32	10	18	24	0.23
CH_3O	15	76	−61	44	−29	−0.27
CH_3S	26	44	18	25	1	−0.05

The differences $\Delta(\Delta\nu) = \Delta\nu_2 - \Delta\nu_{calc}$ are due to a single cause—the change in the effective charge on E as the substituents X are varied. The values of $\Delta(\Delta\nu)$ should therefore vary in parallel with the Hammett σ_n constants of the substituents X; experiment confirmed this. It follows from the relations

$$\Delta(\Delta\nu) = 92\,\sigma_n \quad (RX_2SiH), \tag{9}$$

$$\Delta(\Delta\nu) = 67\,\sigma_n \quad (RX_2GeH) \tag{10}$$

that an increase of the positive charge on the atom E (i.e. an increase of the values of σ_n) leads to an increase of $\Delta(\Delta\nu)$ and hence of $\Delta\nu_2$, i.e. to an enhancement of the π-acceptor properties of the atoms E. Such enhancement is more pronounced for silicon compounds[135,158].

These conclusions were confirmed by a theoretical estimate of the overlap integrals of the Si–X bonds (X = O, S, or Cl) in the SiX_n fragments (n = 1–4) and of the dependence of the overlap integrals on the effective charge on the silicon atom[135]. The dependence of the π-acceptor effects on the atomic charge of E is clearly manifested in the study of the stretching vibration frequencies of the Si–H bonds in the infrared spectra of arylsilanes[105] and of the intensity of the ν(E–H) bands in the spectra of silane and germane derivatives[41,42,50,165,166].

The electron-accepting nature of the group XC_6H_4 in arylsilanes $Alk_{3-n}(XC_6H_4)_nSiH$ becomes significantly more pronounced with enhancement of the electron-accepting properties of the *meta*- or *para*-substituents X. At the same time there is an increase of the positive charge on the silicon atom. The values of $\Delta\nu$ (examined in detail above), which characterise the π-acceptor effect of the silicon atom in relation to the aryl substituent, increase with enhancement of the electron-accepting properties of the aryl substituents, i.e. with increase of the positive charge on the silicon atom. Under these conditions, the following linear relation holds[105]:

$$\Delta\nu = 12\sum\sigma^* + 4, \tag{11}$$

since, according to the data of Fisera et al.,[167] the inductive constants σ^* of the aryl substituents are linearly related to their σ_n constants.

Systematic studies of the integral intensities of the bands associated with the highly characteristic vibrations of the Si–H [41,50] and Ge–H [42,165,166] bonds in the infrared spectra of silane and germane derivatives served as yet another source of information about the dependence of the π-acceptor properties of the atoms E on their charge. While analysis of the frequencies of the highly characteristic M–H vibrations (i.e. analysis of the force constants) yields information about the energies of the E–H bonds, the study of their intensities makes it possible to investigate the polarity (dipole moment) of the E–H bond and in particular the influence on polarity of the π-acceptor effects involving E.

The square roots $A^{1/2}$ of the ν(E–H) absorption band intensity in the infrared spectra are linearly related to the sums of the inductive Taft constants $\sum\sigma^*$ of the substituents, exhibiting only an inductive effect in trisubstituted silane and germane derivatives[166]:

$$A^{1/2}_{ind} = 1.20 - 0.21\sum\sigma^*(R_3SiH), \tag{12}$$

$$A^{1/2}_{ind} = 1.30 - 0.20\sum\sigma^*(R_3GeH). \tag{13}$$

The intensity ($A^{1/2}_{exp}$) of the ν(E–H) bands in compounds with substituents of the n- or π-donor type (X) is higher than the values calculated by Eqns.(12) and (13). The differences $\Delta A^{1/2}_{exp} = A^{1/2}_{ind} - [?]$ are characterised by the π-acceptor effect of the atom E and other conjugation effects. For compounds with E–X bonds in which the π-acceptor effect of the atom E is the dominant conjugation effect, the following linear relations hold[41,166]:

$$\Delta A^{1/2} = 1.47\Sigma\sigma_n + 0.12 \quad \text{(silane derivatives)}, \tag{14}$$

$$\Delta A^{1/2} = 1.09\Sigma\sigma_n + 0.36 \quad \text{(germane derivatives)}. \tag{15}$$

Thus it follows from the intensities of the infrared bands that the π-acceptor properties of the atoms E (characterised by the quantities $\Delta A^{1/2}$ and most pronounced for silicon compounds) increase with increase of the effective positive charge on E (characterised by the sums $\sum\sigma_n$ of the Hammett constants of the substituents linked to E).

Summarising the data presented in the third Section of this review, we may note that these conditions are regarded[3,10–15] as necessary and sufficient for the formation of d_π–p_π bonds. These were enumerated at the beginning of the Section and have been confirmed experimentally.

Thus the available experimental spectroscopic data for the π-acceptor effects of silicon subgroup elements do not require for their interpretation hypotheses other than that based on the d_π–p_π interaction and constitute an indirect confirmation of the widely held view that π-acceptor properties are a manifestation of the effect of the d_π–p_π interaction.

REFERENCES

1. F.G.A.Stone and D.Seyfert, J.Inorg.Nuclear Chem., 1, 112 (1955).
2. H.Burger, Forstschr.chem.Forsch., 79, 934 (1967).
3. E.A.V.Ebsworth in "Organometallic Compounds of the Group IV Elements. The Bond to Carbon, (Edited by A.G.MacDiarmid), M.Dekker, New York, 1968, Vol.1, p.1.
4. K.A.R.Mitchel, Chem.Rev., 69, 157 (1969).
5. C.J.Attridge, Organometal.Chem.Rev., A5, 323 (1970).
6. A.N.Egorochkin, N.S.Vyazankin, and S.Ya.Khorshev, Uspekhi Khim., 41, 828 (1972)[Russ.Chem. Rev., No.5 (1972)].
7. A.W.P.Jarvie, Organometal.Chem.Rev., A6., 153 (1970).

8. J.M.Bellama and A.G.MacDiarmid, J.Organometal Chem., **24**, 91 (1970).
9. L.Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, New York, 1948.
10. W.Moffitt, Proc.Roy.Soc., **A200**, 409 (1950).
11. H.H.Jaffé, J.Phys.Chem., **58**, 185 (1954).
12. D.P.Craig, A.Maccoll, R.S.Nyholm, L.E.Orgel, L.E.Sutton, J.Chem.Soc., 332 (1954).
13. C.A.Coulson, Nature, **221**, 1106 (1969).
14. G.Häfelinger, Topics in Current Chemistry, **28**, 1 (1972).
15. M.E.Dyatkina, "Osnovy Teorii Molekulyarnykh Orbitalei" (Fundamentals of the Molecular Orbital Theory) Izd.Nauka, Moscow, 1975, p.148.
16. D.A.Bochvar, N.P.Gandaryan, and L.M.Epshtein, Uspekhi Khim., **45**, 1316 (1976)[Russ.Chem.Rev., No.7 (1976)].
17. C.G.Pitt, Chem.Comm., 816 (1971).
18. J.I.Musher, Angew.Chem., Int.Ed., **8**, 54 (1969).
19. A.N.Nesmeyanov, Uch.Zap.Moskov.Univ., No.132, 5 (1950).
20. R.Ponec and V.Chvalovsky, Coll.Czech.Chem. Comm., **38**, 3845 (1973).
21. R.Ponec and V.Chvalovsky, Coll.Czech.Chem. Comm., 39, 1185 (1974).
22. C.G.Pitt. J.Organometal.Chem., **61**, 49 (1973).
23. V.F.Sidorkin, V.A.Pestunovich, and M.V.Voronkov, Dokl.Akad.Nauk SSSR, **235**, 1363 (1977).
24. V.I.Nefedov, "Valentyne Urovni Khimicheskikh Soedinenii" (The Valence Levels of Chemical Compounds), Izd.VINITI, Moscow, 1975, Vol.3.
25. A.P.Sadovskii, G.N.Dolenko, L.N.Mazalov, V.D.Yumatov, E.S.Gluskin, Yu.I.Nikonorov, and Gal'tsova, Izv.Akad.Nauk SSSR, Ser.Fiz., 606 (1974).
26. K.S.Krasnov, V.S.Timoshinin, T.G.Danilova, and S.V.Khandozhko, "Molekulyarnye Postoyannye Neorganicheskikh Soedinenii" (Molecular Constants of Inorganic Compounds), Izd.Khimiya, Leningrad, 1968.
27. L.O.Brockway and F.T.Wall, J.Amer.Chem.Soc., **56**, 2373 (1934).
28. H.Burger, Spectrochim.Acta, **24A**, 1863 (1968).
29. H.Burger and A.Ruoff, Spectrochim Acta, **24A**, 2015 (1968).
30. H.Burger, W.Kilian, and K.Burszyk, J.Organometal.Chem., **21**, 291 (1970).
31. H.Burger, U.Goctze, and W.Sawodny, Spectrochim. Acta, **26A**, 685 (1970).
32. F.Hofler, W.Sawodny, and E.Hengge, Spectrochim. Acta, **26A**, 819 (1970).
33. S.Cradock and E.A.V.Ebsworth, Chem.Comm., 57 (1971).
34. P.J.Bassett and D.R.Lloyd, J.Chem.Soc., (A), 641 (1971).
35. S.Cradock and R.A.Whiteford, Trans.Faraday Soc., **67**, 3425 (1971).
36. S.Cradock, E.A.V.Ebsworth, and R.A.Whiteford, J.Chem.Soc., Dalton Trans., **22**, 2401 (1973).
37. M.Jakoubkova, Z.Paoouskova, J.Pola, and V.Chvalovsky, Coll.Czech.Comm., **42**, 2793 (1977).
38. G.K.Semin, T.A.Babushkina, and G.G.Yakobson, "Primenenie Yadernogo Kvadrupol'nogo Rezonansa v Khimii" (Chemical Applications of Nuclear Quadrupole Resonance), Izd.Khimiya, Leningrad, 1972, Chapter 6.
39. A.N.Egorochkin, N.S.Vyazankin, S.Ya.Khorshev, T.I.Chernysheva, and O.V.Kuz'min, Izv.Akad.Nauk SSSR, Ser.Fiz., 1651 (1970).
40. A.N.Egorochkin, S.Ya.Khorshev, N.S.Ostasheva, J.Satge, P.Riviere, J.Barrau, and M.Massol, J. Organometal.Chem., **76**, 29 (1974).
41. A.N.Egorochkin, S.Ya.Khorshev, N.S.Ostasheva, M.G.Voronkov, N.S.Vyazankin, T.V.Kashik, O.V.Kuz'min, N.S.Nametkin, and N.A.Pritula, J. Organometal.Chem., **99**, 47 (1975).
42. A.N.Egorochkin, S.Ya.Khorshev, N.S.Ostasheva, E.I.Sevast'yanova, J.Satge, P.Riviere, and J.Barrau, J.Organometal Chem., **105**, 311 (1976).
43. A.N.Egorochkin, N.S.Vyazankin, A.I.Burov, and S.Ya.Khorshev, Izv.Akad.Nauk SSSR, Ser.Fiz., 1279 (1970).
44. S.Sorriso, A.Ricci, and R.Danielli, J.Organometal Chem., **87**, 61 (1975).
45. M.G.Voronkov, V.P.Mileshkevich, and Yu.A.Yuzhelevskii, "Siloksanovaya Svyaz'" (The Siloxane Bond), Izd.Nauka, Novosibirsk, 1976, Chapter 1.
46. I.F.Kovalev, Doctoral Thesis Saratov University, 1974.
47. C.Glidewell, D.W.H.Rankin, A.G.Robiette, G.M.Sheldrick, B.Beagley, and S.Cradock, J.Chem. Soc., (A), 315 (1970).
48. L.V.Vilkov and N.A.Tarasenko, Zhur.Strukt.Khim., 10, 1102 (1969).
49. A.N.Egorochkin, N.S.Vyazankin, and S.Ya.Khorshev, Izv.Akad.Nauk SSSR, Ser.Fiz., 2394 (1970).
50. A.N.Egorochkin, N.S.Vyazankin, N.S.Ostasheva, O.V.Kuz'min, N.S.Nametkin, I.F.Kovalev, and M.G.Voronkov, J.Organometal.Chem., **59**, 117 (1973).
51. A.N.Egorochkin, M.N.Bochkarev, N.S.Vyazankin, S.E.Skobeleva, and S.Ya.Khorshev, Dokl.Akad.Nauk SSSR, **198**, 96 (1971).
52. A.N.Egorochkin, S.Ya.Khorshev, and N.S.Vyazankin, Dokl.Akad.Nauk SSSR, **185**, 353 (1969).
53. E.M.Arnett, in "Sovremennye Problemy Fizicheskoi Organicheskoi Khimii" (Modern Problems in Physical Organic Chemistry), (Translated into Russian), Izd. Mir, Moscow, 1967, p.195.
54. R.West, R.H.Baney, and D.L.Powell, J.Amer.Chem. Soc., **82**, 6269 (1960).
55. R.West, H.Ronald, and R.H.Baney, J.Amer.Chem. Soc., **81**, 6145 (1959).
56. R.M.Salinger and R.West, J.Organometal.Chem., 11, 631 (1968).
57. A.N.Egorochkin, G.A.Domrachev, N.S.Vyazankin, S.Ya.Khorshev, O.S.D'yachkovskaya, and V.T.Bychkov, Izv.Akad.Nauk SSSR, Ser.Fiz., 164 (1971).
58. C.Glidewell, D.W.H.Rankin, A.G.Robiette, G.M.Sheldrick, B.Beagley, and J.M.Freeman, Trans. Faraday Soc., **65**, 2621 (1969).
59. E.W.Abel, D.A.Armitage, and B.D.Brady, Trans. Faraday Soc., **62**, 3459 (1966).
60. "Spravochnik Khimika" (The Chemist's Handbook), Izd.Khimiya, Leningrad, 1966, Vol.1.
61. B.Beagley and A.R.Conrad, Trans.Faraday.Soc., **66**, 2740 (1970).
62. B.Beagley and A.R.Medwid, J.Molec.Struct., **38**, 239 (1977).
63. D.W.H.Rankin, J.Chem.Soc., **(A)**, 1926 (1969).
64. J.D.Murdoch, D.W.H.Rankin, and B.Beagley, J. Mol.Struct., 31, 291 (1976).
65. N.A.Tarasenko, Candidate's Thesis, Moscow State University, Moscow, 1970.
66. V.Schomaker and D.P.Stevenson, J.Amer.Chem.Soc., **63**, 37 (1941).

67. N.G.Bokii and Yu.T.Struchkov, Zhur.Strukt.Khim., **9**, 722 (1968).
68. A.N.Egorochkin, N.S.Vyasankin, and S.Ya.Khorshev, Izv.Akad.Nauk SSSR, Ser.Khim., 2609 (1970).
69. C.K.Ingold, "Theoretical Principles of Organic Chemistry" [Structure and Mechanism in Organic Chemistry ?] (Translated into Russian), Izd.Mir, Moscow, 1973.
70. J.W.Rakhys, R.W.Taft, and W.A.Sheppard, J. Amer.Chem.Soc., **90**, 5236 (1968).
71. E.N.Tsvetkov, D.A.Bochvar, and M.I.Kabachnik, Teor.Eksper.Khim., **3**, 3 (1967).
72. E.W.Abel, D.A.Armitage, and G.R.Willey, Trans. Faraday Soc., **60**, 1257 (1964).
73. J.Mack and C.H.Yoder, Inorg.Chem., **8**, 278 (1969).
74. M.Jakoubkova and V.Chvalovsky, Coll.Czech.Chem. Comm., **33**, 3062 (1968).
75. Z.Pacl, J.Jakoubkova, V.Chvalovsky, and V.Bazant, Coll.Czech.Chem.Comm., **36**, 1682 (1971).
76. Z.Pacl, M.Jakoubkova, R.Rericha, and V.Chvalovsky, Coll.Czech.Chem.Comm., **36**, 2181 (1971).
77. J.Reijhou, J.Hetflejs, M.Jakoubkova, and V.Chvalovsky, Coll.Czech.Comm., **37**, 3054 (1972).
78. D.Seyferth, A.W.Dow, H.Menzel, and T.C.Flood, J.Amer.Chem.Soc., **90**, 1080 (1968).
79. E.Lukevics, M.G.Voronov, V.E.Shestakov, and A.E.Pestunovich, Zhur.Obshch.Khim., 41, 2218 (1971).
80. E.Popowski, G.Zinder, and H.Kelling, Z.Chem., **14**, 289 (1974).
81. J.R.During and P.J.Cooper, J.Phys.Chem., **81**, 637 (1977).
82. J.Plazanet, F.Metras, A.Marchand, and J.Valade, Bull.Soc.chim.France, 1920 (1967).
83. S.E.Skobeleva, A.N.Egorochkin, N.S.Vyazankin, D.Ya.Zhinkin, G.M.Mal'nova, M.M.Morgunova, and Zh.V.Gorislavskaya, Izv.Akad.Nauk SSSR, Ser. Khim., 644 (1973).
84. S.Ya.Khorshev, A.N.Egorochkin, E.I.Sevast'yanova, and S.P.Korneva, Zhur.Obshch.Khim., **47**, 1795 (1977).
85. E.W.Randall and J.J.Zuckerman, J.Amer.Chem.Soc., **90**, 3167 (1968).
86. R.A.N.McLean, Canad.J.Chem., **51**, 2089 (1973).
87. G.Distefano, S.Pignataro, L.Szepes, and J.Borossay, J.Organometal.Chem., **104**, 173 (1976).
88. Y.Limouzin and J.C.Maire, J.Organometal Chem., **92**, 169 (1975).
89. Y.Limouzin and J.C.Maire, J.Organometal.Chem., **105**, 179 (1976).
90. Yu.A.Zhdanov and V.I.Minkin, "Korrelyatsionnyi Analiz v Organicheskoi Khimii" (Correlation Analysis in Organic Chemistry), Izd.Rostov.Univ., 1966, Chapter VII.
91. M.E.Freeburger and L.Spialter, J.Amer.Chem.Soc., **93**, 1894 (1971).
92. P.N.Preston, L.H.Sutcliffe, and B.Taylor, Spectrochim.Acta, **28A**, 197 (1972).
93. A.J.Smith, W.Adcock, and W.Kitching, J.Amer. Chem.Soc., **92**, 6140 (1970).
94. J.P.Bremonde, M.Donnier, and Y.Limouzin, J. Organometal.Chem., **90**, 279 (1975).
95. J.M.Angelelli, M.A.Delmas, J.C.Maire, and J.P.Zahra, J.Organometal.Chem., **128**, 313 (1977).
96. J.M.Angelelli, M.A.Delmas, J.C.Maire, and J.P.Zahra, J.Organometal.Chem., **128**, 325 (1977).
97. J.M.Angelelli, M.A.Delmas, and J.C.Maire, J.Organometal.Chem., **131**, 225 (1977).
98. W.Caminati, G.Cazzoli, and A.M.Mirri, Chem.Phys. Letters, **35**, 475 (1975).
99. A.N.Egorochkin, N.S.Vyazankin, S.E.Skobeleva, S.Ya.Khorshev, N.A.Pritula, and E.A.Chernyshev, Zhur.Obshch.Khim., **42**, 904 (1972).
100. V.A.Kuznetsova, A.N.Egorochkin, S.E.Skobeleva, G.A.Razuvaev, N.A.Pritula, and G.Ya.Zueva, Zhur.Obshch.Khim., **45**, 2439 (1975).
101. H.Bock and T.Alt, J.Amer.Chem.Soc., **92**, 1569 (1970).
102. V.A.Kuznetsov, A.N.Egorochkin, G.A.Razuvaev, S.E.Skobeleva, and N.A.Pritula, Dokl.Akad.Nauk SSSR, **216**, 812 (1974).
103. V.F.Traven', B.A.Korolev, T.V.Pyatkina, and B.I.Stepanov, Zhur.Obshch.Khim., **45**, 954 (1975).
104. C.J.Attridge, J.Organometal.Chem., **13**, 259 (1968).
105. A.N.Egorochkin, N.S.Vyazankin, N.A.Pritula, T.I.Chernysheva, and G.K.Spiridonova, Dokl.Akad. Nauk SSSR, **199**, 352 (1971).
106. V.Vaisarova and V.Chvalovsky, Coll.Czech.Chem. Comm., **33**, 859 (1968).
107. H.H.Huang and K.M.Hui, J.Organometal.Chem., **11**, 515 (1968).
108. V.Vaisarova, J.Hetflejas, and V.Chvalovsky, J. Organometal.Chem., **22**, 395 (1970).
109. J.Nagy and J.Reffy, J.Organometal.Chem., **22**, 565 (1970).
110. I.P.Gol'dshtein, V.F.Traven', V.I.Kozlov, T.V.Pyatkina, E.N.Gur'yanova, and B.I.Stepanov, Zhur.Obshch.Khim., **46**, 2540 (1976).
111. H.Bock, H.Alt,, F.Gerson, and J.Heinzer, Angew. Chem., **79**, 932 (1967).
112. H.Bock and H.Seidl, J.Organometal.Chem., **13**, 87 (1968).
113. H.Bock, H.Seidl, and M.Focheer, Chem.Ber., **101**, 2815 (1968).
114. F.Gerson, J.Heinzer, H.Bock, and H.Seidl, Helv. Chim.Acta, **51**, 707 (1968).
115. A.L.Allred and L.W.Bush, J.Amer.Chem.Soc., **90**, 3352 (1968).
116. V.A.Kuznetsov, A.N.Egorochkin, S.Yu.Khovryakov, and D.V.Muslin, Zhur.Obshch.Khim., **44**, 1958 (1974).
117. A.G.Evans, B.Jerome, and N.H.Rees, J.Chem.Soc., Perkin Trans.II, 447 (1973).
118. V.A.Kuznetsov, A.N.Egorochkin, A.I.Burov, E.A.Chernyshev, V.I.Savushkina, V.Z.Anisimova, and O.V.Kuz'man, Dokl.Akad.Nauk SSSR, **216**, 1062 (1974).
119. V.A.Kuznetsov, A.N.Egorochkin, V.A.Savin, E.Lukevics, and N.P.Erchak, Dokl.Akad.Nauk SSSR, **221**, 107 (1975).
120. M.Magi, E.Lippmaa, and N.P.Ercak, Org.Magn. Reson, **9**, 297 (1977).
121. H.Bock and H.Seidl, J.Amer.Chem.Soc., **90**, 5694 (1977).
122. R.West and C.S.Kraihauzel, Inorg.Chem., **1**, 967 (1962).
123. O.A.Novikov, V.P.Kuznetsov, and K.A.Kornev, Zhur.Obshch.Khim., **38**, 178 (1968).
124. J.Parker and J.A.Ladd, Trans.Faraday Soc., **66**, 1907 (1970).
125. A.N.Egorochkin, N.S.Vyazankin, S.E.Skobeleva, S.Ya.Khorshev, V.F.Mironov, and T.K.Gar, Zhur. Obshch.Khim., **42**, 643 (1972).
126. M.G.Voronkov, N.I.Shergina, L.V.Sherstyannikova, R.G.Mirskov, N.P.Ivanova, and A.I.Kuznetsov, Dokl.Akad.Nauk SSSR, **233**, 613 (1977).

127. M.Bock and H.Alt, Chem.Ber., **103**, 1784 (1970).
128. V.A.Kuznetsov, A.N.Egorochkin, G.A.Razuvaev, V.F.Mironov, V.D.Shcheludyakov, and V.V.Shcherbinin, Dokl.Akad.Nauk SSSR, **220**, 376 (1975).
129. M.F.Shostakovskii, N.I.Shergina, T.I.Ermolaeva, and N.V.Komarov, Izv.Akad.Nauk SSSR, Ser.Khim., 1565 (1970).
130. E.A.Gastilovich, K.V.Zhukova, D.N.Shigorin, O.G.Yarosh, and I.S.Aknurina, Optika i Spektrosk., **29**, 41 (1970).
131. R.A.Bogatkin, O.V.Sverdlova, and V.A.Gindin, Zhur.Obshch.Khim., **41**, 2220 (1971).
132. A.A.Petrov, I.V.Elsakov, V.F.Zavgorodnii, and B.V.Lebedev, Teor.Eksper.Khim., 1, 697 (1965).
133. L.A.Leites, I.D.Pavlova, and Yu.P.Egorov, Teor. Eksper.Khim., 1, 311 (1965).
134. A.N.Egorochkin, Yu.D.Semchikov, N.S.Vyazankin, and S.Ya.Khorshev, Izv.Akad.Nauk SSSR, Ser. Khim., 152 (1970).
135. A.N.Egorochkin and N.S.Vyazankin, Izv.Akad.Nauk SSSR, Ser.Khim., 342 (1972).
136. G.Guillerm, M.Lequon, and M.P.Simonnin, Bull.Soc. chim.France, 1649 (1973).
137. V.S.Zavgorodnii, E.T.Bogoradovskii, V.L.Maksimov, V.B.Lebedev, B.I.Rogozev, and A.A.Petrov, Zhur. Obshch.Khim., **45**, 2466 (1975).
138. M.T.W.Hearn, J.Magn.Reson., **22**, 521 (1976).
139. J.Schraml, V.Chvalovsky, M.Magi, and E.Lippmaa, Coll.Czech., Chem.Comm., **42**, 306 (1977).
140. E.V.Arshavskaya, N.A.Vasneva, and A.M.Sladkov, Dokl.Akad.Nauk SSSR, **234**, 833 (1977).
141. H.Bock and H.Alt, J.Organometal.Chem., **13**, 103 (1968).
142. J.Nagy and P.Henscei, J.Organometal.Chem., **24**, 285 (1970).
143. E.D.Lavrenenko-Ometsinskaya, V.V.Pen'kovskii, T.I.Krasnova, and E.A.Chernyshev, Teor.Eksper. Khim., **10**, 756 (1974).
144. A.P.Sadimenko, Yu.V.Kolodyazhnyi, L.P.Gudkova, N.I.Sizova, G.S.Gol'din, M.M.Morgunov, L.S.Baturina, and O.A.Osipov, "Tezisy Dokladov IV Mezhdunarodnogo Simpoziuma po Khimii Kremniiorganicheskikh Soedinenii" (Abstracts of Reports at the IVth International Symposium on the Chemistry of Organosilicon Compounds), Moscow, 1975, Vol.1, p.52.
145. P.Hencsei, E.Zimonyi-Hegedus, and J.Nagy, "Tezisy Dokladov IV Mezhdunarodnogo Simpoziuma po Khimii Kremniiorganicheskikh Soedinenii" (Abstracts of Reports at the IVth International Symposium on the Chemistry of Organosilicon Compounds), Moscow, 1975, Vol.1, p.88.
146. Yu.V.Kolodyazhnyi, N.I.Sizova, A.P.Sadimenko, L.G.Loi, E.V.Serebrennikova, N.V.Komarov, and O.A.Osipov, "Tezisy Dokladov IV Mezhdunarodnogo Simpoziuma po Khimii Kremniiorganicheskikh Soedinenii" (Abstracts of Reports at the IVth International Symposium on the Chemistry of Organosilicon Compounds), Moscow, 1975, Vol.1, p.155.
147. D.R.Armstrong, J.Jamieson, and P.G.Perkins, Theoret.Chim.Acta, **25**, 396 (1972).
148. V.I.Danilova, V.P.Shcherbina, and L.V.Gorchakov, Article deposited at the All-Union Institute of Scientific and Technical Information (VINITI) (No.1191-75 Dep.1975).
149. P.G.Perkins, Chem.Comm., 268 (1967).
150. P.G.Perkins, Theoret.Chim.Acta, **12**, 427 (1968).
151. J.Nagy and J.Reffy, J.Organometal.Chem., **23**, 71 (1970).
152. M.I.Drews and P.R.Jones, J.Organometal.Chem., **82**, 57 (1974).
153. E.D.Lavrenenko-Ometsinskaya, V.V.Pen'kovskii, and V.V.Strelko, Teor.Eksper.Khim., 11, 535 (1975).
154. M.T.Vandorci, T.N.Marchenko, and A.E.Lutskii, Teor.Eksper.Khim., 11, 530 (1975).
155. J.Reffy, T.Veszpremi, and J.Nagy, "Tezisy Dokladov IV Mezhdunarodnogo Simpoziuma po Khimii Kremniiorganicheskikh Soedinenii" (Abstracts of Reports at the IVth International Symposium on the Chemistry of Organosilicon Compounds), Moscow, 1975, Vol.1, p.58.
156. J.Kroner and H.Bock, Theoret.Chim.Acta, 12, 214 (1968).
157. A.N.Egorochkin and N.S.Vyazankin, Dokl.Akad. Nauk SSSR, **193**, 590 (1970).
158. A.N.Egorochkin, S.Ya.Khorshev, J.Satge, P.Riviere, and J.Barrau, J.Organometal.Chem., **99**, 239 (1975).
159. V.P.Feshin and M.G.Voronkov, Dokl.Akad.Nauk. SSSR, **236**, 1166 (1977).
160. S.Ya.Khorshev, A.N.Egorochkin, E.I.Sevast'yanov, and O.V.Kuz'min, Zhur.Obshch.Khim., **48**, 1348 (1978).
161. W.Adcock, B.D.Gupta, W.Kitching, and D.Doddrell, J.Organometal.Chem., **102**, 297 (1975).
162. W.Adcock, D.P.Cox, and W.Kitching, J.Organometal. Chem., **133**, 393 (1977).
163. R.D.Bach and P.A.Scherr, Tetrahedron Letters, 1099 (1973).
164. U.Weidner and A.Schmeig, Angew.Chem., Int.Ed., **11**, 146 (1972).
165. A.N.Egorochkin, S.Ya.Khorshev, E.I.Sevast'yanova, S.Kh.Ratushnaya, J.Satge, P.Riviere, J.Barrau, and S.Richelme, J.Organometal.Chem., **155**, 175 (1978).
166. A.N.Egorochkin, E.I.Sevast'yanova, S.Ya.Khorshev, S.Kh.Ratushnaya, J.Satge, P.Riviere, J.Barrau, and S.Richelme, J.Organometal.Chem., **162**, 25 (1978).
167. L.Fisera, J.Sura, J.Kovac, and M.Lucky, Coll. Czech.Chem.Comm., **39**, 1711 (1974).

Institute of Chemistry,
USSR Academy of Sciences,
Gorky

Translated from *Uspekhi Khimii*, **49**, 1711-1729 (1980) U.D.C. 541.124.547.54-39

The Mechanisms of the Rearrangements of Peroxides

V.A.Yablokov

The results of studies on the mechanisms of the rearrangements of organic and organoelemental peroxides are surveyed and the similarity of the mechanisms regardless of the structure of the peroxides is emphasised. The rearrangements of peroxides are regarded as intramolecular processes involving a concerted redistribution of bonds in a polar or radical-ion activated complex.
The bibliography includes 151 references.

CONTENTS

I. Introduction 833
II. Acid-catalysed rearrangement of hydroperoxides 833
III. Thermal rearrangement of peroxyesters 835
IV. Thermal and catalytic rearrangements of diacyl peroxides 836
V. Rearrangement of alkyl (aryl) peroxides 837
VI. Rearrangement of organoelemental peroxides 837

I. INTRODUCTION

The rearrangements of organic and organoelemental peroxides involve a change in the structure of the initial molecule to that of an isomeric compound without the peroxy-group. The peroxides undergoing the rearrangement do not induce the polymerisation of unsaturated compounds and are unaffected by inhibitors and initiators of radical reactions, but are extremely sensitive to the action of protic and Lewis acids. The rearrangement of organic peroxides was observed by Wieland and Maier[1] as early as the 1930's. The oxidation of aldehydes and ketones by hydrogen peroxide or peracids (the Baeyer–Villiger reaction) is also classified as a process involving an intramolecular rearrangement of intermediate peroxyesters[2]. In essence, it was not until the beginning of the 1950's that attention was drawn to reactions of this type; at that time the first factory in the work manufacturing phenol by the cumene method, based on the acid-catalysed rearrangement of peroxides, was set up in the USSR.[3,4] The possibility, in principle, of the catalytic rearrangement of cumenyl hydroperoxide was also demonstrated by Hock and Lang[5].

Since the determination of the principal products of the thermal decomposition of diacyl peroxides by Wieland and Razuvaev[6] and the introduction of Waters' concept of the homolysis of the peroxy-bond[7], a considerable time elapsed before practical applications of the reactions of peroxides were discovered. The urgent need for polymeric materials brought peroxides to the forefront as effective initiators of radical polymerisation and vulcanisation processes[8,9]. As knowledge of the reactions of peroxides deepened, investigators observed with increasing frequency simultaneous non-radical reactions.

The rearrangements of peroxides are encountered much more frequently than might have been supposed at the time when the chemistry of peroxides was established. They have been observed for all classes of peroxy-compounds (hydroperoxides, diacyl peroxides, peroxyesters, and organoelemental peroxides), in certain cases as the only possible reaction pathway.

There is not yet a unanimous view concerning the mechanism of the rearrangement. In some cases the rearrangement is regarded as a heterocytic process and in others as a homolytic process. The asymmetry of peroxyester and hydroperoxide molecules suggests the polarisation of the O–O bond already in the initial state. Even when the initial state is only weakly polar, for example, in symmetrical diacyl and silyl peroxides, the polarisation of the activated state has been postulated. The significant influence of the polar effects of substituents and the medium on the rate of reaction as well as the non-radical nature of the reaction products were regarded as the principal features of a heterolytic process[10]. However, an increasing amount of experimental data indicating that the above features are characteristic also of radical reactions has appeared. The radical formation reactions undergone by certain t-butylperoxesters constitute a homolytic fragmentation of a polar activated state[11].

The study of homolytic and heterolytic reactions led to the observation of an increasing number of facts which make it possible to treat these processes as inter-related. It is not fortuitous that evidence has been adduced in a number of studies for a radical-ion mechanism of the rearrangement of peroxides[12].

The aim of the present review was to analyse the mechanisms of the rearrangements of peroxides known at the present time and to determine how far they are consistent with the modern ideas of theoretical and experimental chemistry.

II. ACID-CATALYSED REARRANGEMENT OF HYDROPEROXIDES

The rearrangements of hydroperoxides of different structures involve their sensitivity to the action of electrophiles, which is common to all of them. Here the hydroperoxide behaves as a base in relation to protic or aprotic acids. The most effective electrophiles exhibiting catalytic activity are protic acids[13–15]. Acid anhydrides and chlorides as well as Lewis acids cannot be regarded as true catalysts of the rearrangement, because in the course of the reaction they interact irreversibly with the hydroperoxide[14].

The acid-catalysed rearrangement of the hydroperoxide takes place readily in polar and non-polar solvents. Depending on the direction of attack by the electrophile (HA), there is a possibility of either a rearrangement, if the oxygen atom O_β is attacked,

$$(R_f)_3 - C - O_\alpha - O_\beta - H,$$

or of a transformation of the hydroperoxide molecule into a carbinol and hydrogen peroxide if the oxygen atom O_α is attacked. The latter reaction occurs with triphenylmethyl hydroperoxide and its derivatives in water-containing media[16,17]: it is not characteristic of cumenyl hydroperoxide[16,17].

On the basis of general considerations concerning acid–base reactions, in early studies of catalytic reactions of hydroperoxides it was assumed[18,19] that the interaction of alkyl hydroperoxide with a strong acid leads to the formation of a peroxyester in which the O–O bond is ionic. The process was represented by two consecutive elementary reactions:

$$PhMe_2COOH + H_2SO_4 \rightarrow PhMe_2\overset{+}{C}O\overline{O}SO_2H + H_2O\ , \quad (1)$$

$$PhOH + Me_2CO + H_2SO_4 \xleftarrow{H_2O} (PhO)\,Me_2COSO_2H\ . \quad (2)$$

However, the attempts to demonstrate the existence of the cation $\geq C-O^{(+)}$ were unsuccessful. Even under the influence of superacids of the type FSO_3H/SbF_5, only the formation of alkoxycarbonium ions was detected (by NMR).[20]

The following objections were raised against the above mechanism[21]. First, it was shown that the peroxyesters of strong acids decompose via the reactions

$$PhMe_2COOSO_2R \rightarrow (PhO)\,Me_2COSO_2R\ , \quad (3)$$

$$(PhO)\,Me_2COSO_2R \rightarrow PhOC(Me)=CH_2 + RSO_3H \quad (4)$$

and cannot be intermediates in reactions (1) and (2). Secondly, when reactions (1) and (2) take place, the phenol and the ketone should contain the ^{18}O isotope on decomposition of the hydroperoxide in the presence of $H_2S^{18}O_4$ and $H_2{}^{18}O$.[22] Isotopic studies showed that the phenol did not contain an excess of ^{18}O compared with its natural abundance. In the ketone ^{18}O was detected in amounts corresponding to direct isotope exchange between $H_2{}^{18}O$ and the ketone[22]. The following mechanism is most plausible[21]:

$$(R_i)_3COOH + HA \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (R_i)_3COOH_2A\ ; \quad (5)$$

$$(R_i)_3COOH_2A \xrightarrow{k_2} \left[\begin{array}{c} R_i \quad R_i \\ \diagdown\ \ \diagup \\ C \\ R_i\,\delta+ \quad \delta-\,OH_2A \\ \diagdown\ \ \diagup \\ O \end{array}\right]^{\#} \rightarrow R_iO(R_i)_2COH + HA\ ; \quad (6)$$

(I)

$$R_iO(R_i)_2COH \xrightarrow{k_3} R_iOH + (R_i)_2C{=}O\ . \quad (7)$$

The protonation of the hydroperoxide is a rapid reversible reaction [reaction (5)]. In the rate-limiting stage [reaction (6)] the electron density is redistributed and the internal nucleophile migrates to one of the peroxide oxygens.

The linear dependence of the logarithm of the rate constant for the rearrangement of the hydroperoxide on the acidity function[23,24] as well as the positive kinetic isotope effect[25] support a rapid reversible interaction of hydroperoxides with the acid, leading to the formation of a hydroperoxide–acid complex. Simple calculations[26] lead to an expression for the experimental rate constant k for the rearrangement:

$$k = \frac{k_1}{k_{-1}} k_2 [HA]_0, \quad (8)$$

where $[HA]_0$ is the initial concentration of the acid.

Kinetic measurements[27–30] have shown that there is a linear relation between the apparent rate constant and the initial acid concentration. The order of the reaction with respect to the acid can be greater than unity if the acid is associated[31]. The experimental rate constants are effective quantities [see Eqn.(8)]. It is therefore difficult to expect the activation parameters to reflect fully the nature of the rate-determining stage of the process. Nevertheless one should turn attention to the fact that the pre-exponential factors correspond to a negative entropy of activation[26,32]. This agrees to some extent with the claim[26] that the rate-determining stage in the rearrangement of hydroperoxides involves a rigid cyclic complex.

Kinetic measurements have made it possible to elucidate a number of significant factors: firstly, the sequence in which the capacity for migration of the groups R_i varies has been established and, secondly, the nature of the interaction of the migrating group with the peroxide oxygen has been determined.

The aryl group in arylalkyl hydroperoxides is known to migrate in preference to the methyl group[23]. In substituted cumenyl hydroperoxides $Y_iC_6H_4C(Me)_2OOH$ the capacity of aryl groups for migration increases with enhancement of the electron-donating properties of the substituent Y.[23,26] The observed dependence of the logarithm of the reaction rate constant on the substituent constant σ^+ confirms the occurrence of a steric interaction between the migrating aryl group and the α-peroxide oxygen. The heterolysis of the peroxide linkage is accompanied by the simultaneous weakening of the Ar–C bond. This results in a transition from the sp^3-hybridisation of the tertiary carbon atom to the sp^2-hybridisation, which leads to an alteration of the valence angles in the activated state. The presence in the hydroperoxide molecule of a group acting as an internal nucleophile whose capacity for migration is comparable to that of the phenyl group, is the main condition for a high rate of the rearrangement.

In the acid-catalysed rearrangement of 2,2,4-trimethyl-2-pentyl hydroperoxide the neopentyl group migrates[33]:

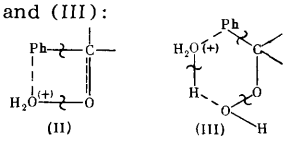
$$Me_3C{-}CH_2{-}CMe_2OOH \xrightarrow{HA} Me_3C{-}CH_2OH + Me_2CO\ . \quad (9)$$

9-Decalinyl hydroperoxide[34,35] rearranges with insertion of one of the peroxide oxygen atoms in the ring. A rearrangement with cleavage or expansion of the ring is characteristic of hydroperoxides derived from polynuclear hydrocarbons which have been partly or completely hydrogenated, as well 9-decalinyl hydroperoxide[36].

Competing reactions involving the migration of phenyl and cycloalkyl groups have been noted[37]. According to the proposed mechanism [reactions (5)–(7)], the rearrangement can be accounted for by the reaction of the hydroperoxide in a polar activated complex. Acid-catalysed rearrangements of tertiary hydroperoxides containing two or three hydroperoxy-groups are also known[38].

In tertiary arylalkyl hydroperoxides the methyl group cannot compete with the aryl group in the rearrangement. The consecutive replacement of the methyl group in cumenyl hydroperoxide by the ethyl, isopropyl, or t-butyl groups showed that the ethyl group, like the methyl group, does not migrate. The isopropyl group competes with the phenyl group as regards migration, while the t-butyl group has a much higher capacity for migration than the phenyl group[30].

In discussing the structure of the activated complex [structure (I), reaction (6)], mention should be made of a study[39] in which the mechanisms of molecular and acid-base catalytic reactions were considered. The authors[39] suggested that the rearrangement of the hydroperoxide can take place in complexes (II) and (III):

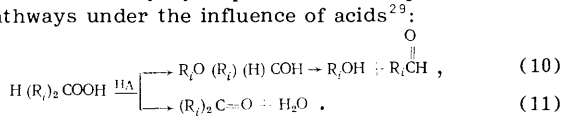


(II) (III)

The formation of the above complexes is inconsistent with experimental data. According to reactions (5)–(7), the hydroperoxide rearranges in the rate-limiting stage to a hemiketal [reaction (6)]. Such hemiketals are not always stable, but in some cases it has been possible to isolate them[40]. Complex (II) is a closed structure in which the protonated hydroperoxide molecule is converted into a phenol and a ketone, by-passing the stage involving the formation of a hemiketal.

There is a well-founded objection also against the transformation of the hydroperoxide in complex (III). The structure of the complex presupposes the involvement of the H_3O^+ ion in the reaction. According to the ring structure, the reaction in $H_2{}^{18}O$ could lead to the formation of [^{18}O] phenol, while studies have shown[21,22] that the phenol does not contain an excess of ^{18}O.

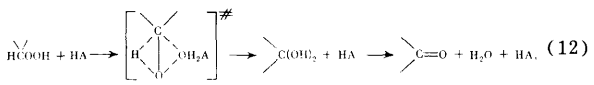
Primary and secondary hydroperoxides decompose via two parallel pathways under the influence of acids[29]:



$$\mathrm{H(R_i)_2COOH} \xrightarrow{\mathrm{HA}} \begin{cases} \longrightarrow \mathrm{R_iO(R_i)(H)COH} \rightarrow \mathrm{R_iOH} + \mathrm{R_iCH}, & (10) \\ \longrightarrow \mathrm{(R_i)_2C{=}O} + \mathrm{H_2O}. & (11) \end{cases}$$

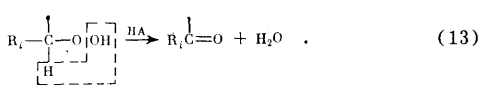
With enhancement of the electron-donating properties of the substituent R_i, the fraction of the products of the rearrangement involving the migration of the group R_i increases.

It is not at present clear which mechanism operates in the formation of water and carbonyl compounds from primary and secondary hydroperoxides. It may be that the acid-catalysed decomposition proceeds either via the reaction



$$\mathrm{HCOOH} + \mathrm{HA} \longrightarrow \left[\begin{array}{c} \mathrm{H} \\ \mathrm{C} \\ \mathrm{O} \end{array}\right]^{\#} \longrightarrow \mathrm{C(OH)_2} + \mathrm{HA} \longrightarrow \mathrm{C{=}O} + \mathrm{H_2O} + \mathrm{HA}, \quad (12)$$

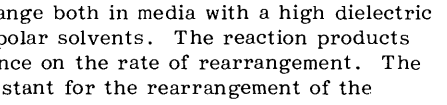
or constitutes a dehydration reaction:



$$\mathrm{R_i{-}C(H){-}O{-}OH} \xrightarrow{\mathrm{HA}} \mathrm{R_iC{=}O} + \mathrm{H_2O}. \quad (13)$$

III. THERMAL REARRANGEMENT OF PEROXYESTERS

Peroxyesters (PE) are the most convenient objects for the investigation of the mechanism of the rearrangement. These compounds can rearrange both in media with a high dielectric constant and in non-polar solvents. The reaction products have almost no influence on the rate of rearrangement. The experimental rate constant for the rearrangement of the peroxyester (k_{exp}) is formally a complex quantity. However, it can be regarded as equal to the rate constant for the elementary reaction of the rearrangement (k_2), provided that the equilibrium in the reaction between the peroxyester and an electrophile, which can be a solvent molecule (SH), is strongly displaced to the right [reaction (14)]:

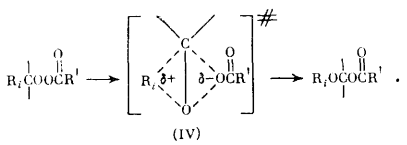


$$\mathrm{PE} + \mathrm{SH} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{PE.SH(fast)}, \quad (14)$$

$$[\mathrm{PE.SH}] \xrightarrow{k_2} \mathrm{P} + \mathrm{SH(slow)} \quad (15)$$

(P is the product of the rearrangement).

The activated state in reaction (15) is a highly structured polar complex. It was shown, first, that there is no transesterification during the rearrangement, because the peroxyester anion is not exchange for a salt anion[41,42] and, secondly, that the ^{18}O oxygen of the carbonyl group is fully retained in the isomeric product of the rearrangement[43,44]:



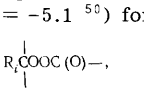
$$\mathrm{R_iCOOCR'} \longrightarrow \left[\begin{array}{c} \mathrm{C} \\ \mathrm{R_i}\delta+ \quad \delta-\mathrm{OCR'} \\ \mathrm{O} \end{array}\right]^{\#} \longrightarrow \mathrm{R_iOCOCR'}. \quad (16)$$

(IV)

Peroxyesters containing the R_i aryl group rearrange on heating in polar and non-polar solvents regardless of the strength of the acid whose anion enters the peroxyester. The aryl group has a high capacity for migration, behaving as an internal nucleophile [activated complex (IV), reaction (16)]. An alkyl group R_i participates in the rearrangement only under severe conditions, where the medium consists of a superacid[45] or when the anion entering the peroxyester is a powerful electron acceptor[46].

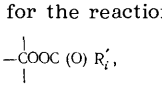
The claim that the highly structured activated state is polar and exhibits the features of a heterolytic process is based on kinetic measurements published by different workers. The rate of rearrangement increases with enhancement of the electron-donating properties of the groups R_i [47,48] and of the electron-accepting properties of R_i'.[42,49]

The reaction constant ($\rho = -5.1$ [50]) for the reaction series



$$\mathrm{R_iCOOC(O)}-,$$

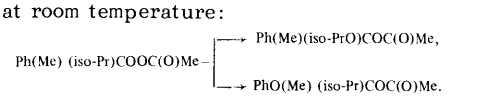
in which R_i is varied, is much larger than the reaction constants ($\rho = 1.1$,[49] 1.21 [51]) for the reaction series



$$-\mathrm{COOC(O)R_i'},$$

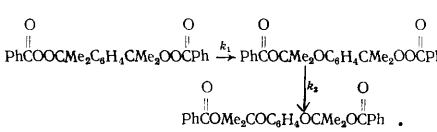
involving variable R_i'. The high sensitivity of the reaction to the electronic effects of R_i is probably caused by the involvement of the nucleophilic migrating group in direct interaction with the peroxide oxygen. Only this can explain the appreciable deviation of the reaction series of *para*-substituted cumenyl peroxybenzoates from the linear relation between $\lg k$ and σ.[52]

The role of the direct polar conjugation of the substituents with the reaction centre has been observed in the analysis of kinetic data[21] for the rearrangement of 2-propyl *p*-nitroperoxybenzoates in methanol, published by Hedaya and Winstein[47]. An increase in the size of the groups located in the alkyl fragment of the peroxyester should give rise to steric hindrance in the ground state and should remove it from the activated state. For peroxyesters containing alkyl or cycloalkyl groups R_i, such effects have an insignificant influence on the rate of rearrangement[47]. However, it was shown in a later study[51] that the rate of migration of the phenyl group increases with increase of the size of the adjacent alkyl group in the sequence methyl < ethyl < isopropyl. In the latter case the rate of rearrangement is so high that the peroxyester rearranges in the course of synthesis in toluene solution at room temperature:



$$\mathrm{Ph(Me)(iso\text{-}Pr)COOC(O)Me} \begin{cases} \longrightarrow \mathrm{Ph(Me)(iso\text{-}PrO)COC(O)Me}, & (17) \\ \longrightarrow \mathrm{PhO(Me)(iso\text{-}Pr)COC(O)Me}. & (18) \end{cases}$$

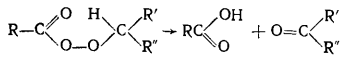
The successive transformation of the peroxy-groups in polyperoxyesters has been postulated[51]:



$$\mathrm{PhCOOCMe_2C_6H_4CMe_2OOCPh} \xrightarrow{k_1} \mathrm{PhCOCMe_2OC_6H_4CMe_2OOCPh}, \quad (19)$$

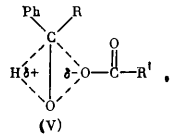
$$\mathrm{PhCOCMe_2OC_6H_4CMe_2OOCPh} \xrightarrow{k_2} \mathrm{PhCOMe_2COC_6H_4OCMe_2OCPh}. \quad (20)$$

Derivatives of secondary and primary alcohols occupy a special place among peroxyesters. These peroxyesters are extremely unstable and decompose to acids and carbonyl compounds[9]:



(21)

The simultaneous presence of a hydrogen atom and a phenyl group in the alkyl component of the peroxyester does not alter the nature of the decomposition. The thermal decomposition of peroxyesters having the structure PhRCHOOC(O)Me (R = Me or Ph) involves the quantitative formation of acetic acid and acetophenone or benzophenone; not even traces of phenol have been detected. Either the phenyl group is unable to compete with the proton in the rearrangement occurring in the cyclic complex[51]



(V)

or the rearrangement proceeds via a many-centre mechanism [reaction (21)].

The study of the influence of solvent polarity on the rate of rearrangement of peroxyesters[44,52-57] showed that, with increase of solvent polarity, the rate of rearrangement also increases. For example, in nitromethane ($\varepsilon = 38.6$) the rate constant for the rearrangement of cumenyl peroxybenzoate is 20 times greater and in aqueous ethanol ($\varepsilon = 31.8$, mole fraction of water 0.35) 100 times greater than in benzene ($\varepsilon = 2.28$).

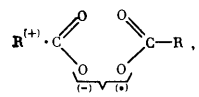
The choice of the Kirkwood parameter $(\varepsilon - 1)/(2\varepsilon + 1)$ as a measure of solvent polarity made it possible to observe a linear relation between $\lg k$ and $(\varepsilon - 1)/(2\varepsilon + 1)$ for the rearrangement of cumenyl peroxybenzoate. For each pair of the binary mixtures nitrobenzene–octane, methanol–water, and ethanol–water, the Kirkwood equation holds, but a general correlation could not be obtained for all the binary solvents[53].

The reason for the deviation from linearity and for the appearance of independent linear relations is the occurrence of specific interactions of the solvents with the peroxyester involving the formation of a hydrogen bond or coordination. Calculations have shown[53] that an increase of solvent polarity and specific solvation of the peroxyester favour the rearrangement of cumenyl peroxybenzoate involving the transition of the initial molecule to a more polar activated state. When the solvent polarity becomes sufficiently high, peroxyesters, which decompose via a radical mechanism in media with a low dielectric constant, undergo a rearrangement[58].

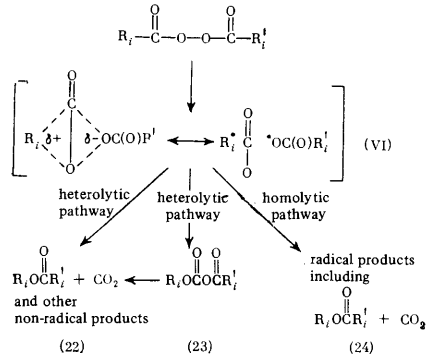
IV. THERMAL AND CATALYTIC REARRANGEMENTS OF DIACYL PEROXIDES

One of the possible pathways leading to the rearrangement of diacyl peroxides is carboxy-inversion, similar in type to the rearrangement of hydroxyperoxides and peroxyesters.

Several years ago studies were published[59-61] in which the thermal decomposition of diacyl peroxides, leading to the formation of radical and polar products, was regarded as a single process. Walling[59] believes that in the activated state a diacyl peroxide exists simultaneously as an ion pair and a biradical. Leffler and Moore[61] adhere to the same concept: they proposed the resonance hybrid intermediate

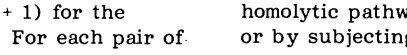


which is converted either into an ion pair or a radical pair, ensuring the development of a homolytic or a heterolytic reaction pathway. The most probable mechanism, which agrees with the available experimental literature data, can be represented by reactions (22)–(24):[62]



(VI)

The formation of a radical pair in the thermolysis of diacyl peroxides and the subsequent reactions of the radicals in the solvent cage or outside it are well known[62,63]. A quantitative transformation of a diacyl peroxide via the homolytic pathway can be achieved by altering its structure or by subjecting it to photochemical decomposition[64]:



(25)

The high polarity of the medium[65] as well as the electron-donating properties of the migrating group R_i or the electron-accepting properties of R_i' are factors favouring a heterolytic rearrangement.

The above mechanism (22)–(24) takes into account an important factor. It follows from the mechanism that the rearrangement need not necessarily lead initially to the intermediate carbonate $R_iOC(O)OC(O)R_i'$ and only then to the ester $R_iOC(O)R_i'$. There is also a possibility of another pathway, leading to the formation of the ester without the stage involving the formation of the rearrangement product [reaction (22)]. The main cause which makes it necessary to regard the process as one of the radical-ion type is that the majority of the factors (solvent polarity and the influence of substituents) are equally significant for the homolytic and heterolytic reaction pathways[65]. It is known[10], for example, that in certain thermal radical formation reactions the transition state in the homolytic fragmentation of peroxides is stabilised or destabilised by polar substituents or solvents, which have a significant effect on the rate of the process.

The attempts to separate competing homolytic and heterolytic processes with the aid of the ^{18}O oxygen isotope introduced into the carbonyl group of the diacyl peroxide proved unsuccessful[65-68]. In some cases isotope exchange of the oxygen atoms of the carbonyl and peroxy-groups in the rearrangement of a diacyl peroxide was observed[67], while in others the rearrangement took place with retention of ^{18}O in the carbonyl group of the isomeric product and did not entail

a change in the optical activity of the migrating group[68]. It has been shown[67] that carboxy-inversion, radical decomposition, and the isotope exchange between the [^{18}O]carbonyl group and the peroxide oxygen take place at comparable rates, which may be an argument in support of a radical-ion mechanism of the decomposition of diacyl peroxides [reactions (22)–(24)] if one rules out the possibility of a sigmatropic rearrangement[69,70].

The successive transformation of diacyl peroxides into alkyl cyclocarbonates and then into esters is catalysed by Lewis acids[71,72]. The optical properties and isotope composition of the carbonyl oxygen in the diacyl peroxide are fully retained in the rearrangement product when the reaction is catalysed by antimony pentachloride[73]. Together with the detection of the intermediate carboxyanhydride, this is evidence for the similarity of the mechanism of this reaction to the mechanism already discussed [reactions (22)–(24)].

Comparison of kintic data for diacyl peroxides of different structure makes it possible to observe the following feature. In the homolytic propagation of the process the reaction constants ρ have small negative values in the range between -0.2 and -0.9.[74–78] It is believed that the decrease of the dipole–dipole repulsion between the oxygen atoms in the molecule due to electron-accepting substituents reduces the rate of the homolytic decomposition[75]. In the thermal decomposition of substituted benzoyl isobutyryl peroxides a high yield of rearrangement products is observed, which increases after the introduction of electron-accepting substituents ($\rho > 0$); the rate of reaction also increases[70]. This is attributed to the heterolytic propagation of the process. The sign of the reaction constant can apparently serve as a criterion for differentiation between the homolytic and heterolytic reaction pathways in accordance with mechanisms (22)–(24).

Reutov and coworkers[79–81] have shown convincingly that the rearrangement of cyclobutanoyl, acetyl cyclobutyl, and acetyl cyclopropyl peroxides is neither a "purely" homolytic nor a "purely" heterolytic process. On formation of esters as a result of the rearrangement of diacyl peroxides, a radical pair is not produced, as shown by CINP data[80]. Carbonium ions were not formed either, as shown by studies of the thermolysis of acetyl cyclobutyl peroxide labelled with ^{13}C in the methylene group of the side chain[81,82]. Thus the rearrangement of diacyl peroxides must be regarded at the present time as a radical-ion process [reactions (22)–(24)].

V. REARRANGEMENT OF ALKYL(ARYL) PEROXIDES

The rearrangement is not characteristic of symmetrical or asymmetric alkyl peroxides R_iOOR_i' (R_i and R_i' are primary, secondary, and tertiary alkyl groups). Cases are known where the migration of the aryl groups in alkyl aryl peroxides cannot be regarded as intramolecular processes. Kharasch et al.[83] showed that the conversion of triphenylmethyl peroxide into the diphenyl ether of benzopinacol on heating in xylene, described by Wieland[84], is a homolytic reaction:

$$(Ph_3CO)_2 \rightarrow 2Ph_3CO^{\cdot} \rightarrow 2Ph_2\dot{C}OPh \rightarrow Ph_2(PhO)C{-}C(PhO)Ph_2 \ . \qquad (26)$$

The same type of reaction is observed in the thermolysis of t-butyl triphenylmethyl and t-butyl diphenyl-*p*-tolylmethyl peroxides[83]:

$$YC_6H_4Ph_2COOCMe_3 \rightarrow YC_6H_4Ph_2CO^{\cdot} + {}^{\cdot}OCMe_3 \qquad (27)$$
$$\swarrow \quad \searrow$$
$$Ph_2\dot{C}OC_6H_4Y \qquad YC_6H_4(Ph)\dot{C}OPh \ .$$

Under the influence of protic acids, alkyl aryl peroxides decompose with formation of phenol[85,86]. The bimolecular reaction between the peroxide and the acid probably gives rise to a hydroperoxide, which then undergoes an acid-catalysed rearrangement. Thus organic peroxides R_3COOCR_3 constitute a class of peroxy-compounds for which the homolysis of the O–O bond is most typical[8,9].

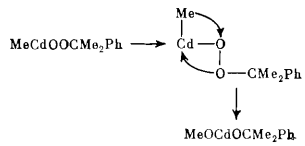
VI. REARRANGEMENT OF ORGANOELEMENTAL PEROXIDES

The monographs and reviews published in recent years[87–92] characterise the field of organoelemental peroxides as one offering promise and developing rapidly. More than five hundred organoelemental peroxides, many of which are capable of rearranging, are now known.

Among organoelemental peroxides of Group II elements rearrangements are known for magnesium and cadmium compounds. When trimethylsilylmethylmagnesium chloride is oxidised by oxygen, the product is a peroxide, which rearranges under the conditions of the synthesis via the reaction[93]

$$Me_3Si{-}CH_2OOMgCl \rightarrow Me_3SiOCH_2OMgCl \ . \qquad (28)$$

Davies and Packer[94,95] pointed out that methylcumenylperoxycadmium, which is stable at room temperature, decomposes at 50 °C with formation of an isomeric compound:



(29)

The reaction of diphenylcadmium with t-butyl hydroperoxide leads to the formation of an intermediate peroxide, which either participates in the disproportionation reaction or rearranges[96]:

$$PhCdOOCMe_3 \xrightarrow{Ph_2Cd} PhCdOCMe_3 + PhCdOPh \qquad (30)$$
$$PhCdOOCMe_3 \rightarrow PhOCdOCMe_3 \ . \qquad (31)$$

Among organoelemental peroxides of Group III elements, boron compounds have been studied in greatest detail and to a lesser extent aluminium, thallium, gallium, and indium compounds.

It has been established[97] that the reaction of phenylboronic acid with hydrogen peroxide results in the formation of phenol. The phenol isolated from the reaction mixture did not contain an excess of heavy oxygen[98] when phenylboronic acid $C_6H_5B(^{18}OH)_2$ was oxidised by the peroxide $H_2{}^{16}O_2$ in the presence of $H_2{}^{18}O$. An unstable hydroperoxide is probably formed and then rearranges like organic hydroperoxides.

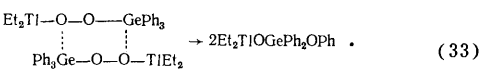
The rearrangement of certain organoboron peroxides take place quantitatively[99] or constitutes an appreciable proportion of the overall process[100–102]. Thus dimethylmethylperoxyboron is converted into a non-peroxide compound of the same molecular weight in the condensed and gas phases via the reaction[99]

$$Me_2BOOMe \rightarrow (MeO)_3BMe. \qquad (32)$$

Organoaluminium peroxides are extremely unstable under normal conditions and readily decompose with formation of several products[103]. A rearrangement has been postulated as one of the possible reaction pathways[105,106].

A reliable demonstration of the rearrangement of organothallium peroxides has been achieved by Razuvaev et al.[106], who showed that, on heating diethylthalliumperoxy (triphenyl)

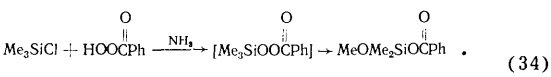
germane in an inert solvent at 80 °C, the rearrangement product is formed quantitatively via the second-order reaction



(33)

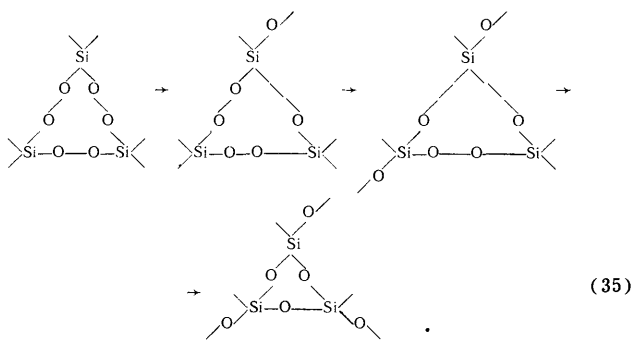
The syntheses of organogallium and organoindium peroxides have been achieved in recent years[107]. The products of the thermal decomposition reaction indicate that their rearrangement takes place simultaneously with homolytic decomposition[107].

The possibility of the rearrangement of peroxide compounds of Group IV elements was first pointed out by Buncel and Davies[108,109]. When an attempt was made to synthesise trimethylsilyl peroxybenzoate, the product isolated was dimethylmethoxysilyl benzoate, which the authors believe to be the product of the rearrangement of an intermediate peroxide:



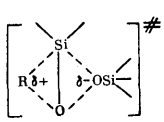
(34)

Approximately at the same time Jenkner[110] reported that dialkyldihalogenosilanes react with H_2O_2 to form cyclopolysiloxanes containing the Si–O–O–Si, Si–O–Si, and Si–O–C groups. The presence of the Si–O–C group was explained erroneously by the oxidation of the Si–C bond. It has been shown[111], that hexamethylcyclotrisilperoxane, which is the first representative of cyclic silyl peroxides, rearranges with contraction of the ring and migration of the methyl group:

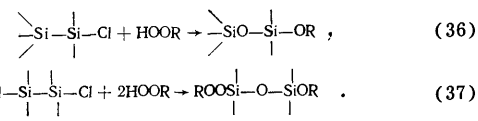


(35)

X-Ray diffraction studies have shown that the average value of the Si–O–O–Si torsional angle is 135.6°, i.e. peroxide bridges have a nearly *trans*-conformation. The negative entropy $\Delta S^{\#} = -13.7$ e.u. and the spatial disposition of the atoms indicate a cyclic transition state:



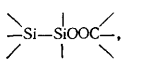
Kawazumi and Murai[112] observed that siloxanes are formed in the synthesis of t-butylperoxypentamethyldisilane and 1,2-di-t-butylperoxytetramethyldisilane:



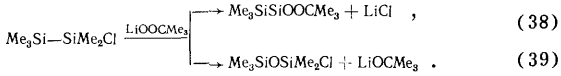
(36)

(37)

It has been suggested that an unstable intermediate silyl peroxide is formed:



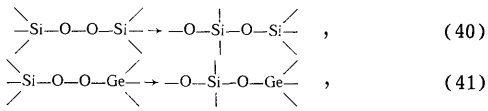
which rearranges under the conditions of the synthesis. However, Razuvaev and coworkers[113–115] established that chlorine-containing di- and tri-silanes are oxidised at the Si–Si bond by the hydroperoxide or its lithium salt before the silyl peroxide is formed:



(38)

(39)

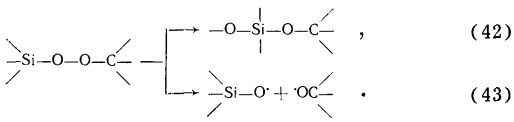
In the thermal and catalytic decomposition of the organoelemental peroxides R_3EOOH [116–120] a rearrangement is observed when E = Si or Ge.[116–118] Silicon and silicon-germanium peroxides rearrange quantitatively to the isomeric siloxanes[121–124]:



(40)

(41)

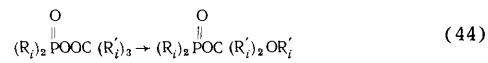
while organosilicon peroxides decompose via two parallel reactions[125]:



(42)

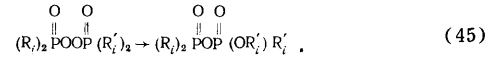
(43)

Peroxide compounds of Group V elements are capable of rearranging with migration of an alkyl or aryl group from a tertiary carbon atom[126–128]:



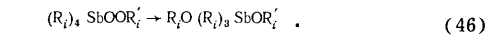
(44)

or from a phosphorus atom[129,130]:



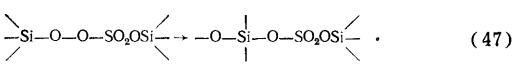
(45)

Such reactions are also characteristic of antimony derivatives[131–134]:



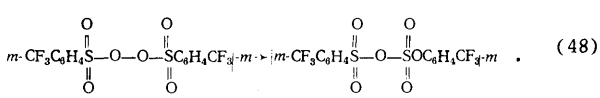
(46)

Bressel and Blaschette[135] observed a rearrangement of bis-(trimethylsilyl) peroxomonosulphate in methylene chloride at a temperature below 0 °C:



(47)

The decomposition of *m*-trifluoromethylbenzenesulphonyl peroxide in ethylbenzene and in cumene and also in the absence of a solvent is, according to the authors[136], an ionic reaction and involves the migration of the aryl group:



(48)

In essence, the consideration of the mechanism of the rearrangement of organoelemental peroxides involves the study of compounds of Group IV elements and in the first place silicon compounds. There is as yet no unanimous view concerning the mechanism of the rearrangement of organoelemental peroxide compounds. Some authors tend to regard the rearrangement as one occurring in a radical pair, while others treat it as a heterolytic process. The results of experimental studies do not provide an unambiguous answer. Investigators have frequently observed that the same factors, which had been believed earlier to be features of either heterolytic or homolytic processes, have the same influence on on both processes.

Dannley suggested that the rearrangement of organoelemental hydroperoxides has a free-radical mechanism[116,118,121]. The author believes that the radicals $\rangle EO^{\cdot}$ (E = Si or Ge), formed as a result of the homolysis of the peroxide linkage, rearrange in a solvent cage or are liberated into space and participate in radical reactions:

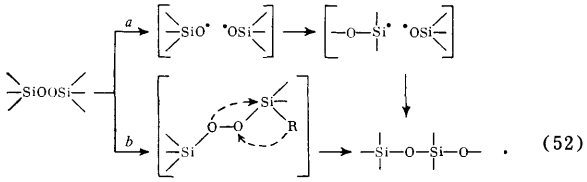
$$(R_i)_3EOOH \rightarrow (R_i)_3EO^{\cdot} + {}^{\cdot}OH\ ; \qquad (49)$$

$$(R_i)_3EO^{\cdot} \xrightarrow{SH} (R_i)_3EOH + S^{\cdot}\ , \qquad (50)$$

$$(R_i)_3EO^{\cdot} \rightarrow R_iO(R_i)_2E^{\cdot} \xrightarrow{{}^{\cdot}OH} R_iO(R_i)_2EOH \rightarrow R_iOH + [(R_i)_2EO]_x\ . \qquad (51)$$

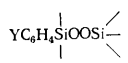
A study of the decomposition of triphenylsilyl hydroperoxide[116] established that the reaction is insensitive to a change in the polarity of the solvent (nitrobenzene, methyl benzoate, anisole, *o*-dichlorobenzene), is accelerated on irradiation with ultraviolet light, and is not catalysed by acids (monochloro- and trichloro-acetic acids in *o*-dichlorobenzene).

In contrast to silyl hydroperoxide, the silyl peroxides $\rangle SiOOSi\langle$ rearrange quantitatively to isomerise siloxanes; the liberation of siloxy-radicals into space is not observed. In order to account for the mechanism of his process, Shubber and Dannley[121] were forced to assume that the rearrangement has a latent radical mechanism [reaction (52), pathway *a*], although they do not rule out the possibility of a concerted rearrangement of the bonds [reaction (52), pathway *b*] without the formation of free radicals:



(52)

The principal argument in support of the rearrangement in a radical pair reduces to the fact that in the silyl peroxides



a relatively slight increase of the capacity for the migration of the aryl groups is observed in the sequence phenyl (1.0) < *p*-tolyl (1.1) < anisyl (6.0), which is more likely to be a property of homolytic than heterolytic processes[121].

This finding can hardly be regarded as sufficient justification for a radical mechanism of the rearrangement. The sequence in which the capacity for migration of the aryl groups YC_6H_4 varies is different in radical reactions and in the rearrangements. It is known[83,137] that, following the rearrangement in an alkoxy-radical,

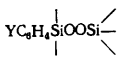


(53)

the capacity for migration of the YC_6H_4 group increases after the introduction of electron-accepting substituents Y. The same behaviour has been observed in isomerisation in an alkyl radical[138]:

$$YC_6H_4CMe_2\dot{C}H_2 \rightarrow Me_2\dot{C}CH_2C_6H_4Y\ , \qquad (54)$$

while in rearrangements of silyl peroxides

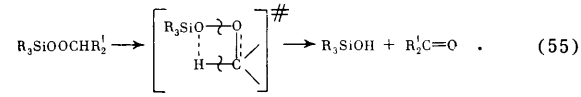


the rate of reaction diminishes after the introduction of an electron-accepting substituent Y.[21] Furthermore, it has been shown that siloxy- and germyloxy-radicals do not isomerise[139,140].

Experimental data indicating a heterolytic mechanism of the rearrangement show that the reactions involved in the rearrangement of silyl peroxides are sensitive to changes in solvent polarity[141] and are accelerated under the influence of nucleophiles such as F^- and CN^-.[142] An increase of pressure to several thousand atmospheres increases the rate of rearrangement of silyl peroxides severalfold[143]. If the rearrangement occurred in a radical pair, the opposite relation would have been observed.

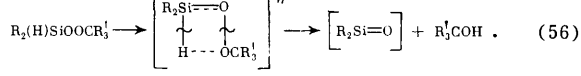
Silyl peroxides $R_3SiOOSiR_3$ do not rearrange quantitatively via reaction (40) in solution alone. For example, in the gas phase there is no solvent cage effect. However, even in this case it has been established that the rearrangement of $Me_3Si.OOSiMe_3$ takes place quantitatively, which indicates a non-radical mechanism of the process. The only difference between the gas-phase and liquid-phase reactions consists in the difference between the rates of the process[144].

Organosilicon peroxides containing an α-hydrogen atom at a silicon or carbon atom undergo thermolysis with migration of the hydrogen atom to one of the peroxide oxygen atoms. It has been shown that the migration of hyrogen constitutes an intramolecular rearrangement, which takes place simultaneously with the radical decomposition[145,146]:



(55)

The rearrangement of silyl peroxides in which there is an α-hydrogen atom at the silicon atom is of special interest[145,146]:



(56)

Reaction (56) makes it possible to generate silanones in different solvents at 160–180 °C.

Since 1977 systematic studies have begun on the structure of organoelemental peroxides by electron diffraction[147] and X-ray diffraction[111,148–150]. The results of the studies on silyl peroxides agreed with the concept of rearrangement in a "rigid" cyclic complex.

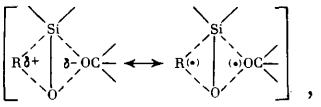
In analysing the arguments for and against the homolytic and heterolytic mechanisms of the rearrangements of silyl peroxides one should probably not pose the question unduly categorically and one should postulate, for example, that "in the same reacting system some of the bonds undergo homolytic dissociation, while another fraction of the same bonds... are ruptured heterolytically".[151] It is quite probable that the elementary reaction in the rearrangement of the molecular skeleton is preceded by electron transfer. For example, two parallel reactions are observed in the thermolysis of cumenylperoxy(triphenyl)silane:

$$Ph_3SiOOCMe_2Ph \xrightarrow[\text{anisole}]{160^\circ} \begin{cases} \rightarrow PhOPh_2SiOCMe_2Ph \\ \quad (\Delta G^{\#} = 138\ \text{kJ mol}^{-1}; \end{cases} \qquad (57)$$

$$\begin{cases} Ph_3SiO^{\cdot} + {}^{\cdot}OCMe_2Ph \\ \rightarrow (\Delta G^{\#} = 142\ \text{kJ mol}^{-1}\ . \end{cases} \qquad (58)$$

The values of $\Delta G^{\#}$ calculated by Yablokov et al.[123] are the same, within the limits of the error of the measurement (±4 kJ), for the rearrangement and the homolytic reaction

and are consistent with the hypothesis of a radical-ion mechanism of thermolysis in an activated state:



which is analogous to that proposed by Leffler and More[61] for the rearrangement of diacyl peroxides.

REFERENCES

1. H.W.Wieland and J.Maier, Ber., **64**, 1205 (1931).
2. R.Criegee and R.Kaspar, Annalen, **560**, 127 (1948).
3. P.G.Sergeev and B.D.Kruzhalov, Khim.Nauka i Prom., No.3, 287 (1956).
4. M.S.Nemtsov, I.I.Radchenko, and S.L.Fisher, Khim. Nauka i Prom., No.2, 306 (1957).
5. H.Hock and S.Lang, Ber., **77b**, 257 (1944).
6. H.Wieland and G.A.Razuwaev, Annalen, **480**, 157 (1930).
7. H.P.Hey and N.A.Waters, Chem.Rev., **21**, 169 (1937).
8. V.L.Antonovskii, "Organicheskie Perekisnye Initsiatory" (Organic Peroxide Initiators), Izd.Khimiya, Moscow, 1972.
9. A.I.Rakhimov, "Khimiya i Tekhnologiya Organicheskikh Perekisnykh Soedinenii" (The Chemistry and Technology of Organic Peroxide Compounds), Izd. Khimiya, Moscow, 1979.
10. C.Rüchardt, Fortschr.chem.Forsch., **6**, 251 (1966).
11. C.Rüchardt, Forschungsberichte des Landes Nordrhein-Westfalen, No.2471, Westdeutscher Verlag, 1975.
12. T.Migita, J.Synth.Org.Chem.Japan, **34**, 477 (1976).
13. J.Vodnar, Rev.Roum.Chim., **18**, 797 (1973).
14. G.A.Razuvaev, V.A.Shushunov, and V.A.Yablokov, Dokl.Akad.Nauk SSSR, **139**, 1128 (1961).
15. V.A.Yablokov, Candidate's Thesis, Gorky University, Gorky 1964.
16. D.E.Blissing, C.W.Matuszak, and W.E.McEwen, Tetrahedron Letters, 763 (1962).
17. D.E.Bissing, C.W.Matuszak, and W.E.McEwen, J.Amer. Chem.Soc., **86**, 3824 (1964).
18. F.H.Seubold and W.E.Vaughan, J.Amer.Chem.Soc., **75**, 3790 (1953).
19. V.A.Shushunov and Yu.A.Shlyapnikov, Dokl.Akad. Nauk SSSR, **128**, 341 (1959).
20. R.A.Sheldon and J.A.Doorn, Tetrahedron Letters, 1021 (1973).
21. V.A.Yablokov, Doctoral Thesis, Lensovet Leningrad Technological Institute, Leningrad, 1977.
22. V.A.Yablokov and O.N.Druzhkov, Trudy po Khim.i Khim.Tekhnol., Gorky, No.1, 15 (1964).
23. A.W.de Ruyter van Stevenink, Rec.Trav.chim., **79**, 413 (1960).
24. A.W.de Ruyter van Stevenink, J.Chem.Soc., 2066 (1958).
25. V.P.Maslennikov and V.A.Shushunov, Trudy po Khim. i Khim.Tekhnol., Gorky, No.2, 3 (1965).
26. V.A.Yablokov, S.A.Petrova, and A.B.Livadonova, Kinetika i Kataliz, **11**, 51 (1970).
27. Yu.A.Shlyapnikov, Kinetika i Kataliz, 1, 365 (1960).
28. N.G.Kostyuk, I.D.Sinovich, I.M.Lezhneva, and A.G.Kostyuk, Kinetika i Kataliz, **14**, 1389 (1973).
29. V.A.Yablokov, V.A.Shushunov, S.A.Petrova, and T.M.Nazarova, Kinetika i Kataliz, **14**, 341 (1973).
30. V.A.Yablokov, S.A.Petrova, and V.A.Shushunov, Kinetika i Kataliz, **14**, 584 (1973).
31. A.V.Antyukhina and V.P.Maslennikova, Trudy po Khim.i Khim.Tekhnol., Gorky, No.2, 184 (1967).
32. G.Burtzlaff, U.Felder, H.Hubner, W.Pritzkow, and W.Kolle, J.prakt.Chem., **28**, 305 (1965).
33. J.Hoffman and C.E.Boord, J.Amer.Chem.Soc., 77, 3139 (1955).
34. C.F.H.Tipper, J.Chem.Soc., 1675 (1953).
35. H.E.Holmquist, H.S.Rothrock, C.W.Theobald, and B.E.Englund, J.Amer.Chem.Soc., **78**, 5339 (1956).
36. W.Triebs, Chem.Ber., **94**, 1915 (1961).
37. H.Anderson and J.G.Smith, Canad.J.Chem., **46**, 1561 (1968).
38. I.E.Pokrovskaya, L.A.Fil'mankova, G.P.Pavlov, T.I.Kubasova, and T.N.Aleskovskaya, Symposium, "Neftepererabotka i Neftekhimiya" (Petroleum Processing and Petrochemistry), 1974, No.4, p.32.
39. Ya.K.Syrkin and I.I.Moiseev, Uspekhi Khim., **29**, 425 (1960) [Russ.Chem.Rev., No.4 (1960)].
40. W.Webster and D.P.Young, J.Chem.Soc., 4785 (1956).
41. P.D.Bartlett and J.L.Kice, J.Amer.Chem.Soc., **75**, 5591 (1953).
42. H.L.Goering and A.G.Olson, J.Amer.Chem.Soc., **75**, 5853 (1953).
43. D.B.Denney and D.G.Denney, J.Amer.Chem.Soc., **79**, 4806 (1957).
44. N.V.Yablokova, V.A.Yablokov, and V.A.Shushunov, Symposium, "Uspekhi Khimii Organicheskikh Perekisnykh Soedinenii i Autookisleniya" (Advances in the Chemistry of Organic Peroxide Compounds and in Autoxidation), Izd.Khimiya, Moscow, 1969, p.208.
45. C.A.Olah, D.G.Parker, and N.Voneda, J.Org.Chem., **42**, 32 (1977).
46. P.D.Bartlett and T.G.Traylor, J.Amer.Chem.Soc., **83**, 856 (1961).
47. E.Hedaya and S.Winstein, J.Amer.Chem.Soc., 89, 1661 (1967).
48. S.Winstein and G.C.Robinson, J.Amer.Chem.Soc., **80**, 169 (1958).
49. N.V.Yablokova, V.A.Yablokov, and V.K.Mamushkin, Zhur.Org.Khim., **9**, 82 (1973).
50. N.V.Yablokova, V.A.Yablokov, and V.A.Shushunov, Kinetika i Kataliz, **7**, 165 (1966).
51. S.A.Ivanova, Candidate's Thesis, Gorky University, Gorky 1973.
52. N.V.Yablokova, V.A.Yablokov, A.P.Tarabarina, and M.A.Dikii, Reakts.Sposobn.Org.Soed., No.3, 154 (1966).
53. N.V.Yablokova, Candidate's Thesis, Gorky State University, Gorky, 1967.
54. N.V.Yablokova, V.A.Yablokov, and O.F.Rachkova, Reakts.Sposobn.Org.Soed., No.2, 223 (1966).
55. V.A.Yablokov, S.A.Petrova, and V.A.Shushunov, Kinetika i Kataliz, **11**, 1054 (1970).
56. G.A.Razuvaev, T.N.Brevnova, N.F.Cherepennikova, and S.Kh.Ratushnaya, Zhur.Obshch.Khim., **46**, 857 (1976).
57. T.N.Brevnova, N.F.Cherepennikova, and N.S.Vyazankin, Zhur.Obshch.Khim., **44**, 1937 (1974).
58. R.A.Sheldon and J.K.Kochi, J.Org.Chem., **35**, 1223 (1970).
59. C.Walling, H.P.Waits, J.M.Milovanovic, and C.G.Pappiannou, J.Amer.Chem.Soc., **92**, 4927 (1970).
60. R.A.Cooper, R.G.Lawler, and H.R.Ward, J.Amer.Chem. Soc., **94**, 545 (1972).

61. J.E.Leffler and A.A.More, J.Amer.Chem.Soc., **94**, 2483 (1972).
62. R.G.Linhardt and L.Murr, Tetrahedron Letters, 1007 (1979).
63. R.G.Lawer, P.F.Barbara, and D.Yacobs, J.Amer. Chem.Soc., **100**, 4912 (1978).
64. R.A.Sheldon and J.K.Kochi, J.Amer.Chem.Soc., **92**, 4395 (1970).
65. R.Hiatt, Intra.Science Chemistry Reports, **5**, 163 (1971).
66. T.Kashiwagi, M.Kozuka, and S.Oae, Tetrahedron, **26**, 3619 (1970).
67. K.Fujimori and S.Oae, Tetrahedron, **29**, 65 (1973).
68. S.Oae and K.Fujimore, J.Chem.Soc., Perkin Trans.II, **15**, 1844 (1974).
69. M.J.Goldstein and H.A.Judson, J.Amer.Chem.Soc., **92**, 4114 (1970).
70. M.J.Goldstein and H.A.Judson, J.Amer.Chem.Soc., **92**, 4120 (1970).
71. F.D.Greene, H.P.Stein, C.C.Chu, and F.M.Vane, J.Amer.Chem.Soc., **86**, 2080 (1964).
72. J.K.Kochi, J.Amer.Chem.Soc., **85**, 1958 (1963).
73. T.Kashiwogi and S.Oae, Tetrahedron., **26**, 3631 (1970).
74. R.C.Lamb and J.R.Sanderson, J.Amer.Chem.Soc., **91**, 5034 (1969).
75. C.G.Swain, W.T.Stockmayer, and J.T.Clarke, J.Amer. Chem.Soc., **72**, 5245 (1950).
76. A.T.Blomquist and A.J.Busell, J.Amer.Chem.Soc., **73**, 3883 (1951).
77. R.Hisada, N.Komigata, H.Minato, and M.Kobayashi, Bull.Chem.Soc.Japan, **44**, 3475 (1971).
78. R.C.Lamb, L.L.Vestal, G.R.Cipan, and S.Debnath, J.Org.Chem., **39**, 2096 (1974).
79. T.N.Shatkina, A.N.Lovtsova, K.S.Mazel', and O.A.Reutov, Dokl.Akad.Nauk SSSR, **227**, 112 (1976).
80. E.T.Lippmaa, T.N.Shatkina, A.N.Lovtsova, P.E.Pirn, K.S.Mazel', and O.A.Reutov, Dokl.Akad.Nauk SSSR, **231**, 1362 (1976).
81. T.N.Shatkina, A.N.Lovtsova, K.S.Mazel', T.N.Pekhk, E.T.Lippmaa, and O.A.Reutov, Dokl.Akad.Nauk SSSR, **237**. 368 (1977).
82. K.S.Mazel', Candidate's Thesis, Moscow State University, Moscow, 1980.
83. M.S.Kharasch, A.C.Poshkus, A.Fono, and W.Nudenberg, J.Org.Chem., **16**, 1458 (1951).
84. H.W.Wieland, Ber., **44**, 2553 (1911).
85. M.S.Kharasch, A.Fono, and N.Nudenberg, J.Org. Chem., **15**, 775 (1950).
86. V.P.Maslennikov, V.P.Sergeeva, and V.A.Shushunov, Zhur.Obshch.Khim., **37**, 1727 (1967).
87. D.Brandes and A.Blaschette, J.Organometal.Chem., **78** 1 (1974).
88. G.A.Razuvaev and T.G.Brilkina, Uspekhi Khim., **45**, 2196 (1976) [Russ.Chem.Rev., No.12 (1976)].
89. Yu.A.Aleksandrov, "Zhidkofaznoe Avtookislenie Elementoorganicheskikh Soedinenii" (Liquid-Phase Autoxidation of Organoelemental Compounds), Izd. Nauka, Moscow, 1978.
90. V.A.Yablokov, N.V.Yablokova, V.E.Mikhlin, and D.Ya.Zhinkin, "Kremniiorganicheskie Perekisi. Reaktsionnaya Sposobnost'" (Organosilicon Peroxides. Reactivity), Izd.NIITEKhim., Moscow, 1978.
91. V.A.Yablokov, V.E.Mikhlin, N.V.Yablokova, D.Ya.Zhinkin, and N.A.Luk'yanov, "Seriya Elementoorganicheskie Soedineniya" (Organoelemental Compound Series), Izd.NIITEKhim., 1979, No.3, p.12.
92. Yu.A.Aleksandrov, N.V.Yablokova, V.A.Yablokov, V.P.Sergeeva, and V.P.Maslennikov, Symposium, "Khimiya Elementoorganicheskikh Soedinenii" (The Chemistry of Organoelemental Compounds), Izd. Gor'k.Univ., 1979, No.7, p.3.
93. J.J.Eisch and G.R.Husk, J.Org.Chem., **29**, 254 (1964).
94. A.G.Davies and J.E.Packer, Chem.Ind.(London), 1177 (1958).
95. A.G.Davies and J.E.Packer, J.Chem.Soc., 3164 (1959).
96. G.A.Razuvaev, V.N.Pankratova, V.A.Murav'ev, and I.V.Bykova, Zhur.Obshch.Khim., **39**, 2490 (1969).
97. H.G.Kuivila and A.G.Armour, J.Amer.Chem.Soc., **79**, 5659 (1957).
98. A.G.Davies and R.B.Moodie, J.Chem.Soc., 2372 (1958).
99. R.C.Petry and F.H.Verhock, J.Amer.Chem.Soc., **78**, 6416 (1956).
100. V.A.Zhushunov, V.P.Maslennikov, and G.I.Makin, "Trudy po Khimii i Khimicheskoi Teckhnologii" (Studies in Chemistry and Chemical Engineering), Gorky, 1970, No.2, p.214.
101. G.I.Makin, V.P.Maslennikov, and Yu.A.Aleksandrov, Zhur.Obshch.Khim., **43**, 2270 (1973).
102. P.B.Brindeg, J.C.Hodson, and M.J.Scatten, J.Chem. Soc., Perkin Trans.II, 45 (1979).
103. T.G.Brilkina and V.A.Shushunov, "Reaktsii Metalloorganicheskikh Soedinenii s Kislorodom i Perekisyami" (Reactions of Organometallic Compounds with Oxygen and Peroxides), Izd.Nauka, Moscow, 1966.
104. A.G.Davies and C.D.Hall, J.Chem.Soc., 1192 (1963).
105. G.A.Razuvaev, L.P.Stepovik, and V.A.Dodonov, Zhur.Obshch.Khim., **40**, 1800 (1970).
106. G.A.Razuvaev, V.A.Dodnov, T.J.Starostina, and T.A.Ivanova, J.Organometal.Chem., **37**, 233 (1972).
107. Yu.A.Aleksandrov, N.V.Chikinova, G.I.Makin, N.V.Kornilova, and V.N.Bregadze, Zhur.Obshch. Khim., **48**, 467 (1978).
108. E.Buncel and A.G.Davies, Chem.Ind.(London), 492 (1957).
109. E.Buncel and A.G.Davies, J.Chem.Soc., 1550 (1958).
110. H.Jenkner, Z.Naturforsch., **11b**, 734 (1956).
111. G.A.Razuvaev, V.A.Yablokov, A.V.Ganyushkin, V.E.Shklover, Ts.Tsinker, and Yu.T.Struchkov, Dokl.Akad.Nauk SSSR, **242**, 132 (1978).
112. R.Kawazumi and B.Murai, Bull.Chem.Soc.Japan, **39**, 1951 (1966).
113. G.A.Razuvaev, T.N.Brevnova, and V.V.Semenov, Zhur.Obshch.Khim., **47**, 2270 (1977).
114. T.N.Brevnova, V.V.Semenov, and G.A.Razuvaev, Zhur.Obshch.Khim., **48**, 1380 (1978).
115. T.N.Brevnova and V.V.Semenov, Zhur.Obshch.Khim., **49**, 142 (1979).
116. R.L.Dannley and G.Jalics, J.Org.Chem., **30**, 3848 (1965).
117. V.A.Yablokov and A.P.Tarabarina, Kinetika i Kataliz, **10**, 200 (1969).
118. R.L.Dannley and G.Farrant, J.Org.Chem., **34**, 2432 (1969).
119. V.A.Yablokov, A.P.Tarabarina, and N.V.Yablokova, Trudy po Khim.Tekhnol., Gorky, No.2, 167 (1970).
120. R.L.Dannley and W.A.Aue, J.Org.Chem., **30**, 3845 (1965).
121. A.Shubber and R.L.Dannley, J.Org.Chem., **36**, 3784 (1971).
122. V.A.Yablokov, A.P.Tarabarina, N.V.Yablokova, and M.I.Stal'nova, Zhur.Obshch.Khim., **41**, 887 (1971).

123. V.A.Yablokov, A.P.Tarabarina, and N.V.Yablokova, Zhur.Obshch.Khim., **42**, 157 (1972).
124. V.A.Yablokov, A.P.Tarabarina, and N.V.Yablokova, Syn.React.Inorg.Metal.-Org.Chem., **4**, 339 (1974).
125. V.A.Yablokov, N.V.Yablokova, and A.P.Tarabarina, Zhur.Obshch.Khim., **42**, 1051 (1972).
126. V.P.Maslennikov and V.P.Sergeeva, Zhur.Org.Khim., **7**, 686 (1971).
127. V.P.Maslennikov, V.P.Sergeeva, and V.A.Shushunov, Dokl.Akad.Nauk SSSR, **209**, 1109 (1973).
128. G.Sosnovskt and E.H.Zaret, Z.Naturforsch., **31b**, 820 (1979).
129. R.L.Dannley, R.L.Waller, and R.V.Hoffman, J.Chem. Soc.D, 1362 (1971).
130. R.L.Dannley, R.L.Waller, R.V.Hoffmann, and R.F.Hudson, J.Org.Chem., **37**, 418 (1972).
131. G.A.Razuvaev and T.I.Zinov'eva, Izv.Akad.Nauk SSSR, Ser.Khim., 2007 (1969).
132. G.A.Razuvaev, T.I.Zinov'eva, and T.G.Brilkina, Dokl. Akad.Nauk SSSR, **188**, 830 (1969).
133. J.Dahlmann and K.Wensel, Z.Chem., **14**, 232 (1974).
134. J.Dahlmann and K.Wensel, J.prakt.Chem., **318**, 390 (1976).
135. B.Bressel and A.Blaschette, Z.anorg.Chem., **377**, 182 (1970).
136. R.L.Dannley and P.K.Tornstrom, J.Org.Chem., **40**, 2278 (1975).
137. P.D.Bartlett and J.D.Cottman, J.Amer.Chem.Soc., **72**, 3095 (1950).
138. E.T.Denisov, "Konstanty Skorosti Gomoliticheskikh Zhidkofaznykh Reaktsii" (The Rate Constants for Homolytic Liquid-Phase Reactions), Izd.Nauka, Moscow, 1971, p.156,
139. E.A.Artemova, M.P.Plitakova, N.K.Shchennikova, and V.A.Yablokov, Trudy po Khim.Tekhnol., Gorky, No.4, 79 (1974).
140. E.A.Artemova, M.P.Plitakova, and M.K.Shchennikova, Trudy po Khim.Tekhnol., No.4, 82 (1974).
141. V.A.Yablokov, A.N.Sunin, N.V.Yablokova, and Yu.A.Aleksandrov, Zhur.Obshch.Khim., **46**, 2726 (1976).
142. G.A.Razuvaev, V.A.Yablokov, A.V.Ganyushkin, N.V.Yablokova, and G.S.Kalinina, J.Organometal. Chem., **165**, 281 (1979).
143. V.A.Yablokov, A.V.Ganyushkin, M.Ya.Botnikov, and V.M.Zhulin, Izv.Akad.Nauk SSSR, Ser.Khim., 484 (1976).
144. V.A.Yablokov, A.V.Ganyushkin, and N.V.Yablokova, Zhur.Obshch.Khim., **47**, 2553 (1977).
145. A.B.Tomadze, N.V.Yablokova, and V.A.Yablokov, Zhur.Obshch.Khim., **49**, 1171 (1979).
146. V.A.Yablokov, A.V.Tomadze, N.V.Yablokova, and G.A.Razuvaev,"The IXth International Conference on Organometallic Chemistry (Abstr.), Dijon, France, 1979", p.A-2.
147. D.Kass, H.Oberharmer, D.Brandes, and A.Blaschette, J.Mol.Struct., **40**, 65 (1977).
148. V.A.Lebedev, Yu.N.Drozdov, E.A.Kuz'min, A.V.Ganyushkin, V.A.Yablokov, and N.V.Belov, Dokl.Akad.Nauk SSSR, **246**, 601 (1979).
149. Z.A.Starinova, T.M.Shcheglova, V.K.Trunov, I.E.Pokrovskaya, and E.N.Kanunnikova, Kristallografiya, **24**, 1211 (1979).
150. V.E.Shklover, A.V.Ganyushkin, V.A.Yablokov, and Yu.T.Struchkov, Cryst.Struct.Comm., **8**, 869 (1979).
151. O.Yu.Okhlobystin, "Perenos Elektrona v Organicheskikh Reaktsiyakh" (Electron Transfer in Organic Reactions), Izd.Rostovsk.Univ., 1974, p.7.

Chkalov Gorky
Institute of Civin Enginnering,
Gorky

Translated from *Uspekhi Khimii*, **49**, 1730-1750 (1980) U.D.C. 661.718.1+547.455

α-Ketophosphonic Acid Esters—Synthesis, Structure, and Reactions

Yu.A.Zhdanov, L.A.Uzlova, and Z.I.Glebova

Studies on the synthesis and properties of α-ketophosphonic acid esters (KPE)—a class of highly reactive organophosphorus compounds—are surveyed. Data are presented concerning instances of the anomalous course of the process in the synthesis of KPE by the Arbuzov reaction. The reactions of KPE with nucleophiles, including those which lead to the rupture of the phosphorus-carbon bond, are examined in detail. The problems of the stereochemistry of KPE are dealt with briefly. The bibliography includes 162 references.

CONTENTS

I. Introduction 843
II. Methods of synthesis 843
III. Structure 844
IV. Chemical properties 846
V. Carbohydrate-containing α-ketophosphonic acid esters 849

I. INTRODUCTION

For a long time, α-ketophosphonic acid esters (KPE) were comparatively little known and the chemistry of this unusual group of organophosphorus compounds began to be studied vigorously only in recent times. The experimental data for the properties of KPE obtained in the period 1962–71 have been partially surveyed in a short review[1]. Despite the lability of the phosphorus-carbon bond, KPE proved to be interesting key compounds in a number of syntheses based on the use of the increased reactivity of the carbonyl group, particularly in the preparation of α-aminophosphonic acids[2] and phosphorylcarbenes[3]. Even a superficial acquaintance with the chemical properties of KPE reveals an analogy with α-dicarbonyl compounds. On the other hand, the stereochemical aspects of the formation of the KPE molecule and its structure have been shown by the first studies[4,5] to be more varied compared with the same problems in the case of α-dicarbonyl compounds.

The synthesis of carbohydrate derivatives with a phosphorus–carbon bond using traditional methods for the formation of the latter is frequently accompanied by side reactions[6,7], one of the causes of which is the involvement in the reaction of the acetoxy-group of the protected monosaccharide. This feature was fully manifested also in the synthesis of carbohydrate-containing KPE, where the initial compounds were the chlorides of acetylated aldonic acids.

II. METHODS OF SYNTHESIS

The synthesis of KPE is based on the acylation of phosphite esters. Different versions of this reaction are distinguished by the nature of the acylating agent and the structure of the tervalent phosphorus acid derivative.

KPE (I) were first synthesised by Kabachnik et al.[8] from acyl chlorides and trialkyl phosphites:

$$\underset{}{RCOCl} + P(OR')_3 \rightarrow \underset{(I)}{RC(O)P(O)(OR')_2} + R'Cl \qquad [RC(O)OP(OR')_2] \text{ (II)}$$

In subsequent years a large number of a wide variety of KPE were synthesised by the interaction of the full esters of phosphorous acid with aliphatic[9–19] and aromatic[20–25] carboxylic acid chlorides. The method of synthesis has undergone certain changes compared with the initial procedure[8] (reaction in an inert gas atmosphere[10,13,20] and in a number of instances the reverse order of mixing of the reactants[13,16,21]).

KPE can be obtained by the reaction of acyl halides with other derivatives of tervalent phosphorus acids—tetraethyl pyrophosphite[26], hypodiphosphites[27,28], and phosphoramidite esters[29–32]. Attempts have been frequently made to employ dialkyl phosphites and their salts for the synthesis of KPE, but their reaction with halides does not proceed unambiguously and the yield of KPE is only 10–30%. This is because the KPE formed initially react further with dialkyl phosphites to form diphosphoryl compounds[15,33,34]; in other cases the enolic form of the α-ketophosphonate is acylated by the initial acyl halide[35]. The chlorides of halogeno-substituted acids give rise to high yields of KPE on interaction with dialkyl phosphites. The chlorides of trichloroacetic[36], trifluoroacetic[37], and other perfluorocarboxylic acids[38] have been used in this reaction.

Apart from acyl halides, carboxylic acid anhydrides can be used to acylate phosphite esters. The interaction of acetic anhydride with triethyl phosphite leads to a 10% yield of diethyl acetylphosphonate[39]. The main reaction product is a compound without an active carbonyl group. Referring to earlier studies, the authors[39] attributed the structure of tetraethyl 1-hydroxyethylidenediphosphonate (III) to this compound. However, it was shown later[34] that, under the conditons of the reaction described, the diphosphonate (III) rearranges to the phosphonophosphate (IV):

$$\underset{\text{OH}}{\underset{|}{CH_3C}}\text{—[P(O)(OC}_2\text{H}_5\text{)}_2\text{]}_2 \xrightarrow{t^\circ} \underset{\text{OP(O)(OC}_2\text{H}_5\text{)}_2}{\underset{|}{CH_3CHP(O)(OC_2H_5)_2}}$$

(III) (IV)

Trialkyl phosphite reacts anomalously with phthalic anhydride–biphthalyl was obtained in 70% yield instead of the expected α-ketophosphonate[40].

Mixed anhydrides of carboxylic and dialkylphosphorous acids (II) are converted into KPE under the influence of alkyl iodides, acyl iodides, and iodine, which function as catalysts in this reaction. The reaction has been carried out[41,42] with the anhydrides of a number of aliphatic acids, including those with the iso-structure. The anhydrides of carboxylic acids apparently interact analogously with dialkyl phosphorochloridites[43], whereupon the mixed anhydride (V) formed in the first stage isomerises to the ketophosphonate under the catalytic influence of the acyl chloride (VI):

$$(C_3H_7CO)_2O + (RO)_2PCl \rightarrow \underset{(V)}{C_3H_7C(O)OP(OR)_2} + \underset{(VI)}{C_3H_7COCl};$$

$$(V) + (VI) \rightarrow C_3H_7C(O)P(O)(OR)_2.$$

The formation of acetyl phosphonate $CH_3C(O)P(O)(OC_2H_5)_2$ (VII) by the reaction of acetyl acylals with diethyl phosphorochloridite can be explained satisfactorily[44] within the framework of the same mechanism.

KPE are frequently formed as intermediates in various reactions and their involvement in further chemical transformations has been confirmed by specific syntheses. The formation of the phosphonate (VII), which is then converted into the phosphonophosphate (IV), has been demonstrated[45,46] in the acetylation of dialkyl phosphite with vinyl acetate. The prototropic isomerisation of the esters of α-hydroxyallyl- and α-hydroxypropargyl-phosphonic acids to KPE has been observed recently[47,48]:

$$\underset{\text{(VIII)}}{CH_2{=}CHCH(OH)P(O)(OCH_3)_2} \xrightarrow{Na} \underset{\text{(IX)}}{CH_3CH_2C(O)P(O)(OCH_3)_2} .$$

The KPE (IX) formed in the intermediate stage acylates another molecule of the initial hydroxyacid ester (VIII).

The presence of halogen atoms in the α-position in the acyl halide frequently results in the reaction of the KPE (X) formed initially with the trialkyl phosphite via the mechanism of the Perkow reaction and the ultimate formation of unsaturated phosphonophosphates (XI):

$$\underset{\text{X=Cl or Br}}{RCH(X)COX} + P(OR')_3 \rightarrow \underset{\text{(X)}}{[RCH(X)C(O)P(O)(OR')_2]} \xrightarrow{P(OR')_3} \underset{\text{(XI)}}{RCH{=}\underset{\displaystyle OP(O)(OR')_2}{\underset{|}{C}}P(O)(OR')_2} ;$$

Such a complex course of the reaction of the halides of α-halogeno-derivatives of acids with trialkyl phosphites, observed in a few instances, can be explained[11,36,49-52] on the basis of the modern interpretation of the mechanism of the Perkow reaction[53,54]. However, α-ketophosphonates of type (X) can be obtained not only from the halides of perhalogenocarboxylic acids and dialkyl phosphites[36-38] (see above), but also as a result of the reaction of hexafluorodimethylketen with dialkyl phosphite[55] or of the chlorides of chloroacetic acids with acetyl dialkyl phosphite[52].

The latter reaction has been used to elucidate the mechanism of the formation of unsaturated phosphonophosphates from α-halogenoacyl halides and trialkyl phosphites[52]. In principle, the interaction of chloroacetyl chloride with trialkyl phosphite, which leads to the unsaturated phosphonophosphate (XIV), could proceed either via chloroacetyl phosphonate (XII) (pathway *1*) or via chlorovinyl phosphate (XIII) (pathway *2*):

$$ClCH_2COCl + P(OR)_3 \rightarrow \left[\begin{array}{l} \xrightarrow{(1)} \underset{\text{(XII)}}{ClCH_2C(O)P(O)(OR)_2} \\ \xrightarrow{(2)} \underset{\displaystyle Cl}{\underset{|}{CH_2{=}C}OP(O)(OR)_2} \text{ (XIII)} \end{array}\right] \rightarrow \underset{\displaystyle P(O)(OR)_2}{\underset{|}{CH_2{=}C}OP(O)(OR)_2} \text{ (XIV)} .$$

When the less reactive acetyl diethyl phosphite is used, it is possible to isolate the chloro-substituted KPE (XIIa) together with a small amount of high-boiling products formed as a result of further reactions:

$$ClCH_2COCl + (C_2H_5O)_2P(O)COCH_3 \rightarrow \underset{\text{(XIIa)}}{ClCH_2C(O)P(O)(OC_2H_5)_2} .$$

Thus pathway 1—the initial Arbuzov reaction with subsequent Perkow reaction—is more probable.

In the synthesis of KPE by the classical version of the Arbuzov reaction phosphites of different structures have been used[11,17,28-32,52]. The study of the kinetics of this reaction with phosphoramidite esters in benzene and acetonitrile solutions showed[31] that its direction depends on the structure of the phosphoramidite: cyclic phosphoramidites are less reactive and tend to react anomalously when acted upon by benzoyl chloride. An analogous phenomenon has been described in a number of other studies[29,30,32]. It has been noted[32] that the direction of the reaction of phosphoroamidite esters with acetyl chloride depends on the environment of the phosphorus and nitrogen atoms—the introduction of more electron-donating groups at the phosphorus atom promotes the preferential formation of acetyl phosphonate. The full amides of phosphorous acid react with acetyl and benzoyl chlorides at the nitrogen atom and, when benzoyl chloride was used, it was possible to isolate[32] intermediate benzoylphosphonium halides.

On interaction with acyl chlorides in diethyl ether, fully *O*-triorganosilylated phosphorous acids give rise to KPE in high yields[56]. When mixed alkyl triorganosilyl phosphites are used in this reaction, the most electrophilic triorganosilyl group is always split off[17,18,57]:

$$(R_3SiO)_nP(OR')_{3-n} + R''COCl \rightarrow R''C(O)P(O)(OR')_{3-n}(OSiR_3)_{n-1} + R_3SiCl .$$

Among the specific methods for the synthesis of bis(triethylsilyl)acetylphosphonates, mention should be made of procedures based on the reactions of acetoxytriethylsilane under the influence of halogeno-derivatives of tervalent phosphorus[57,58].

The reactions of sulphur analogues of carboxylic and phosphorous acids have been less investigated. While trimethyl phosphite reacts with thiobenzoyl chloride via the standard mechanism[59], the interaction of acyl chlorides with phosphorothioites does not lead to the synthesis of thioanalogues of KPE.

III. STRUCTURE

The products of the reaction of trialkyl phosphites with acyl halides can have the structure of ketophosphonates (I) or the isomeric structure of mixed phosphites with a tervalent phosphorus atom (II). The structure (I) has proved to be fully consistent with the pronounced carbonyl functions of these compounds and the usually easy hydrolysis, leading to the regeneration of phosphorous acid, was fully accounted for by the isomeric phosphite structure (II). However, the first investigators of this reaction[8] were forced to recognise on the basis of the chemical properties (and later infrared spectroscopic studies) that the reaction products are α-ketophosphonates (I) and that the interaction therefore proceeds via the mechanism of the Arbuzov reaction. If one assumes a reaction mechanism involving the formation of phosphonium salts as intermediates (there is also evidence[60,61] for the formation of intermediate pentacovalent derivatives in some reactions), then evidently adducts with a tetrahedral configuration are formed as intermediates in this case[62]:

$$RCOCl + P(OR')_3 \rightarrow \left[\begin{array}{c} R \\ | \\ (R'O)_3\overset{+}{P}CCl \\ | \\ O^- \end{array}\right] \rightarrow (R'O)_3\overset{+}{P}COR\ Cl^- \rightarrow \underset{\text{(I)}}{RC(O)\overset{O}{\overset{\|}{P}}(OR')_2} .$$

Summarising the result of earlier studies[8,9,22], Hudson[63] claims that the phosphonates (I) are thermodynamically more stable that the isomeric phosphites (II). The formation of thermodynamically stable isomers is consistent with the concept that the transition states resemble the intermediate addition products, so that the energy of bond formation plays a decisive role.

Spectroscopic studies of KPE and in recent years comprehensive investigation of their chemical reactions confirmed the phosphonate structure of these compounds. The low frequency of the carbonyl vibrations is a consequence of the

conjugation between the C=O and P→O bonds and demonstrates[22] the absence of an oxygen atom between the acyl group and the phosphorus atom.

In the KPE containing cycloalkane and aliphatic acyl groups the absorption by the C=O and P→O groups varies over a short range. The introduction of the phenyl group[16], alkoxy- and thioalkoxy-groups[14], and halogens[52] in the β-position in the KPE displaces the frequency of the carbonyl vibrations to the region 1715–1733 cm^{-1}, while in KPE with a β,γ-unsaturated bond the C=O vibrations appear[10] at 1645 to 1660 cm^{-1}. A low absorption frequency of the C=O group (1639–1672 cm^{-1}) compared with α-diketones and aliphatic KPE (1685–1695 cm^{-1}) is observed in the series of aroylphosphonates[20,22,23,64] and the extreme values correspond respectively to *o*-chlorobenzoyl- and *p*-anisoyl-phosphonates.

The study of the infrared spectra of *para*- and *ortho*-substituted bis(triorganosilyl)benzoylphosphonates showed that the shift of the frequencies of the C=O groups depends on the electronic effects of the substituents in the aromatic ring and a correlation between the frequency shifts of the stretching vibrations of the carbonyl group with the Hammett σ constants was clearly observed[64].

The structure of the acyl group in KPE has a slight influence on the position of the P→O absorption band: in thiobenzoylphosphonate[59] the P→O group absorbs at 1280 cm^{-1}, while in alkoxyacetylphosphonate[14] it absorbs at 1260 to 1270 cm^{-1}. The structure of the ester groups at the phosphorous atom has a more significant influence and the phosphoryl group in alkyleneacylphosphonates[28] can absorb at 1280–1290 cm^{-1}.

The infrared spectra of the phosphonates obtained from the chlorides of mono- and di-chloroacetic acids contain, apart from the frequencies characteristic of the C=O and P→O groups, absorption bands at 1605 and 3000–3400 cm^{-1}. These data suggested[52] the occurrence of keto–enol tautomerism, which was subsequently confirmed by ^1H NMR[65]:

$$\underset{(87\%)}{ClCH_2C(O)P(O)(OR)_2} \rightleftarrows \underset{(13\%)}{ClCH{=}C(OH)P(O)(OR)_2}\ .$$

The ratio of the tautomers of dichloroacetylphosphonate is the same, while the phenylacetylphosphonate molecule is 82% enolised. The keto–enol equilibrium is apparently based[65] on the free energy of the enol form and not on the acid properties of the CH protons.

Chemists soon ceased to be satisfied with spectroscopic data as an additional confirmation of the structure of KPE and the problem of the study of their steric structure was posed. It proved to be complex, primarily because of two factors—the uncertainty of the function performed by the vacant 3*d* orbitals of the phosphorus atom and the possibility of different steric configurations—different relative positions of the carbonyl and the neighbouring phosphoryl group, in which the phosphorus atom can be asymmetric depending on the structure of the other two substituents. Apart from the importance of the study of the steric structure of KPE from the theoretical point of view, investigation of the nature of the mutual influence of adjacent phosphoryl and carbonyl groups is necessary to elucidate many anomalous reactions of KPE.

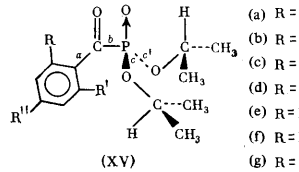
Remarkably low absorption frequencies of the carbonyl group in KPE have been observed by Berlin and Taylor[22], who explained this phenomenon by the reaction of the non-bonding orbital of the oxygen atom in the phosphoryl group with the π orbital of the carbon atom in the C=O group. The overlap of the orbitals then reaches a maximum when the P→O bond is at right angles to the plane in which the aromatic ring, the carbonyl carbon, and phosphorus are located. Thus Berlin and Taylor not only interpreted the spectroscopic characteristics of KPE from the standpoint of conjugation between the C=O and P→O groups, but also proposed a possible version of their relative positions in space. The additional interaction between the carbonyl group and the phosphoryl centre, presupposing the involvement of the 3*d* orbitals of the phosphorus atom, can be investigated by spectroscopic methods in KPE. Laskorin and coworkers[37,66] investigated different spectroscopic characteristics of ketophosphoryl compounds, in particular a series of dimethyl esters of acylphosphonic acids, differing from one another in the structure of the acyl group. It was noted that the decrease of ν(C=O) and the appreciable bathochromic shift of the $n \rightarrow \pi^*$ transition in dimethylacylphosphonates compared with the corresponding ketones indicate the conjugation of the carbonyl group with the phosphorus atom. After comparing ultraviolet, infrared, and ^1H NMR spectroscopic data, the authors[66] concluded that the effective positive charge on the phosphorus atom increases with increasing electronegativity of the acyl residue in dimethylacylphosphonates and that the carbonyl group is involved in conjugation with the 3*d* orbitals of the phosphorus atom to a greater extent.

The same workers[5] made a detailed study of different spectroscopic characteristics of KPE in order to detect the conformers whose existence had been suggested[67]. Different sterically hindered KPE, containing bulky substituents at the carbonyl group and the phosphorus atom, were synthesised. Their infrared spectra showed that they do not exhibit the *cis-trans* isomerism involving the P(O)–C(O) bond, since the ν(C=O) frequency is not split. A detailed study of the ultraviolet and ^1H NMR spectra of KPE showed[5] that the dynamic equilibrium between the isomers cannot be observed by spectroscopic methods. The occurrence of $p_\pi - d_\pi$ conjugation in KPE was again confirmed; the adoption of this concept implies that the rotation about the C–P bond cannot be free.

The first investigators[68] of the electronic spectra of the acylphosphonates also expressed the view that there is a significant conjugation in the P(O)–C(O) system. Ultraviolet spectroscopic data have been frequently invoked to characterise KPE [4,37,66–70] (the bathochromic shift of the $n \rightarrow \pi^*$ transition relative to the corresponding methyl ketone reaches 68 nm). In the studies enumerated above correlations are presented between the bathochromic shift of the $n \rightarrow \pi^*$ transition, as a measure of the $p_\pi - d_\pi$ conjugation, and the structure of the acyl group.

The application of NMR to the conformational analysis of KPE is at present restricted to several investigations[4,5,67], although the ^{31}P NMR spectra of diethyl acetylphosphonate had been published in still earlier studies[33]. The ^1H NMR spectra published in various communications[4,5,10,13,15,32,37,65–67,71,72] are of interest from the standpoint of the study of the spin–spin coupling constants between the P and H nuclei. In the case of dialkyl acetylphosphonates J_{P-H} for the methyl group adjoining the carbonyl group is 5 Hz, which is significantly less than *J* for trimethyl phosphate (11.2 Hz), dimethyl methylphosphonate (CH_3, $J = 17.5$ Hz; OCH_3, $J = 11$ Hz), and trimethyl phosphite ($J = 11$ Hz).

Clark et al.[4] used NMR for the conformational analysis of KPE in relation to diisopropyl esters of aroylphosphonic acids (XV, a-i):



(XV)

(a) R = R′ = R″ = H
(b) R = R″ = H, R′ = CH_3
(c) R = R′ = H, R″ = CH_3
(d) R = R′ = CH_3, R″ = H
(e) R = R″ = H, R′ = OCH_3
(f) R = R′ = H, R″ = OCH_3
(g) R = R′ = OCH_3, R″ = H
(h) R = R″ = H, R′ = Cl
(i) R = R′ = H, R″ = Cl

it was suggested[4] that the bulky isopropyl groups influence the preferred conformation of the system in which the angle between the C=O and P→O bonds can vary as a function of the nature of the substituents in the aromatic ring. A splitting, unusual for KPE, of the doublets due to the methyl group in the isopropyl group in consequence of their non-equivalence has been observed in the ^{1}H NMR spectra measured at temperatures from -50° to +100 °C. In compounds (XV, a, c, f, and i) the non-equivalence of the protons is observed between -50° and +20 °C, in the esters (XV, d, g, and h) between -50° and +100 °C, and in the compounds (XV, b and e) only at temperatures below -20 °C and at approximately +100 °C. Furthermore, the non-equivalence of the methylidyne protons of the isopropyl groups follows from the ^{31}P NMR spectra of the esters (XV, b and c). This fact suggests that, whatever the angle between the C=O and P→O bonds, the rotation about the P–O bond in these compounds (*c* and *c'*) must be restricted. On the basis of NMR data, the determination of dipole moments, infrared absorption, and theoretical calculations, the authors[4] concluded that the possibility of the existence of the system in a preferred conformation and of a restricted rotation about the C–P and possibly P–O bonds is ruled out. The authors[4] state that the earlier conclusion[73] that acylphosphonates exist as equilibrium systems of *s-cis*- and *s-trans*-isomers cannot be correct for the isopropyl esters (XV) according to their dipole moments. The C(O)–P(O) system does not need to be coplanar to achieve the overlap of the *d* and *p* orbitals of different sizes which ensure the d_π–p_π conjugation. The authors claim that the dihedral OPCO angle in the system can assume a series of values for which conjugation is achieved between the C=O and P→O bonds.

The study of the mass spectra of KPE showed[74] that, on electron impact, fragmentation evidently begins with ionisation of the oxygen of the carbonyl group and the dissociation of the P–C bond in consequence of the formation of the stable ion R–C ≡ O$^+$ (the latter is formed from the unstable KPE molecular ion). Among the fragments produced, other ions as well as keten and carbon monoxide were detected, but the formation of a fragment containing carbonyl and phosphoryl groups with simultaneous dissociation of other bonds at the phosphorus atom could never be observed. The P(O)–C(O) bond is least stable in KPE and this structural feature is reflected in a wide variety of chemical reactions of KPE.

IV. CHEMICAL PROPERTIES

The phosphorus–carbon bond, readily formed in the synthesis of α-ketophosphonates, is also readily ruptured under the influence of various nucleophiles. The decomposition of KPE under the influence of a weak nucleophile such as water is one of the chemical reactions observed for these compounds. The reactions of KPE with nucleophiles have been successfully classified by Pudovik and Gareev[75], who proposed a mechanism for the reactions of acetylphosphonate with compounds of type XH (or XNa) and diazoalkanes. The authors state that, when proton-containing compounds react with acetylphosphonate, the latter is cleaved at the P–C bond with formation of an acetic acid derivative and dialkyl phosphite. On the other hand, if the nucleophile is aprotic, the dissociation of the P–C bond is accompanied by the migration of the phosphorus-containing fragment. Numerous experimental facts confirm that the reactions take place generally via these pathways.

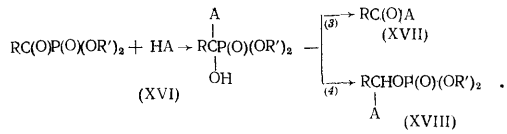
1. Interaction with Proton-Containing Compounds

The hydrolysis of KPE, which leads to a carboxylic acid, can be carried out in a neutral medium[76], but it proceeds faster and reaches completion in the presence of acids[8,22] and alkalies[8,22]. Bertin and Taylor[22] made the first attempt to elucidate the mechanisms of the alkaline and acid hydrolyses by making a detailed study of the decomposition of *p*-anisoylphosphonate. The authors state that the alkaline hydrolysis proceeds more readily and explain this phenomenon by the fact that in the acid hydrolysis the protonation of the phosphoryl group is reversible and the positive charge on the phosphorus atom hinders attack on the carbonyl group. They do not rule out an alternative mechanism, i.e. the slow protonation of the carbonyl group with subsequent rapid attack by water on the carboxonium cation. The formation of an intermediate in the alkaline catalysis resembles the hydrolysis of carboxylic acid esters. However, the true mechanism of the hydrolysis of acylphosphonates is probably more complex[77].

Acylphosphonates and halogeno-substituted KPE react with alcohols in an acid medium[78] or in the presence of a tertiary amine[79], forming unstable adducts; the latter decompose into the corresponding carboxylic acid esters and dialkyl phosphites. Benzoylphosphonate behaves as a benzoylating agent in reactions with thiophenoxides[21]. The rupture of the phosphorus–carbon bond is observed when KPE are acted upon by various amines–aniline[79,80], dialkylamines in the presence of a catalyst (magnesium bromide),[24] and liquid ammonia[81].

In the above reactions with water, alcohols, and amines KPE play the role of acylating agents. It has been shown[24] for dimethylbenzoylphosphonate that these reactions (which the authors[24] called "direct benzoylation") are accelerated by magnesium chloride and bromide. A similar catalytic effect for magnesium salts had been observed earlier in a study of the interaction of Grignard reagents with phosphonates[82].

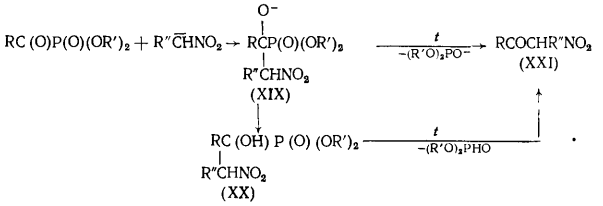
However, the reactions of KPE with proton-containing compounds can proceed also via different pathways, where the addition of the elements of HA to the carbonyl group leads to the formation of the α-hydroxyphosphonic acid ester (XVI). Under the conditions of alkaline catalysis, depending on the nature of A, the latter either decomposes with formation of the corresponding acylated compounds (XVII) or rearranges to a phosphoric acid derivative (XVIII):



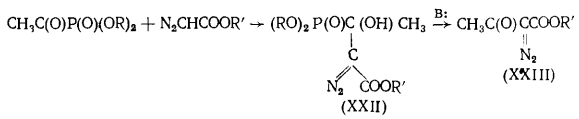
Reactions via pathway *3* are known as "indirect acylation" and have been thoroughly investigated[24] in relation to the reaction of benzoylphosphonate with *N*-magnesium derivatives of amines. The adducts formed under these conditions, containing a hydroxy-group and a substituted amino-group attached to the same carbon atom, proved to be unexpectedly stable; they can be distilled without decomposition. Under the influence of sodium methoxide, the adduct decomposes with liberation of dialkyl phosphite and an acylated amine. It has been suggested[47,48] that the same mechanism is valid for the acylation of β,γ-unsaturated *d*-hydroxyphosphonic acid esters [for example (VIII)] by α-ketophosphonates (IX), which are formed as a result of protoropic isomerisation when esters of type (VIII) are acted upon by metallic sodium.

Apart from the reactions discussed above, in which KPE behave as *O*- and *N*-acylating agents, it has been shown in recent studies[75,83,84] that they can acylate the carbon atoms

in nitroalkanes, alkylmagnesium bromides, and diazoacetic ester. In these reactions the α-hydroxyacid ester formed initially decomposes in the presence of bases at the carbon–phosphorus bond with elimination of the phosphorus-containing group and the *C*-acylated nucleophile. The acylated nitroalkane[83] (XXI) can be formed from the corresponding α-hydroxy-β-nitroalkylphosphonates (XX) while from the intermediate anion (XIX):

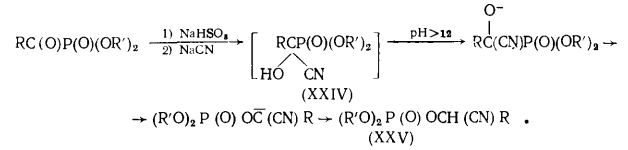


When acetylphosphonate condenses with diazoacetic ester, the product is the ester (XXII),[85,86] stable under neutral conditions, which decomposes under the influence of basic compounds (sodium methoxide, amines, diazomethane) [75] with formation of the ester of 1-diazo-2-oxobutanoic acid (XXIII):



In their study of the stability of compounds containing the O=P–C–OH fragment in the molecule, Pudovik and Gareev[75] suggested that the decomposition of α-hydroxyphosphonates is due to the mobility of the hydrogen atom of the hydroxy-group and the highly nucleophilic properties of the oxygen atom of the phosphoryl-group. The reactions of α-hydroxyphosphonate derivatives, formed when benzoylphosphonate interacts with Grignard and Reformatskii reagents, can be assigned to the same group of reagents (pathway *3*)–the adducts are cleaved with formation of alkyl phenyl ketones and benzoylacetate esters respectively[24,84].

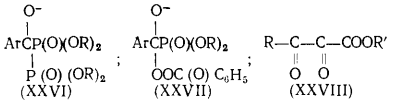
The conditions for the rearrangement[87,88] of α-hydroxyphosphonates to phosphoric acid derivatives (pathway *4*) have now been thoroughly investigated. The first reactions of this type were observed by Hall and Stephen when sodium cyanide was allowed to react with bisulphite compounds of KPE. Instead of the expected α-cyano-α-hydroxyphosphonic acid esters (XXIV), the isomeric phosphates (XXV) were obtained:



The pyrolysis of the phosphates (XXV) has been studied recently and the nitriles of α,β-unsaturated carboxylic acids were obtained in high yields[89]. The reactions of KPE with partially esterified phosphorus acids have been studied in fair detail. Such reactions sometimes accompany as side processes reactions involving the synthesis of α-ketophosphonate as the desired product. It was believed for a long time that the interaction of acetylphosphonate with sodium dialkyl phosphite and with dialkyl phosphite in the presence of amines leads to the hydroxydiphosphonate (III). The study of ^{31}P NMR spectra showed[33] that the products contain two non-equivalent phosphorus atoms. Under mild conditions (0 °C), it was possible to isolate diphosphonates of type (III), which are converted on distillation into the phosphonophosphates (IV). The conditions for the rearrangement were studied in greater detail by Pudovik and coworkers[34,45,46]. The phosphonophosphate (IV) has been obtained as a side product on heating acetylphosphonate with ethanol in the presence of triethylamine. The rearrangement to phosphates takes place readily[90] when dialkyl phosphites react with β-halogeno-substituted α-ketophosphonates without a catalyst.

In the case of asymmetric hydroxydiphosphonates (such diphosphonates have been obtained by the reaction of dialkyl acylphosphonates with derivates of ethylphosphinothioic[20] or dialkylphosphorothioic[91,92] acids as well as ethyl *N,N*-diethylphosphoramidite[93]) the structure of the isomerisation products (phosphates) was established by chemical and additional physicochemical methods[93].

In the course of the phosphonate–phosphate rearrangement the dialkoxyphosphono-group migrates from carbon to oxygen. α-Hydroxydiphosphonates obtained from aroylphosphonates isomerise particularly readily; the unstable intermediate ion (XXVI), containing three electron-accepting groups, is then stabilised by conversion into a phosphate:

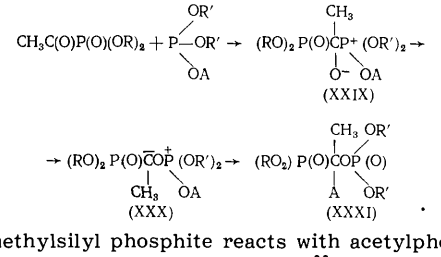


The preferred migration of the dialkoxyphosphono-group compared with the aryl group is observed in the oxidation of aroylphosphonates by perbenzoic acid[94]. The mixed anhydride of dialkylphosphorous and substituted benzoic acids is formed in high yield in this reaction from the intermediate addition product (XXVII).

2. Reactions with Aprotic Nucleophiles

For the majority of reactions of KPE with aprotic reagents, the attack of the nucleophile is directed to the carbon atom of the carbonyl group. The dipolar ion formed can be stabilised in different ways; however, the migration of the electrophilic group (frequently the dialkoxyphosphono-group) is characteristic of all cases of stabilisation.

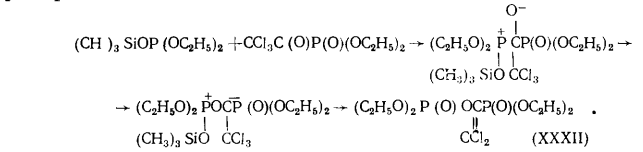
Part of the review of Konovalova and Pudovik[95] is devoted to the reactions of KPE and α-dicarbonyl compounds with trialkyl phosphites. They draw attention to the lower reactivity of KPE in the reaction with phosphites compared with α-ketocarboxylic acid esters (XXVIII) [96] and to a different course of the reaction. The interaction of trialkyl phosphites with the esters (XXVIII) usually leads to compounds having the 1,3,2-dioxophospholan structure, while KPE give rise to the phosphonophosphates (XXXI, A = alkyl). The reaction, occurring at 100–120 °C, probably begins with attack by the phosphite on the carbon atom of the carbonyl group and in the resulting zwitter-ion (XXX) the alkyl group migrates to the carbanionic centre of the molecule[97,98]:



When trimethylsilyl phosphite reacts with acetylphosphonate, the product is a diphosphonate[99]. Evidently[100] in this case the dipolar ion (XXIX, A = Si(CH$_3$)], which has

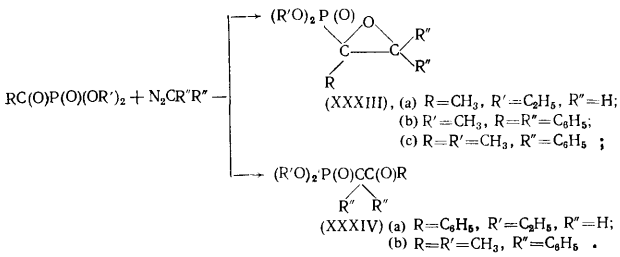
a harder electrophilic centre A, is rapidly stabilised as a result of the migration of the trimethylsilyl group and not the dialkoxyphosphono-group. The intermediate ion [XXIX, A = C(O)CH_3], formed by the interaction[101] of acetylphosphonate with acetyl phosphite, isomerises analogously.

The interaction of triethyl phosphite with β-halogeno-substituted KPE proceeds in a complex manner[36,52], discussed previously, with formation of a mixture of compounds including unsaturated phosphates. The reaction of trichloroacetyl phosphonate with mixed phosphites (trimethylsilyl and acetyl diethyl phosphite) is exothermic and leads to the same compound (XXXII). It has been suggested that, in the reaction with trimethylsilyl phosphite[102], the zwitter-ion is converted by the mechanism of the Perkow reaction into the phosphono-phosphate (XXXII):



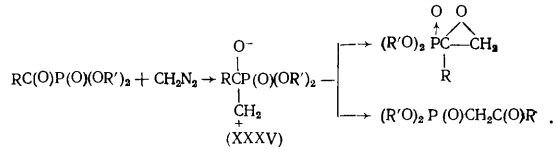
Aldehydes, which have a potentially mobile hydrogen atom in the formyl group (trichloroacetaldehyde, benzaldehyde), react with KPE via a mechanism of the type of benzoin condensation at 80 °C in the presence of piperidine. At a higher temperature the resulting "benzoins" isomerise to phosphates[103,104]. When trichloroacetylphosphonate was allowed to react with chloral, the product was an unsaturated phosphate[105], formed evidently from the initial "benzoin" anion as a result of the elimination of the chloride ion.

The reactions of KPE with diazoalkanes take place in different ways. Data have been published[106] on the interaction between certain KPE and diazomethane. The reaction of acetylphosphonate with diazomethane leads to the oxiran derivative (XXXIIIa) and benzoylphosphonate is converted into the β-ketophosphonate (XXXIVa). Acetyl- and benzoyl-phosphonates react with diphenyldiazomethane at 80 °C via one pathway with formation[107] of the epoxy-compounds (XXXIII, b and c). When the reaction of acetylphosphonate with diphenyldiazomethane was carried out at 0 °C, a mixture of products was obtained[108], consisting of derivatives of oxiran (XXXIIIc) and β-ketophosphonate (XXXIVb):



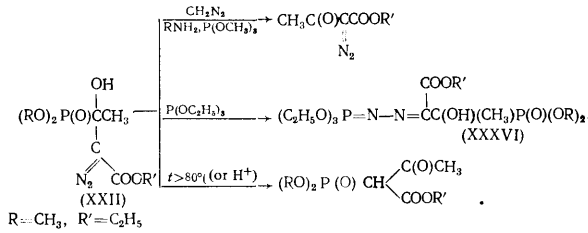
The authors[108] suggest that in the latter case both products are formed from the same intermediate ion. It was later shown[109] that, when benzoylphosphonate is acted upon by a threefold excess of diazomethane, the only reaction product is a compound to which the structure of the methyl ether of the enolic form of the β-ketophosphonate was attributed on the basis of spectroscopic data; evidently the carbonyl form enolises under the influence of diazomethane as a base. Under analogous conditions, diazoethane does not promote the enolisation of the corresponding ketophosphonate.

The mechanism of the reactions of KPE with diazoalkanes can be treated in different ways from the standpoint of the possible pathways leading to the formation of intermediates[109,110], but there is no doubt about the formation of a bond between the carbon atoms of the diazo-component and the carbonyl group of KPE [110]. The elimination of molecular nitrogen results subsequently in two pathways leading to the stabilisation of the ion (XXXV); for R = CH_3, both pathways operate, while for R = C_6H_5 only the second pathway is active:



In the transformation of the dipolar ion (XXXV, R = C_6H_5) to the stable β-ketophosphonate, the phosphorous-containing fragment migrates to the electron-deficient carbon atom. Contrary to expectation, the interaction of dimethyl acetylphosphonate with diazoethane leads to an oxiran derivative and not a β-ketophosphonate. On the basis of data obtained in the study of this reaction, it was concluded[111] that the nature of the final product of the reaction of KPE with diazoethane is independent of the type of substituent at the carbonyl group of the initial ketophosphonate.

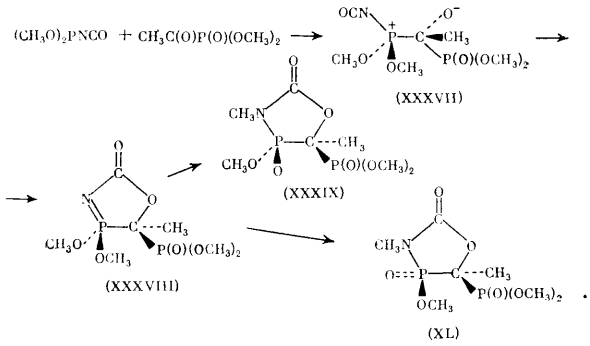
As already mentioned previously, the condensation of diazoacetate ester with acetylphosphonate led unexpectedly to the formation of a product of the aldol type (XXII), [86] which undergoes interesting reactions. Under the influence of diazomethane[75] or trimethyl phosphite[112] as bases, the ester (XXII, R = CH_3, R′ = C_2H_5) is cleaved at the carbon–phosphorus bond with liberation of dimethyl phosphites. Under these conditions, the reaction with triethyl phosphite leads to the phosphazine system (XXXVI),[112] which is cleaved hydrolytically with elimination of triethyl phosphate. On heating above 80 °C or under the influence of acids, the ester (XXII) undergoes 1,2-fragmentation of a new type, which yields dialkoxyphosphonylacetoacetic ester. The mechanism of the formation and the structure of the latter have been studied in detail[113–115]:



A series of studies by Japanese workers were devoted to the investigation of KPE with thiazolium and benzimidazolium salts. A derivative of 2-substituted 1,4-thiazine was obtained from benzoylphosphonate and thiamine in the presence of bases[21,116,117]. Subsequently the reaction was extended to different *N*-substituted thiazolium salts[118–123] and 1,3,4-oxadiazolium salts[124], and in some cases intermediate isomerisation products were isolated[121]. It has been suggested that in all cases the nucleophilic thiazolium centre adds to the carbon atom of the carbonyl group in KPE. This is followed by isomerisation to a phosphate, which hydrolyses on treatment with alkali with formation of an enol. Ring expansion then takes place as a result of the insertion of a new carbon atom with formation of a 1,4-thiazine derivative. The reactions of KPE with benzimidazolium salts yielded adducts[125], which do not give rise to quinoxaline derivatives on alkaline hydrolysis.

The interaction of KPE with phosphoroisocyanatidites results in the formation of zwitter-ions [for example, (XXXVII)], the pathway leading to the stabilisation of which

is determined by the presence of several reaction centres. In the case of dialkyl phosphoroisocyanatidites, three structural isomers are formed[126,127] (demonstrated by infrared spectroscopy). A detailed study of the reaction[128] between dimethyl phosphoroisocyanatidite and acetylphosphonate at reduced temperatures made it possible to observe a new type of isomerisation of the zwitter-ion to the intermediate (XXXVIII) with subsequent conversion into a mixture of two configurational isomers of the substituted phosphaoxazolidinone, (XXXIX) and (XL), with a P–C bond in the ring:



The reaction of dialkyl phosphoroisocyanatidites with chloro-substituted acetylphosphonates does not proceed unambiguously. Whereas the only product of the interaction with trichloroacetylphosphonate is[129] a phosphonophosphate, resulting from the Perkow reaction, the interaction with mono- and di-chloroacetylphosphonate under analogous conditions leads[130] to a mixture of products. One of these is a phosphonophosphate and the other is a substituted phosphaoxazolidinone with a P–O–C linkage in the ring. A similar feature was noted in the behaviour of chloro-substituted acetylphosphonates in relation to alkyl phosphorodi-isocynatidites[65,131]. The migration of the alkyl group to the nitrogen atom is characteristic of the formation of cyclic products in the reactions indicated.

The C,O- and C,C-migration of the electrophilic dialkoxyphosphono-group in the intermediate dipolar ion, formed as a result of the nucleophilic addition of the carbonyl group of the ketophosphonate to carbon, is characteristic of the majority of the reactions of KPE with aprotic nucleophiles examined above. However, one can postulate also direct attack by phosphorus on the oxygen atom of the carbonyl group in the reaction of KPE with phosphoramidite[132]:

$$(C_2H_5O)_2PNHR + R'C(O)P(O)(OC_2H_5)_2 \rightarrow (C_2H_5O)_2\overset{+}{P}\overset{-}{O}CR'P(O)(OC_2H_5)_2 \rightarrow$$
$$\rightarrow (C_2H_5O)_2POCH(R')P(O)(OC_2H_5)_2 \rightarrow C_2H_5OP(O)OCH(R')P(O)(OC_2H_5)_2 .$$

The complex-forming properties of KPE have been studied inadequately. The formation of a complex on interaction of dimethyl benzoylphosphonate with aluminium chloride has been reported[24]. Molecular complexes[133] of aroylphosphonates with tin and titanium tetrahalides have been described; it has been established by infrared spectroscopy that the metal in the complex is coordinated to the carbonyl and phosphoryl groups. Diethyl acylphosphonates behave as bidentate ligands in the reaction[134,135] with 3*d* metal perchlorates. The reaction between aroylphosphonates and nickel complexes with cyclo-octa-1,5-diene proceeds via a different pathway: the arolyphosphonates are cleaved at the C–P bond[136].

The synthesis of free α-ketophosphonic acids from the esters involves certain difficulties because of the hydrolytic instability of the phosphorus–carbon bond in the KPE molecule mentioned above. In a study of the use of aroylphosphonates as alkylating agents for the synthesis of *p*-toluenesulphonic acid esters, Golborn[137] isolated also acylphosphonic acids. Zygmunt et al.[138] reviewed briefly data on the dealkylation of acylphosphonates and suggested that the dealkylation can be carried out with the aid of trimethylsilyl iodide. KPE are silylated under mild conditions; the resulting trimethylsilyl α-ketophosphonate esters are readily hydrolysed by water under neutral conditions.

3. Reactions Involving the Substitution of the Carbonyl Oxygen

The traditional qualitative reactions of ketones are also undergone by KPE, which form phenylhydrazones and oximes. The methods for the preparation of arylhydrazones are various–heating with arylhydrazine in absolute alcohol, the addition of an ethereal solution of the KPE to solid *p*-nitrophenylhydrazine, and reactions in the presence of sulphuric acid. It is remarkable that β-halogeno-substituted KPE do not form[66,76] *p*-nitrophenylhydrazones and oximes. This fact has been explained[66] by the reduced amount of double bond character in the carbonyl group owing to the p_π-d_π conjugation with the phosphorus atom. KPE oximes (more rarely phenylhydrazones) have been used as the starting compounds in the synthesis of various α-aminophosphonic acids[2]. Apart from aluminium amalgam[23], diborane[139] and hydrogen over Raney nickel[16] have been used as reducing agents.

The conversion of acetylphosphonates into derivatives of α,β-unsaturated phosphonic acids has been described[140]. When acetylphosphonates react with cyanoacetic ester in the presence of amines, it is possible to obtain either the corresponding α-hydroxyphosphonates or their dehydration products, depending on the reaction temperature. α-Hydroxyphosphonates, obtained by the condensation of acetylphosphonate with malonodinitrile, are readily dehydrated[140].

Dialkylphosphonodiazoalkanes have been synthesised by the decomposition of the tosylhydrazones of aliphatic KPE;[10,141,142] subsequently this method was extended[143] to aroylphosphonates. It has been suggested[71] that diazoalkylphosphonates be synthesised from the tosylhydrazones of KPE by treatment with sodium borohydride in methanol. A review has been devoted to the chemistry of aryldiazoalkylphosphonates[3].

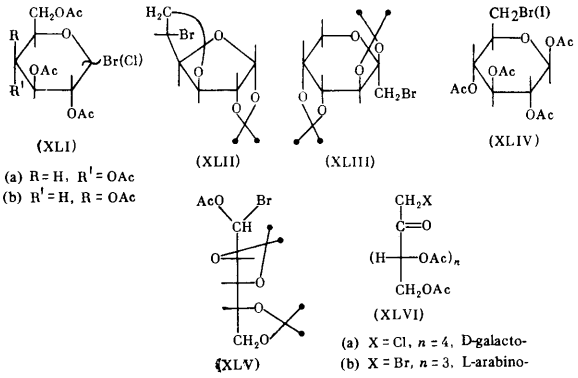
The photochemical reactions of aroylphosphonates[70,144] are distinguished by a wide variety of reaction products. This behaviour is determined by the structure of the aroylphosphonate and the coreactant in the photochemical reaction. When diethyl benzoylphosphonate is irradiated with the light of a mercury lamp, a trioxan derivative is formed as a result of trimerisation; isopropyl and butyl esters undergo the pinacol rearrangement under these conditions. In methanol solution methyl benzoate is formed from these esters. Irradiation of substituted azirine in the presence of benzoylphosphonate leads to a satisfactory yield of a phosphonate-substituted oxazoline, whereupon the diatomic C–O bond is inserted in the ring[144].

The conversion of KPE into alkylphosphonates can be achieved by reducing α-diazoalkylphosphonates with sodium borohydride in boiling tetrahydrofuran[71] or by electrochemical reduction[145].

V. CARBOHYDRATE-CONTAINING α-KETOPHOSPHONIC ACID ESTERS

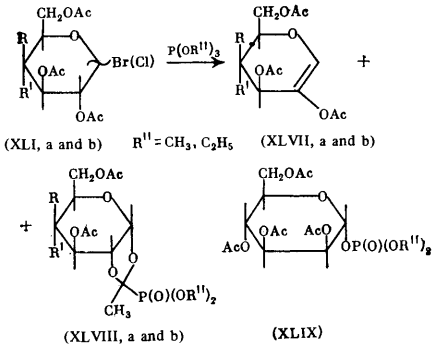
Numerous examples in which the usual organic reactions take place via non-standard pathways are known in carbohydrate chemistry. The Arbuzov reaction, applied to

halogen-containing monosaccharides in order to obtain carbohydrate derivatives with a phosphorus–carbon bond, is no exception in this sense. In the classical version of the Arbuzov reaction the principal types of halogeno-derivatives of monosaccharides (XLI)–(XLVI) have been used:



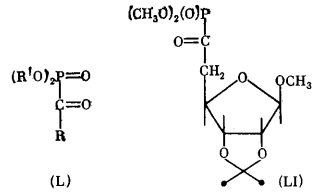
Among these compounds, only (XLIV) and (XLV) yield the "normal" products of the Arbuzov reaction–the corresponding carbohydrate-containing phosphonates[146–148]; compound (XLII) is reduced[149] by triethyl phosphite; acetohalogenoses (acetylated 1-halogeno-monosaccharides), for example, (XLI, a and b), react to form anomalous compounds, while compound (XLIII) does not react with trialkyl phosphites even under severe conditions. Acetylated non-cyclic halogenoketoses (XLVI) undergo the Perkow reaction on treatment with triethyl phosphite to form vinyl phosphates[150].

In the general case the interaction of acetohalogenoses with trialkyl phosphites results in a mixture of compounds[6,7,151], the ratios of which depend on the configuration of the initial halogenose:



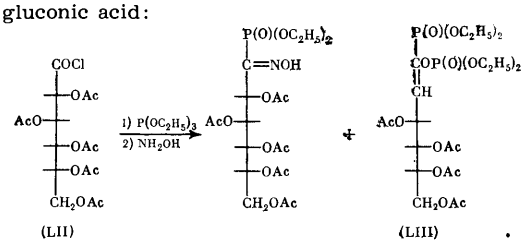
Compounds (XLVIII, a and b) are formed from the acetohalogenoses (XLI, a and b) and trialkyl phosphites in 12–15% yield and by the Michaelis–Becker reaction (using the mercury and silver salts of dialkylphosphorous acids) in 20 to 80% yield. The glucal (XLVIIa) and the phosphate (XLIX) were isolated after the reaction of α-acetobromomannose with trialkyl phosphites. The probable mechanism of the formation of acetylphosphonates (XLVIII) under the conditions of the Arbuzov reaction is believed[151] to involve the formation of an intermediate acetoxonium ion, which combines with triethyl phosphite and then eliminates ethyl halide. It is remarkable that in the acetylphosphonates (XLVIII) the carbon–phosphorus bond is stable and the conversion of these phosphonates into the glycal (XLVII) has not been observed in any one instance. Compound (XLVIII) is a cyclic ketal of acetylphosphonate and exhibits a stability characteristic of KPE ketals[152] with respect to the action of alkaline agents. It has been suggested that α-ketophosphonates are formed in the oxidation of carbohydrate-containing α-hydroxyphosphonates by sodium periodate[153].

The synthesis of carbohydrate-containing α-ketophosphonate (L) (R is a polyol residue with protected hydroxy-groups) from the chlorides of acetylated aldonic acids was first reported by Zhdanov et al.[154]; the synthesis of compound (LI) from the chloride of uronic acid and trimethyl phosphite was described subsequently[72]:



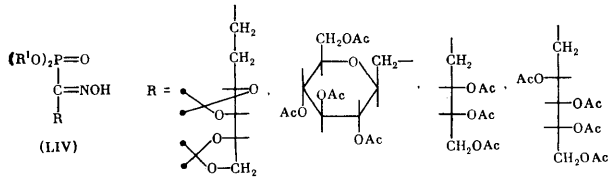
The esters (L) have been isolated in low yields as hydroxyimino-derivatives. The principal reaction products are[155] diphosphoryl-containing compounds, the structure of which has been established with the aid of NMR and infrared specta; the alkyl esters of aldonic acids have also been obtained.

Diphosphorylcarbohydrate reaction products, with non-equivalent phosphorus atoms, an olefinic bond, and a smaller number of acetyl groups than in the initial acid halide, are formed via the Perkow reaction mechanism. α-Ketophosphonates with highly reactive carbonyl groups and an acetoxy-group activated by α-carbonyl and β-phosphoryl functional groups are obtained in the first stage and react with the excess phosphite. The α,β-unsaturated phosphonophosphates formed have been isolated as isomeric compounds. Thus compound (LIII) is formed from the chloride of acetylated D-gluconic acid:



Similarly compound (LII) reacts with tri-isopropyl phosphite and the chlorides of D-galactonic and D-arabonic acids react with triethyl phosphite[155]. It is of interest to note that the Perkow reaction observed for carbohydrate-containing α-ketophosphonates takes place under very mild conditions (at 25 to 30 °C), while in the case of the carbonyl forms of monosaccharides the enol phosphates are formed only on heating with triethyl phosphite to 85–140 °C.[156,157]

The interaction of trialkyl phosphites with the chlorides of desonoic acids gives high yields of carbohydrate-containing α-ketophosphonates, which have been identified as the oximes (LIV).[158] Such phosphonates are phosphorus analogues of 2-oxo-3-deoxyaldonic acids:



Carbohydrate-containing phosphonic acids, obtained from compounds of type (LIV) after removing the protecting groups at the phosphorus atom and in the carbohydrate residue, can apparently be used as substrates and inhibitors in the study of their interaction with a number of enzymes[159, 160]. This conclusion is based on convincing data[161] for the inhibition of pyruvate dehydrogenase by the phosphonate analogue of pyruvate and for the inhibition of acetyl-CoA synthetase when the substrate is acted upon by adenosine 5′-chloroacetylphosphonate[162].

REFERENCES

1. A.N.Pudovik, I.V.Konovalova, R.D.Gareev, R.A.Cherkasov, E.A.Ishmaeva, G.E.Yastrebova, N.G.Khusainova, and M.G.Zimin, "Khimiya i Primenenie Fosfororganicheskikh Soedinenii" (The Chemistry and Applications of Organo-phosphorus Compounds), Izd.Nauka, Moscow, 1974, p.62.
2. K.A.Petrov, V.A.Chauzov, and T.S.Erokhina, Uspekhi Khim., **43**, 2045 (1974)[Russ.Chem.Rev., No.11 (1974)].
3. M.Regitz, Angew.Chem., **87**, 259 (1975).
4. P.E.Clark, K.D.Berlin, J.Mosbo, and J.G.Verkade, Phosphorus, **2**, 265 (1973).
5. B.N.Laskorin, V.V.Yakshin, and L.I.Sokal'skaya, Zhur.Obshch.Khim., **44**, 1716 (1974).
6. H.Paulsen, J.Thiem, and M.Moner, Tetrahedron Letters, 2105 (1971).
7. H.Paulsen and J.Thiem, Chem.Ber., **106**, 132 (1973).
8. M.I.Kabachnik and P.A.Rossiskaya, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 364 (1945).
9. J.A.Cade, J.Chem.Soc., 2272 (1959).
10. R.S.Marmor and D.Seyferth, J.Org.Chem., **36**, 128 (1971).
11. O.E.Nasakin, V.V.Kormachev, and V.A.Kukhtin, Zhur.Obshch.Khim., **45**, 2374 (1975).
12. R.D.Moss, US P.3 012 054 (1961); Chem.Abs. **57**, 4698 (1962).
13. K.D.Berlin, D.M.Hellwege, and M.Nagabhushanam, J.Org.Chem., **30**, 1265 (1965).
14. M.V.Zolotova and T.V.Konstantinova, Zhur.Obshch. Khim., **40**, 2131 (1970).
15. D.A.Nicholson and H.Vaughn, J.Org.Chem., **36**, 3843 (1971).
16. S.Asano, T.Kitahara, T.Ogata, and M.Matsui, Agric.Biol.Chem., **37**, 1193 (1973).
17. N.F.Orlov and B.L.Kaufman, Zhur.Obshch.Khim., **38**, 1842 (1968).
18. T.Kh.Gazizov, Yu.I.Sudarev, and A.N.Pudovik, Zhur.Obshch.Khim., **47**, 1660 (1977).
19. R.M.Khomutov, T.I.Osipova, and Yu.N.Zhukov, Izv.Akad.Nauk SSSR, Ser.Khim., 1391 (1978).
20. A.N.Pudovik, I.V.Gur'yanova, and M.G.Zimin, Zhur.Obshch.Khim., **38**, 1533 (1968).
21. A.Takamizawa, Y.Sato, and S.Tanaka, Yakugaku Zasshi, **85**, 298 (1965); Chem.Abs., **63**, 9940 (1965).
22. K.D.Berlin and H.A.Taylor, J.Amer.Chem.Soc., **86**, 3862 (1964).
23. K.D.Berlin, R.T.Claunch, and E.T.Gaudy, J.Org. Chem., **33**, 3090 (1968).
24. I.Shahak and J.Peretz, Israel J.Chem., **9**, 35 (1971).
25. V.M.D'yakov, N.F.Orlov, G.S.Gusakova, and N.I.Zakharov, "Khimiya i Prakticheskoe Primenenie Kremniiorganicheskikh Soedinenii" (The Chemistry and Practical Applications of Organosilicon Compounds), Izd.Nauka, Leningrad, 1971, p.117.
26. T.Kh.Gazizv, A.P.Pashinkin, and A.N.Pudovik, Zhur.Obshch.Khim., **41**, 2418 (1971).
27. I.F.Lutsenko, A.L.Chekhun, and N.V.Proskurnina, USSR P.389 105 (1972); Byul.Izobret., No.29 (1973).
28. E.E.Nifant'ev, I.V.Komlev, I.P.Konyaeva, A.I.Zavalishina, and V.I.Tul'chinskii, Zhur.Obshch. Khim., **43**, 2368 (1973).
29. P.I.Alimov and L.A.Antokhina, Izv.Akad.Nauk SSSR, Ser.Khim., 1486 (1966).
30. N.P.Grechkin, N.A.Buina, I.A.Nuretdinov, and S.G.Samekhov, Izv.Akad.Nauk SSSR, Ser. Khim., 2131 (1968).
31. C.Brown and R.F.Hudson, Tetrahedron Letters, 3191 (1971).
32. M.A.Pudovik, L.K.Kibardina, M.D.Medvedeva, and A.N.Pudovik, Zhur.Obshch.Khim., **49**, 988 (1979).
33. S.J.Fitch and K.Moedritzer, J.Amer.Chem.Soc., **84**, 1876 (1962).
34. A.N.Pudovik and I.V.Konovalova, Zhur.Obshch.Khim., **33**, 98 (1963).
35. G.F.Gavrilin and B.A.Vovsi, USSR P.189 849 (1963); Byul.Izobret., No.1 (1967).
36. L.Z.Soborovskii and Yu.G.Gololobov, Zhur.Obshch. Khim., **30**, 2586 (1960).
37. B.N.Laskorin, V.V.Yakshin, and L.I.Sokal'skaya, Dokl.Akad.Nauk SSSR, **198**, 1091 (1971).
38. I.L.Knunyants, E.G.Bykhovskaya, and Yu.A.Sizov, Zhur.Vses.Khim.Obshch. im Mendeleeva, **17**, 354 (1972).
39. G.A.Kamai and V.A.Kukhtin, Zhur.Obshch.Khim., **27**, 949 (1957).
40. F.Ramirez, H.Yamanaka, and O.Basedow, J.Amer. Chem.Soc., 83, 173 (1961).
41. A.N.Pudovik, T.Kh.Gazizhov, and A.P.Pashikin, Zhur.Obshch.Khim., **36**, 563 (1966).
42. A.N.Pudovik, T.Kh.Gazizhov, and A.P.Pashikin, Symposium, "Khimiya Organicheskikh Soedinenii Fosfora" (The Chemistry of Organic Phosphorus Compounds), Izd.Nauka, Leningrad, 1967, p.25.
43. M.B.Gazizov and A.I.Razumov, Zhur.Obshch.Khim., **39**, 2600 (1969).
44. M.B.Gazizov, D.B.Sultanova, V.V.Moskva et al., Zhur.Obshch.Khim., **41**, 932 (1971).
45. A.N.Pudovik and I.G.Konovalova, Dokl.Akad.Nauk SSSR, **143**, 875 (1962).
46. A.N.Pudovik and I.G.Konovalova, Zhur.Obshch. Khim., **32**, 467 (1962).
47. A.N.Pudovik, M.G.Zimin, and A.A.Sobanov, Zhur.Obshch.Khim., **43**, 1910 (1973).
48. M.G.Zimin, A.A.Sobanov, and A.N.Pudovik, Zhur. Obshch.Khim., **44**, 2582 (1974).
49. M.I.Kabachnik and P.A.Rossiiskaya, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 48 (1957).
50. A.N.Pudovik and L.G.Biktimirova, Zhur.Obshch. Khim., **27**, 2104 (1957).
51. J.W.Baker and G.A.Saul, US P.2934 469 (1960); Chem.Abs. **54**, 18356 (1960).
52. A.N.Pudovik and T.Kh.Gazizov, Zhur.Obshch.Khim., **39**, 2225 (1969).
53. I.J.Borowitz, F.Firstenberg, G.B.Borowitz, and D.Schuessler, J.Amer.Chem.Soc., **94**, 1623 (1972).
54. I.J.Borowitz and R.K.Crouch, Phosphorus, **2**, 209 (1973).
55. I.L.Knunyants, E.G.Bykhovskaya, V.N.Frosin, and Yu.A.Sizov, USSR P.239 950 (1968); Byul.Izobret., No.12 (1969).
56. N.F.Orlov and B.L.Kaufman, USSR P.193 505 (1965); Byul.Izobret., No.7 (1967).

57. N.F.Orlov and B.L.Kaufman, Izv.Akad.Nauk SSSR, Neorg.Materialy, **2**, 946 (1966).
58. N.F.Orlov and B.L.Kaufman, Symposium, "Kremnii-organicheskie Soedinenya, Trudy Soveshchaniya" (Organosilicon Compounds, Conference Proceedings), Izv.NIITEKhIN), 1966, p.74.
59. V.V.Yakshin and L.I.Sokal'skaya, Zhur.Obshch. Khim., **41**, 484 (1971).
60. G.Bauer and G.Hagele, Angew.Chem., **89**, 493 (1977).
61. A.Skowronska, J.Mikolayczak, and J.Michalski, Chem.Comm., 791 (1975).
62. A.J.Kirby and S.G.Warren, "The Organic Chemistry of Phosphorus" (Translated into Russian), Izd.Mir, Moscow, 1971, pp.45, 70.
63. R.F.Hudson, "Organic Chemistry", Vol.6, "Structure and Mechanisms in Organophosphorus Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1967, pp.122, 169.
64. V.M.D'yakov, G.S.Gusakova, E.I.Pokrovskii, and T.L.D'yakova, Zhur.Obshch.Khim., **41**, 1035 (1971).
65. I.V.Konovalova, R.D.Gareev, L.A.Burnaeva, N.V.Mikhailova, N.K.Novikova, and A.N.Pudovik, Zhur.Obshch.Khim., **48**, 1700 (1978).
66. B.I.Laskorin, V.V.Yakshin, and L.I.Sokal'skaya, Zhur.Obshch.Khim., **42**, 1261 (1972).
67. A.B.Remizov, R.D.Gareev, and A.N.Pudovik, Zhur. Obshch.Khim., **42**, 1238 (1972).
68. K.D.Berlin and D.H.Burpo, J.Org.Chem., **31**, 1304 (1966).
69. K.Terauchi and H.Sakurai, Bull.Chem.Soc.Japan, **42**, 821 (1969).
70. K.Terauchi and H.Sakurai, Bull.Chem.Soc.Japan, **43**, 883 (1970).
71. G.Rosini and G.Baccolini, Synthesis, 44 (1975).
72. A.Hampton, F.Perini, and P.J.Harper, Carbohydr. Res., **37**, 359 (1974).
73. E.A.Ishmaeva, M.G.Zimin, R.N.Galeeva, and A.N.Pudovik, Izv.Akad.Nauk SSSR, Ser.Khim., 538 (1971).
74. B.I.Laskorin, V.V.Yakshin, and L.I.Sokal'skaya, Zhur.Obshch.Khim., **46**, 2545 (1976).
75. A.N.Pudovik and R.D.Gareev, Zhur.Obshch.Khim., **45**, 16 (1975).
76. I.L.Knunyants, E.G.Bykhovskaya, Yu.A.Sizov, and L.I.Zinov'eva, Zhur.Vses.Khim.Obshch.im.Mendeleeva, **20**, 235 (1975).
77. A.J.Kirby and S.G.Warren, "The Organic Chemistry of Phosphorus" (Translated into Russian), Izd.Mir, Moscow, 1971, p.164.
78. S.G.Warren, Angew.Chem., **80**, 649 (1968).
79. A.P.Pashinkin, T.Kh.Gazizov, and A.N.Pudovik, Zhur.Obshch.Khim., **40**, 28 (1970).
80. A.N.Pudovik, T.Kh.Gazizov, and A.P.Pashinkin, Zhur.Obshch.Khim., **38**, 2812 (1968).
81. M.Soroka and P.Mastalerz, Zhur.Obshch.Khim., **44**, 463 (1974).
82. K.D.Berlin and G.B.Butler, Chem.Rev., **60**, 243 (1960).
83. A.V.Serdyukova, G.M.Baranov, and V.V.Perekalin, Zhur.Obshch.Khim., **44**, 1243 (1974).
84. I.Shahak and F.D.Bergmann, Israel J.Chem., **4**, 225 (1966).
85. A.N.Pudovik, A.B.Remizov, L.A.Stabrovskaya, S.E.Shtil'man, I.G.Lushchits, and R.D.Gareev, Zhur.Obshch.Khim., **42**, 1421 (1972).
86. A.N.Pudovik, R.D.Gareev, A.B.Remizov, A.V.Aganov, G.I.Evstaf'ev, and S.E.Shtil'man, Zhur.Obshch.Khim., **43**, 559 (1973).
87. A.N.Pudovik, I.V.Gur'yanova, and E.A.Ishmaeva, "Reaktsii i Metody Issledovaniya Organicheskikh Soedinenii" (Reactions of and Methods for the Investigation of Organic Compounds), Izd.Khimiya, Moscow, 1968, Book 19, p.53.
88. A.N.Pudovik, I.V.Gur'yanova, L.V.Banderova, and G.V.Romanov, Zhur.Obshch.Khim., **38**, 143 (1968).
89. Y.Okamoto, T.Nitta and H.Sakurai, Bull.Chem.Soc. Japan, **42**, 543 (1969).
90. I.L.Knunyants, E.G.Bykhovskaya, Yu.A.Sizov, and L.I.Zinov'eva, Zhur.Vses.Khim.Obshch.im.Mendeleeva, **20**, 236 (1975).
91. A.N.Pudovik, I.V.Gur'yanova, and M.G.Zimin, Zhur. Obshch.Khim., **37**, 2580 (1967).
92. A.N.Pudovik, I.V.Konovalova, and L.V.Dedova, Dokl. Akad.Nauk SSSR, **153**, 616 (1963).
93. A.N.Pudovik, I.V.Gur'yanova, G.V.Romanov, and L.G.Rakhimova, Zhur.Obshch.Khim., **41**, 1485 (1971).
94. M.Sprecher and E.Nativ, Tetrahedron Letters, 4405 (1968).
95. I.V.Konovalova and A.N.Pudovik, Uspekhi Khim., **41**, 799 (1972)[Russ.Chem.Rev. No.5 (1972)].
96. A.N.Pudovik, I.V.Gur'yanova, S.P.Perevezentseva, and T.V.Zykova, Zhur.Obshch.Khim., **37**, 1317 (1967).
97. A.N.Pudovik and I.V.Konovalova, Zhur.Obshch.Khim., **33**, 3100 (1963).
98. A.N.Pudovik, I.V.Gur'yanova, and S.P.Perevezentseva, Zhur.Obshch.Khim., **37**, 1090 (1967).
99. A.N.Pudovik, E.S.Batyeva, and G.U.Zamaletdinova, Zhur.Obshch.Khim., **43**, 680 (1973).
100. L.V.Nesterov and I.E.Krepysheva, Dokl.Akad.Nauk SSSR, **222**, 121 (1975).
101. A.N.Pudovik and T.Kh.Gazizov, Zhur.Obshch.Khim., **38**, 140 (1968).
102. I.V.Konovalova, L.A.Burnaeva, and A.N.Pudovik, Zhur.Obshch.Khim., **45**, 2567 (1975).
103. A.N.Pudovik, V.I.Nikitina, and V.V.Evdokimova, Zhur.Obshch.Khim., **40**, 294 (1970).
104. A.N.Pudovik, M.G.Zimin, and V.V.Evdokimova, Zhur.Obshch.Khim., **43**, 1907 (1973).
105. A.N.Pudovik, M.G.Zimin, and V.V.Evdokimova, Zhur.Obshch.Khim., **44**, 2109 (1974).
106. B.A.Arbuzov, V.S.Vinogradova, M.A.Polezhaeva, and A.K.Shamsutdinova, Izv.Akad.Nauk SSSR, Otd.Khim. Nauk, 675 (1963).
107. A.N.Pudovik, R.D.Gareev, and L.A.Stabrovskaya, Zhur.Obshch.Khim., **40**, 698 (1970).
108. A.N.Pudovik, R.D.Gareev, A.V.Aganov, and L.A.Stabrovskaya, Zhur.Obshch.Khim., **41**, 1232 (1971).
109. R.D.Gareev, A.N.Pudovik, and Yu.Yu.Samitov, Symposium, "Khimiya Elementoorganicheskikh Soedinenii" (The Chemistry of Organoelemental Compounds), Izd.Nauka, Leningrad, 1976, p.135.
110. R.D.Gareev, G.I.Evstaf'ev, and A.N.Pudovik, Dokl. Akad.Nauk SSSR, **246**, 332 (1979).
111. R.D.Gareev and A.N.Pudovik, Zhur.Obshch.Khim., **47**, 475 (1977).
112. R.D.Gareev and A.N.Pudovik, Zhur.Obshch.Khim., **46**, 2487 (1976).
113. A.N.Pudovik, R.D.Gareev, and S.E.Shtil'man, Zhur.Obshch.Khim., **43**, 1646 (1973).
114. A.N.Pudovik and R.D.Gareev, Zhur.Obshch.Khim., **45**, 22 (1975).
115. A.N.Pudovik and R.D.Gareev, Zhur.Obshch.Khim., **46**, 458 (1976).

116. A.Takamizawa, Y.Sato, S.Tanaka, and H.Itoh, Tetrahedron Letters, 3599 (1964).
117. A.Takamizawa, Y.Hamashima, Y.Sato, and S.Tanaka, J.Org.Chem., **31**, 2951 (1966).
118. A.Takamizawa, Y.Hamashima, and H.Sato, J.Org. Chem., **33**, 4038 (1968).
119. A.Takamizawa, Y.Mori, H.Sato, and S.Tanaka, Chem.Parm.Bull.(Tokyo), **16**, 1733 (1968).
120. A.Takamizawa, Y.Hamashima, and H.Sato, Chem. Pharm.Bull.(Tokyo), **17**, 1356 (1969).
121. A.Takamizawa and H.Sato, Chem.Pharm.Bull.(Tokyo), **18**, 1201 (1970).
122. A.Takamizawa and H.Harada, Chem.Pharm.Bull. (Tokyo), **18**, 1402 (1970).
123. A.Takamizawa and H.Sato, Yakugaku Zasshi, **92**, 27 (1972); Chem.Abs., **76**, 126899 (1972).
124. A.Takamizawa and H.Sato, Chem.Pharm.Bull.(Tokyo), **23**, 948 (1975).
125. A.Takamizawa, Y.Hamashima, H.Sato, and Y.Matsumoto, Chem.Pharm.Bull.(Tokyo), **18**, 1576 (1970).
126. I.V.Konovalova, L.A.Burnaeva, L.S.Yuldasheva, and A.N.Pudovik, Zhur.Obshch.Khim., **44**, 2408 (1974).
127. I.V.Konovalova, L.A.Burnaeva, L.S.Yuldasheva, and A.N.Pudovik, Zhur.Obshch.Khim., **46**, 1733 (1976).
128. I.V.Konovalova, R.D.Gareev, L.A.Burnaeva, T.A.Faskhutdinova, and A.N.Pudovik, Zhur.Obshch. Khim., **48**, 284 (1978).
129. I.V.Konovalova, L.A.Burnaeva, N.K.Novikova, N.V.Mikhailova, and A.N.Pudovik, Zhur.Obshch. Khim., **46**, 1411 (1976).
130. I.V.Konovalova, L.A.Burnaeva, N.V.Mikhailova, and A.N.Pudovik, Zhur.Obshch.Khim., **48**, 739 (1978).
131. I.V.Konovalova, L.A.Burnaeva, and A.N.Pudovik, Zhur.Obshch.Khim., **45**, 2558 (1975).
132. A.N.Pudovik, E.S.Batyeva, and V.D.Nesterenko, Zhur.Obshch.Khim., **44**, 1674 (1974).
133. A.A.Shvets, O.A.Osipov, and L.M.Tokina, Zhur. Obshch.Khim., **47**, 2180 (1977).
134. C.M.Mikulski, W.Henry, L.L.Pytlewski, and N.M.Karayannis, Transit.Met.Chem., **2**, 135 (1977).
135. C.M.Mikulski, W.Henry, L.L.Pytlewski, and N.M.Karayannis, J.Inorg.Nuclear Chem., **40**, 769 (1978).
136. G.P.Chiusoli, G.Cometti, and V.Bellotti, Gazzetta, **104**, 217 (1977).
137. P.Golborn, Syn.Comm., **3**, 273 (1973).
138. J.Zygmunt, P.Kafarski, and P.Mastalerz, Synthesis, 609 (1978).
139. K.D.Berlin, N.K.Roy, and R.T.Claunch, J.Amer. Chem.Soc., **90**, 4494 (1968).
140. A.N.Pudovik, M.G.Zimin, and V.V.Evdokimova, Zhur.Obshch.Khim., **42**, 1489 (1972).
141. D.Seyferth, P.Hilbert, and R.S.Marmor, J.Amer. Chem.Soc., **89**, 4811 (1967).
142. D.Seyferth, R.S.Marmor, and P.Hilbert, J.Org.Chem., **36**, 1379 (1971).
143. N.Gurudata, C.Benezza, and H.Cohen, Canad.J. Chem., **51**, 1142 (1973).
144. N.Gakis, H.Heimgartner, and H.Schmid, Helv.Chim. Acta, **58**, 748 (1975).
145. Von W.Jugelt, W.Lamm, and F.Pragst. J.prakt.Chem., **314**, 193 (1972).
146. R.S.Griffin and A.Burger, J.Amer.Chem.Soc., **78**, 2336 (1956).
147. H.Paulsen, W.Greve, and H.Kuhne, Tetrahedron Letters, 2109 (1971).
148. S.Inokawa, Y.Tsuchiya, and H.Yoshida, Bull.Chem. Soc.Japan, **43**, 3224 (1970).
149. S.Inokawa, K.Yoshida, H.Yoshida, and T.Ogata, Carbohydr.Res., **26**, 230 (1973).
150. L.A.Uzlova, Z.I.Glebova, and Yu.A.Zhdanov, Zhur. Obshch.Khim., **42**, 483 (1972).
151. H.Paulsen and J.Thiem, Chem.Ber., **106**, 115 (1973).
152. V.V.Moskva, A.I.Maikov, and A.I.Razumov, Zhur. Obshch.Khim., **39**, 2451 (1969).
153. H.Paulsen and W.Greve, Chem.Ber., **106**, 2174 (1973).
154. Yu.A.Zhdanov, L.A.Uzlova, and Z.I.Glebova, Dokl. Akad.Nauk SSSR, **197**, 1331 (1971).
155. Yu.A.Zhdanov, L.A.Uzlova, and Z.I.Glebova, Zhur. Obshch.Khim., **48**, 227 (1978).
156. J.Thiem and D.Rasch. Synthesis, 481 (1976).
157. J.Thiem, D.Rasch, and H.Paulsen, Chem.Ber., **109**, 3588 (1976).
158. Z.I.Glebova, L.A.Uzlova, G.K.Kist'yan, and Yu.A.Zhdanov, "Tezisy Dokladov VI Vsesoyuznoi Konferentsii po Khimii i Biokhimii Uglevodov" (Abstracts of Reports at the VIth All-Union Conference on the Chemistry and Biochemistry of Carbohydrates), Izd.Nauka, Moscow, 1977, p.33.
159. N.V.Gulyaeva and L.A.Baranova, "Tezisy Dokladov VI Vsesoyuznoi Konferentsii po Khimii i Biokhimii Uglevodov" (Abstracts of Reports at the VIth All-Union Conference on the Chemistry and Biochemistry of Carbohydrates), Izd.Nauka, Moscow, 1977, p.32.
160. R.Engel, Chem.Rev., **77**, 349 (1977).
161. R.Kluger and D.C.Pike, J.Amer.Chem.Soc., **99**, 4504 (1977).
162. N.N.Gulyaev and L.A.Baranova, Dokl.Akad.Nauk SSSR, **213**, 335 (1973).

Rostov State University

Institute of Physical and Organic
Chemistry at Rostov State University

Translated from *Uspekhi Khimii*, **49**, 1751-1773 (1980) U.D.C. 547.514.72

Arylated Cyclopentadienes and Cyclopentadienylides

Ya.N.Kreitsberga and O.Ya.Neiland

Information on the synthesis of arylated cyclopentadienes and their ylide derivatives is systematically reviewed, and the chemical reactions of the compounds are discussed. A list of 110 references is included.

CONTENTS

I.	Introduction	854
II.	Methods for the synthesis of arylated cyclopentadienes	854
III.	Chemical reactions of arylated cyclopentadienes	857
IV.	Preparation of arylated cyclopentadienylides	859
V.	Properties of arylated cyclopentadienylides	860

I. INTRODUCTION

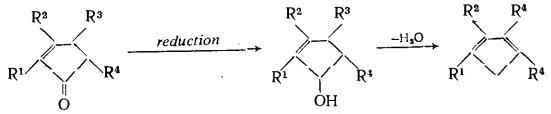
Several phenylated cyclopentadienes have found application as photosensitisers, but arylcyclopentadienes are of interest mainly as starting materials for the synthesis of cyclopentadienylides, fulvenes, ferrocenes, and other compounds.

The Review covers only those arylated cyclopentadienes in which the double bonds of the cyclopentadiene ring do not form part of an aromatic system (indenes are not covered).

II. METHODS FOR THE SYNTHESIS OF ARYLATED CYCLOPENTADIENES

1. Synthesis from Cyclopentenones

Cyclopentenones are used to obtain substituted cyclopentadienes because of the readiness with which the carbonyl group undergoes reduction and the Grignard reaction[1,2]. Cyclopent-2-enones are usually employed, for they are more stable and more readily available than cyclopent-3-enones[3]:

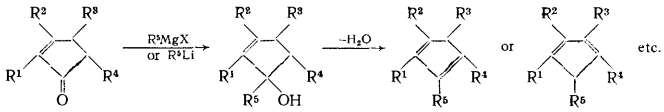


(*a*) $R^1=R^2=R^3=R^4=Ph$;
(*b*) $R^1=R^2=R^3=Ph$, $R^4=H$.

Selective reduction of the carbonyl group in the conjugated enone system is effected with lithium tetrahydroaluminate in ether at room temperature[1] or with sodium tetrahydroborate in aqueous dioxan[2]. The yields of cyclopentadienes reach 70–90% of theoretical, and the preparation can be accomplished in a single stage without isolation of the intermediate cyclopentenols. 1,2,3,4-Tetra- and 1,2,3-tri-phenylcyclopenta-1,3-dienes have been obtained in this way[1,2].

An attempt to use this method to obtain 1,2-diphenylcyclopenta-1,3-diene was unsuccessful[1,4], since 3,4-diphenylcyclopent-2-enol resinifies on acid dehydration, and the desired product is formed in small quantities, while the isomeric 3,4-diphenylcyclopent-3-enol does not eliminate water. 1,2-Diphenylcyclopenta-1,3-diene has been obtained in low yield by reducing 4-chloro-2,3-diphenylcyclopent-2-enone with lithium tetrahydroaluminate[5].

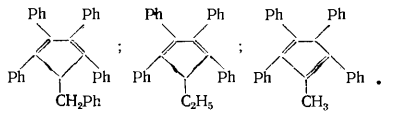
Substituted cyclopentadienes are most often obtained by treating cyclopentenones with organomagnesium and organolithium compounds and then dehydrating without isolating the intermediate carbinols[6-10]:



(*a*) $R^1=R^2=R^3=R^4=H$, $R^5=Ph$;
(*b*) $R^1=R^3=R^4=H$, $R^2=Ph$, $R^5=$ Ph or Alk; k;
(*c*) $R^1=R^2=R^3=R^4=Ph$, $R^5=$pH or Alk; ::
(*d*) $R^4=H$, $R^1=R^2=R^3=Ph$, $R^5=p$-Me–C_6H_4–;
(*e*) $R^1=R^2=Ph$, $R^3=R^4=H$, $R^5=Ph$

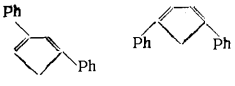
This method has been used to obtain the following cyclopenta-1,3-diene derivatives—1-phenyl[6], 1,4-diphenyl[7,8], 1,2,3,4,5-pentaphenyl[9], 1,2,3-triphenyl-4-*p*-tolyl, and 1,2,3-triphenyl[10].

The structure of the resulting cyclopentadienes cannot be predicted from that of the starting material, in the present case the cyclopentenone, since substituted cyclopentadienes that are isomeric with respect to the cyclic double bonds are in a state of thermodynamic equilibrium[3]. The potential barriers to interconversion of isomers are quite high, so that within certain temperature limits in effect only the thermodynamically more stable isomer can be isolated, but it is not so easy to predict which is the more stable form. Thus 5-benzyl- and 5-ethyl-1,2,3,4-tetraphenylcyclopenta-1,3-dienes are stable, but the methyl analogue has the structure 2-methyl-1,3,4,5-tetraphenylcyclopenta-1,3-diene[9]:



Therefore establishment of the structure of arylated cyclopentadienes requires careful examination of their proton magnetic resonance spectra.

Because of the complexity of determining the structure of the final product doubt attaches to the structure of several cyclopentadienes[7,8,11,12]. For example, it has not been established whether both isomers—1,3- and 1,4-diphenylcyclopenta-1,3-dienes

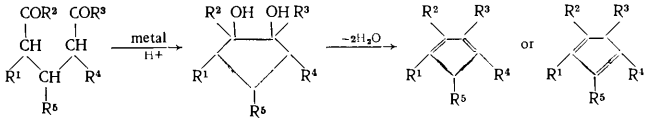


exist or only one of them. It appears more probable that only the 1,4-derivative can exist, since this structure is

supported by the ^{1}H n.m.r. spectra[8] and ozonolysis products of the diene[11], as well as by the identity of its properties with those described much earlier[7] for 1,3-diphenylcyclopenta-1,3-diene. The authors of this last work ascribe to this compound the structure of 1,3-diphenylcyclopenta-1,3-diene, although its properties conform to those of 1,4-diphenylcyclopenta-1,3-diene. However, this is contradicted by a recent report[12] that two diphenylcyclopentadienes have been obtained, giving different fulvenes on reaction with benzaldehyde.

2. Preparation of Arylated Cyclopentadienes from 1,5-Diketones

Arylated cyclopentadienes were first obtained from 1,5-diketones, in two stages. The first stage involves reductive cyclisation to cyclopentanediols (by prolonged boiling with zinc in acetic acid[13-19] or by means of aluminium amalgam in aqueous ethanol[17]). In the second stage these diols are dehydrated by boiling with alcoholic hydrochloric acid[13,14] or by fusing with oxalic acid[13,14]. The yields vary, but do not exceed 50%. Many arylcyclopentadienes have been obtained in this way[13-19]:

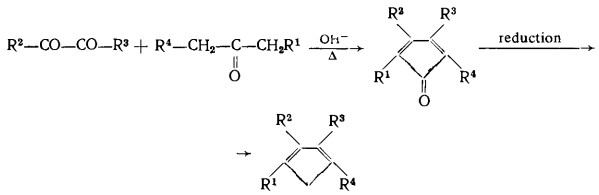


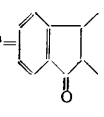
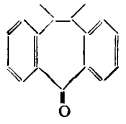
(*a*) $R^1=R^2=R^3=R^4=Ph$, $R^5=H$;
(*b*) R^1, R^2, R^3, $R^4=X-C_6H_4-$ (X=Cl, Me, OMe, NMe_2), $R^5=H$;
(*c*) $R^3=p$-MeO$-C_6H_4-$, $R^1=R^4=R^5=H$;
(*d*) $R^1=R^2=R^3=Ph$, $R^4=R^5=H$;
(*e*) $R^2=R^3=R^5=Ph$, $R^1=R^4=H$.

In acid media 1,2,3,4- and 1,2,3,5-tetraphenylcyclopentane-1,2-diols eliminate water to form the same 1,2,3,4-tetraphenylcyclopenta-1,3-diene[15], which apparently is thermodynamically the most stable isomer.

3. Preparation of Cyclopentadienes from Cyclopentadienones

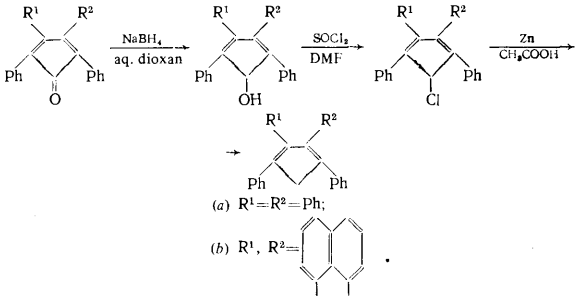
Cyclopentadienones (cyclones) are very reactive, with a strong tendency to dimerise by diene synthesis, so that mono- and di-arylcyclones can exist only as dimers[20]. Therefore cyclopentadienes can be obtained from tri- and tetra-arylcyclones, which are readily formed by the condensation of diaryl-α-diketones with αα′-diarylacetones[21-27]:



(*a*) $R^1=R^2=R^3=R^4=Ph$;
(*b*) $R^1=R^4=Ph$, $R^2=R^3=p$-Ph$-C_6H_4$;
(*c*) $R^1=R^4=n$-Ph$-C_6H_4$, $R^2=R^3=Ph$;
(*d*) $R^1=R^2=R^3=R^4=p$-Ph$-C_6H_4$;
(*e*) $R^1=R^4=Ph$, R^2, R^3=  ;
(*f*) $R^1=R^4=Ph$, R^2, R^3=  or  .

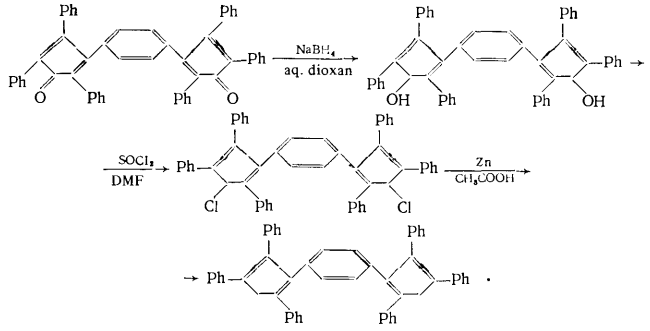
Selective reduction of the carbonyl group in tetraphenylcyclopentadienone (tetracyclone) was first attempted by Sonntag et al.[21], who obtained mixtures of various reduction products by the use of such reductants as zinc dust and lithium tetrahydroaluminate and by Clemmensen, Wolff–Kishner, or Meerwein–Pondorff reduction. Thus 5% and 12% yields of 1,2,3,4-tetraphenylcyclopenta-1,3-diene were obtained respectively on distillation with zinc dust at 270 °C and on reduction with lithium tetrahydroaluminate in dibutyl ether.

Recently, however, methods have been found for reducing tetra-arylcyclones to the corresponding cyclopentadienes. A fairly general scheme for obtaining tetra-arylcyclopentadienes is[22]



(*a*) $R^1=R^2=Ph$;
(*b*) R^1, R^2=.

Sodium tetrahydroborate in aqueous dioxan converts tetra-arylcyclones quantitatively into tetra-arylcyclopentadienols, in which the hydroxy-group is then replaced by a chlorine atom by means of Vilsmeier's reagent. The resulting tetra-arylchlorocyclopentadienes are dechlorinated with zinc in acetic acid to form tetra-arylcyclopentadienes (in 60% yield based on the cyclones). This method can be used[22] to obtain a bistetraphenylcyclopentadiene:

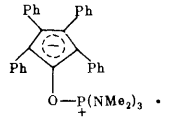


A better yield (93%) of tetraphenylcyclopentadiene was obtained[23] by the reduction of tetracyclone with a mixture of lithium tetrahydroaluminate and aluminium chloride, and a 55% yield by the two-stage reduction to 2,3,4,5-tetraphenylcyclopent-2-enol with sodium tetrahydroborate followed by elimination of water. However, other workers have been unable to repeat these experiments[24,25]. Tetraphenylcyclopentadiene is formed only on prolonged boiling in the presence of a large excess of reductant[24], and isolation of a chromatographically pure product is possible only in an inert atmosphere in the dark and at low temperatures[26]. It has proved possible to reproduce the earlier experiments[23] in only one case[26]. Extending to other cyclones the method of reduction with a mixture of lithium tetrahydroaluminate and aluminium chloride has given mixtures of products, from

which corresponding cyclopentadienes have been isolated in yields of 10–20%[24,25,27].

Tetracyclone can be reduced also with hydrazine dihydrate and dihydrochloride in diethylene glycol[26], under which conditions 1,2,3,4-tetraphenylcyclopenta-1,3-diene is formed in 80% yield.

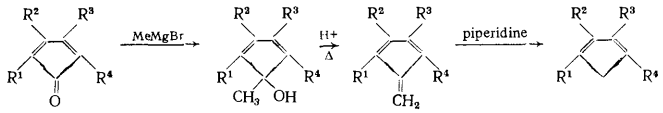
An interesting route from tetracyclone to tetraphenylcyclopentadiene was discovered[28] in an investigation of the action of tervalent phosphorus compounds on the former: with the hexamethyltriamide of phosphorous acid an unstable adduct is formed having the structure of an internal salt



This adduct is readily split by acids to form tetraphenylcyclopentadiene derivatives, but with hydrogen-donors it is reduced to 1,2,3,4-tetraphenylcyclopenta-1,3-diene in 87% yield. There have been no reports of the reactions of other cyclones with the triamide.

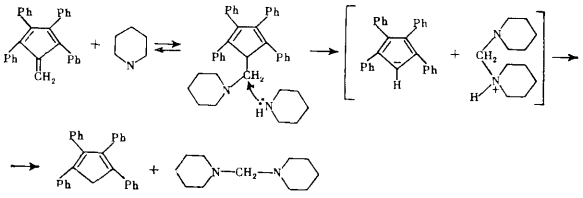
4. Fulvenes for the Preparation of Cyclopentadienes

Several tetra-arylcyclopentadienes can be obtained from tetra-arylfulvenes, which are formed by the action of methylmagnesium bromide on cyclones[29,30]:



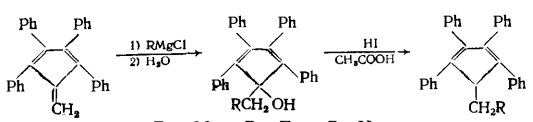
(*a*) $R^1=R^4=Ph$, $R^3=R^2=Ph$ or *p*-MeO—C_6H_4;
(*b*) $R^1=R^2=R^4=Ph$, $R^3=$ *p*-Me—C_6H_4—;
(*c*) $R^1=R^4=Ph$, $R^2=R^3=$ *p*-Me—C_6H_4— .

The mechanism



was suggested[29]. The ease of occurrence of this reaction (on boiling for a short time) is attributed to formation of the stable delocalised anion of tetraphenylcyclopentadiene. However, the reaction cannot be extended to other tetraarylcyclones ($R^2=p$-$X.C_6H_4$, where X = Cl, $(CH_3)_2N$, CH_3O), because the carbinols formed from cyclones and methylmagnesium bromide are unable to eliminate water[30].

Tetraphenylfulvene can be used to obtain alkyl- and arylalkyl-tetraphenylcyclopentadienes by the series of reactions[29,31,32]

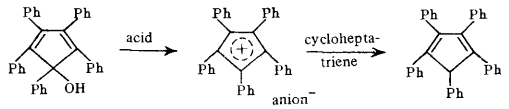


R = Me, t-Bu, Et, n-Pr, H

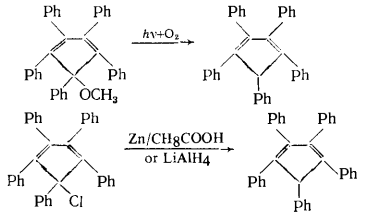
in which the yield is low. If $R=C_6H_5CH_2$ or t-C_4H_9, the carbinols are converted at high temperatures into the corresponding cyclopentadienes (without use of a reductant)[33].

5. Special Methods of Preparation of Arylated Cyclopentadienes

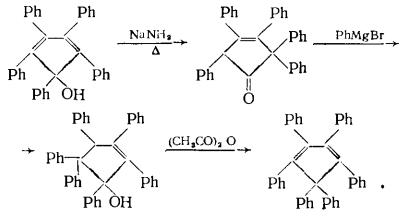
1,2,3,4,5-Pentaphenylcyclopentadiene can be obtained in two ways from 5-substituted derivatives. In the first method 1,2,3,4,5-pentaphenylcyclopenta-2,4-dienol is treated with a Lewis acid (boron trifluoride[34] or antimony pentachloride[35]) or with a strong acid, e.g. sulphuric acid[36,37], to form the pentaphenylcyclopentadienyl cation, stable only at low temperatures (−70 °C) which with a donor of a hydride ion gives 1,2,3,4,5-pentaphenylcyclopentadiene:



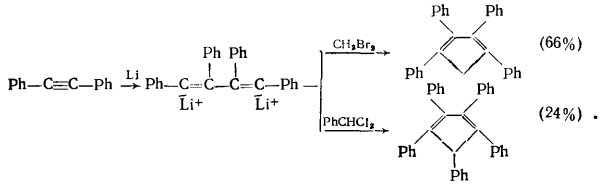
The second method may involve the photo-oxidation of 5-methoxylated[38,39] or the reduction with zinc dust or lithium tetrahydroaluminate of 5-chlorinated 1,2,3,4,5-pentaphenylcyclopenta-1,3-diene[14,38]:



Completely phenylated cyclopentadiene has been obtained by the isomerisation of 1,2,3,4,5-pentaphenylcyclopenta-2,4-dienol in the presence of sodamide into 2,2,3,4,5-pentaphenylcyclopent-3-enone, which reacts with phenylmagnesium bromide and then eliminates water to give a 30–40% yield of hexaphenylcyclopentadiene[40]:



The single-stage formation of 1,2,3,4-tetraphenylcyclopenta-1,3,diene from acetylenic compounds has still been little studied. In the presence of lithium, diphenylacetylene dimerises to form 1,4-dilithiotetraphenylbutadiene, which is alkylated by dibromomethane to give a 66% yield of tetraphenylcyclopentadiene[41]; when alkylation is effected with benzylidene dichloride, a 24% yield of 1,2,3,4,5-pentaphenylcyclopentadiene is obtained[42]:



Yields of 1,2,3,4-tetraphenylcyclopenta-1,3-diene obtained by the action of diphenylacetylene on trimethylchromium[43] or on cyclopentadienylmethylmolybdenum tricarbonyl[44] are below 5%.

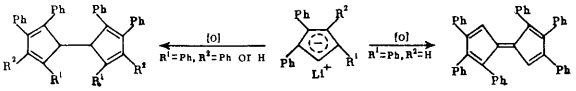
III. CHEMICAL REACTIONS OF ARYLATED CYCLOPENTADIENES

1. Acid-Base Reactions

Unsubstituted cyclopentadiene is a carbon–hydrogen acid, whose aqueous solution has $pK_a = 15.6$.[45] Such high acidity is attributed to stabilisation of the cyclopentadienyl anion by cyclic delocalisation of the six π electrons. The acidity is enhanced by the introduction of aryl substituents into the cyclopentadiene ring: thus for 8*H*-cyclopent[*a*]acenaphthylene in chloroform $pK_a = 14 \pm 0.5$.[46] For other arylated cyclopentadienes pK_a has not been determined, but their acidity is evident in reactions with bases and in many reactions involving condensation, in which they behave as containing an activated methylene group.

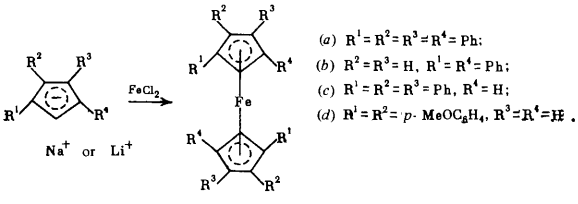
The sodium or lithium salt of 1,2,3,4-tetraphenylcyclopenta-1,3-diene is formed by the action of sodium in oxolan[47], sodamide[48,49], or sodium hydride in dimethyl sulphoxide (dimsylsodium)[47] or of phenyl-lithium or butyl-lithium[50,51]. Salts of 1,4-di- and 1,2,3,4,5-penta-phenylcyclopentadienes have been obtained by reaction of sodamide (or better dimsylsodium) with other substituted cyclopentadienes[49]. Phenyl-lithium has been used to obtain salts of 1,2,3-tri- and 1,2.3,4-tetra-phenylcyclopentadienes[49,2], and those of 1,2-di-*p*-methoxyphenylcyclopenta-1,3-diene by the action of methylmagnesium bromide[17].

Salts of arylated cyclopentadienes are readily oxidised by atmospheric oxygen and other oxidants, e.g. iodine, to form fulvalenes or, when this is prevented by steric hindrance, 1,1-dihydrofulvalenes[2]:



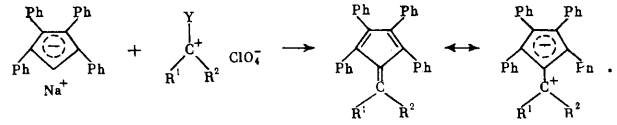
Salts of cyclopentadienes are therefore obtained in an inert atmosphere, and are immediately subjected to further reactions without isolation.

The reaction between salts of arylated cyclopentadienes and iron(II) chloride provides the only method for obtaining polyarylated ferrocenes[17,18,48,49]:

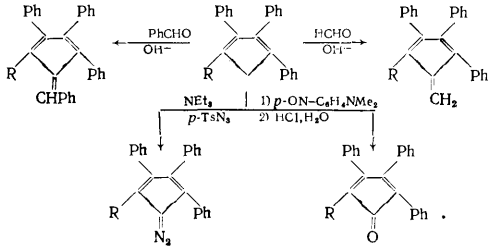


Almost all such compounds have been obtained in this way, with the exception of decaphenylferrocene, which was attributed[49] to steric hindrance.

The sodium and lithium salts of tetraphenylcyclopentadiene undergo nucleophilic substitution with 3,3-dichloro-1,2-diphenylcyclopropene[52], with methoxydiphenylcyclopropenylium[51], 4-chloro-2,6-dimethylthiopyrylium[53], and 2-methylthio-1,3-dithiolium[54] perchlorates, and with tropylium bromide[47] to form deeply coloured compounds of fulvene type, possessing large dipole moments:

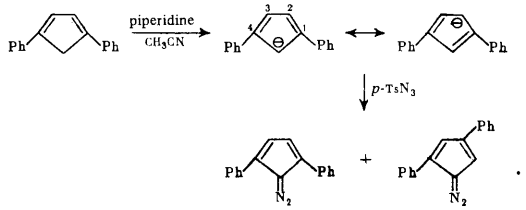


In the presence of bases arylated cyclopentadienes condense with aldehydes[12,55,56], *p*-nitrosodimethylaniline[16,56], and toluene-*p*-sulphonyl azide[3,24,50,56–59]:



The reactions with formaldehyde and benzaldehyde yield fulvenes, but that with *p*-nitrosodimethylaniline after hydrolysis gives cyclones. These reactions have been used repeatedly to characterise newly obtained cyclopentadienes[14,16,29].

The reaction with tosyl azide involves the formation of diazocyclopentadienes, which are starting materials for many cyclopentadiene derivatives, including ylides of arylated cyclopentadienes (Section IV). It is interesting that the reaction of 1,4-diphenylcyclopenta-1,3-diene with tosyl azide in the presence of piperidine gives a mixture of 1-diazo-2,4(and 2,5)-diphenylcyclopentadienes in yields of 30% and 58% respectively[59]. The explanation is that in an intermediate species—the anion of 1,4-diphenylcyclopenta-1,3-diene—the negative charge is delocalised to give an appreciable negative charge on the $C_{(2)}$ atom[59]:



An analogous phenomenon was observed by Freeman and Lloyd[60], who obtained 2,4-diphenyl-1-triphenylarsoniopentadienylide in the reaction between 1,4-diphenylcyclopenta-1,3-diene and triphenylarsine oxide in triethylamine. The course of this reaction is also explained by formation of a conjugated anion of 1,4-diphenylcyclopentadiene. Hence it can reasonably be expected that conjugated anions of mono-, di-, and tri-arylcyclopentadienes will contain more than one nucleophilic centre, owing to delocalisation of the negative charge in the ring.

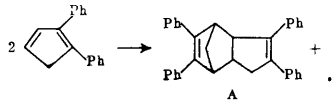
2. Arylated Cyclopentadienes in Diene Synthesis

Like other cyclopentadienes the arylated derivatives are able to undergo diene synthesis with various dienophiles, including cyclopentadienes, although the introduction of

aryl substituents results in steric hindrance to the interaction of two cyclopentadiene molecules.

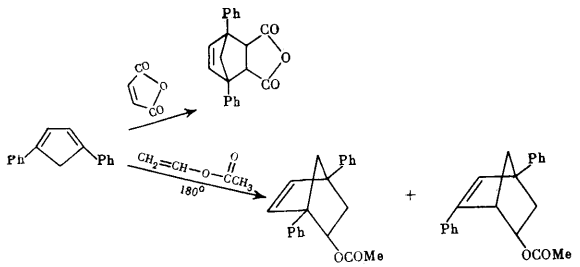
Crystalline phenylcyclopentadiene is monomeric, but its recrystallisation from ligroin leads to formation of a dimer (the structure of the latter has not been established, but dimerisation is supposed to occur by a mechanism of diene synthesis)[6].

On prolonged heating at 120 °C, 1,2-diphenylcyclopenta-1,3-diene dimerises to a mixture of products (with structure A predominating)[4,5,61]:



A

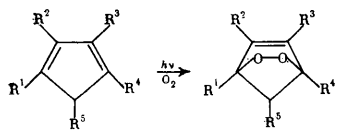
Dimerisation of the 1,4-diphenyl isomer has not been observed, although this compound readily undergoes diene synthesis with maleic anhydride[11,62] and with vinyl acetate[63]:



Dimerisation by a mechanism of diene synthesis does not take place in the presence of three or more aryl substituents. Perhaps interaction between the phenyl *ortho*-hydrogen atoms "twists" the phenyl groups out of the cyclopentadiene plane[18,64]. This impedes a frontal arrangement of two substituted cyclopentadiene molecules and formation of the transition state necessary for diene synthesis.

3. Photo-oxidation and Free Radicals of Pentaarylcyclopentadienes

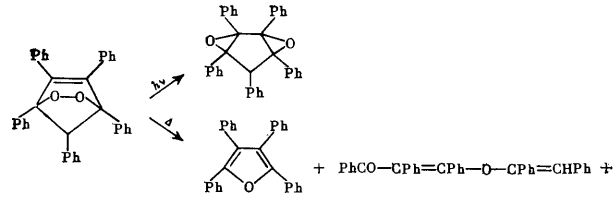
1,4-Diphenylcyclopenta-1,3-diene has been recommended[65,66] for use as a photosensitiser, and is also an oxygen-acceptor (with formation of compounds of the type MO_2). Photo-oxidation has been studied on 1,2,3,4-tetraphenylcyclopenta-1,3-diene and its alkyl derivatives[9,67], and on the 1,2,3,4,5-pentaphenyl[68] and 1,2-diphenyl[5,61] compounds. Oxygen was found to undergo 1,4 addition to the diene system to form *endo*-peroxides:



(*a*) $R^1 = R^2 = R^3 = R^4 = Ph$, $R^5 = H$, Ph, Alk;
(*b*) $R^1 = R^2 = Ph$, $R^3 = R^4 = R^5 = H$;
(*c*) $R^1 = R^2 = R^4 = R^5 = Ph$, $R^3 = Me$.

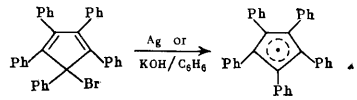
The structures of the latter have been confirmed by various chemical reactions. For example, reduction of the *endo*-peroxide of 1,2-diphenylcyclopentadiene with lithium tetrahydroaluminate gave 3,4-diphenylcyclopent-4-ene-*cis*-1,3-diol, but alkaline hydrolysis gave 4-hydroxy-3,4-diphenylcyclopent-2-enone[61].

When subjected to light or heat, *endo*-peroxides undergo further changes with fission not only of carbon–oxygen and oxygen–oxygen bonds but also of carbon–carbon bonds, so that the photo-oxidation of arylated cyclopentadienes usually gives a complicated mixture of products. For example, under the influence of light and of high temperatures the *endo*-peroxide of 1,2,3,4,5-pentaphenylcyclopentadiene undergoes the reactions[68]



The oxidation of cyclopentadienes in the dark or by means of other oxidants has not been investigated, with the exception of the oxidation of anions of tri- and tetra-phenylcyclopentadienes by iodine[2].

Many extremely stable, deeply coloured free radicals of 1,2,3,4,5-penta-arylcyclopentadienes are known. However, they have been obtained not by the direct oxidation of cyclopentadienes but by the action of silver or potassium hydroxide on penta-arylbromocyclopentadienes[14,69–76]:

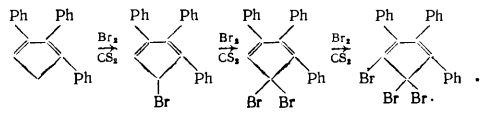


4. Halogenation of Cyclopentadienes

The action of halogens on arylated cyclopentadienes may involve either addition or substitution depending on the conditions and also on the halogenating agent used. Substitution occurs more readily.

Boiling 1,2,3-triphenylcyclopenta-1,3-diene with *N*-bromosuccinimide in tetrachloromethane for 1 h gives a mixture of the 1-bromo-2,3,4-triphenyl- and 5-bromo-1,2,3-triphenylcyclopentadienes[77]; boiling for 2 h yields 5,5-dibromo-1,2,3-triphenylcyclopenta-1,3-diene[2]. Under the same conditions 1,2,4-triphenylcyclopenta-1,3-diene forms the 5-bromo-1,2,4-triphenyl derivative[2,10].

With bromine in carbon disulphide all three hydrogen atoms in the 1,2,3-triphenylcyclopentadiene are successively replaced[2]:



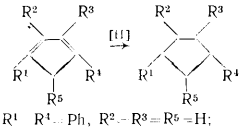
The action of bromine on the 1,2,4-triphenylcyclopentadiene involves a mechanism of addition and elimination with the formation of 2,5-dibromo-1,3,4-triphenylcyclopenta-1,3-diene[19].

With bromine both methylene hydrogen atoms in 1,2,3,4-tetraphenylcyclopenta-1,3-diene are substituted at once to give the 5,5-dibromo-derivative[13]. To obtain the monobromo-compound it is necessary to use *N*-bromosuccinimide or bromopyridinium nitrate[78]. Similarly, iodopyridinium

nitrate gives 5-iodo-1,2,3,4-tetraphenylcyclopenta-1,3-diene[78], and *S*-chloro-*S*-*p*-nitrophenyl-*N*-phenylsulphonylsulphidimine yields the corresponding 5-chloro-compound[79].

5. Hydrogenation of Arylated Cyclopentadienes

The hydrogenation of arylated cyclopentadienes to cyclopentane derivatives is used to establish and confirm the structure of cyclopentadienes obtained for the first time[11,13,19,80]:



(*a*) R^1 = R^4 = Ph, R^2 = R^3 = R^5 = H;
(*b*) R^1 = R^4 = *p*-Me—C_6H_4; R^2 = R^3 = R^5 = H;
(*c*) R^2 = R^3 = R^5 = Ph, R^1 = R^4 = H;
(*d*) R^1 = R^2 = R^3 = R^4 = Ph, R^5 = H.

Hydrogenation is effected with hydrogen in the presence of a catalyst—Raney nickel[80] or palladium black[11]—or with hydriodic acid in the presence of red phosphorus[13,19].

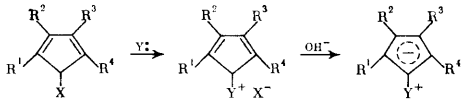
IV. PREPARATION OF ARYLATED CYCLOPENTADIENYLIDES

Much information has been published on the preparation and properties of tri- and tetra-arylcyclopentadienylides, but only in 1974 were the first diarylcyclopentadienylides—1-triphenylphosphonio- and 1-triphenylarsonio-2,4- and -2,5-diphenylcyclopentadienylides—described[60], since when 1-*N*-pyridinio-2,3- and -3,4-diphenylcyclopentadienylides have been obtained[22]. Ylides of monoarylcyclopentadienes are at present unknown.

Two main methods—the salt method and the decomposition of diazocyclopentadienes—have been used to obtain arylated cyclopentadienylides. In addition, triphenylarsoniocyclopentadienylides have been obtained by condensing substituted cyclopentadienes with triphenylarine oxide in the presence of bases[60,77] or phosphorus pentoxide[81].

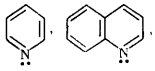
1. Salt Method

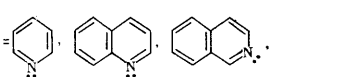
In the salt method onium salts of arylated cyclopentadienes are treated with bases to abstract the proton. Its limits of applicability depend on the accessibility of the onium salts[82]. These can be obtained in three ways, firstly from halogen derivatives of the substituted cyclopentadiene[60,77,83–85]:

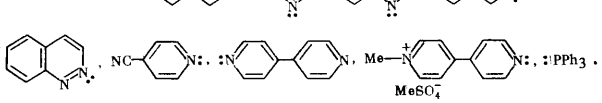


X = Cl or Br;

(a) R^1 = R^2 = R^3 = Ph, R^4 = H, Y: =  , :PPh_3, :$AsPh_3$, :SMe_2, :S=C(NR$_2$)(NR$_2$);

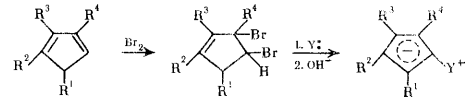
(b) R^1 = R^2 = R^3 = R^4 = Ph, Y: =  , :PPh_3, :S=C(NR$_2$)(NR$_2$);

(c) R^1 = R^4 = Ph, R^2, R^3 =  , Y: = 

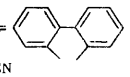
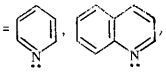


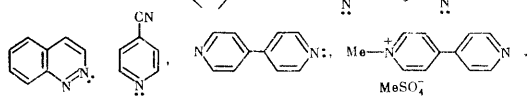
MeSO$_4^-$

In the second process an onium salt of an arylated cyclopentadiene is obtained by the action of a base on a dibromocyclopentene[24,87]:



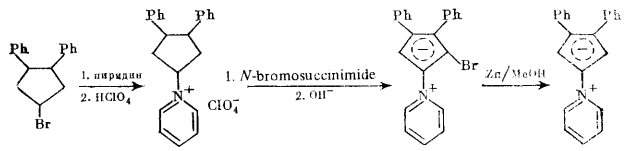
(*a*) R^1 = R^4 = H, R^2 = R^3 = Ph, Y: =  ;

(*b*) R^1 = R^4 = Ph, R^2, R^3 =  , Y: = 



MeSO$_4^-$

The starting compound in the third method is a halogenated cyclopentane, but in this case it is necessary also to dehydrogenate the onium salt[24]:

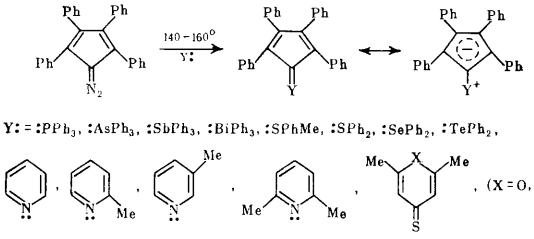


In all cases aqueous–ethanolic sodium hydroxide was used as the base.

Two limitations have been found in obtaining onium salts of arylated cyclopentadienes, the first involving steric hindrance to nucleophilic substitution of the bromine atom. If the cyclopentadiene ring contains 2- and 5-phenyl substituents, the yield of onium salts in the reaction of the corresponding bromocyclopentadiene with 2-methyl- or 2,6-dimethyl-pyridine is 6%, but with quinoline reaction does not occur[84]. From the corresponding chlorocyclopentadiene and quinoline the onium bond is formed in low yield[85], but when the decomposition of diazocyclopentadienes is used, a method in which steric hindrance is absent from the reactant species (a carbene), onium salts are obtained in good yields[86]. The second limitation is due to dehalogenation in the reaction of halogenated cyclopentadienes with triphenylphosphine in acid solvents. This reaction involves the formation not of onium salts but of the original substituted cyclopentadienes[77,85], which is attributed to attack by triphenylphosphine on the bromine atom.

2. Decomposition of Diazocyclopentadienes

The thermal decomposition of arylated diazocyclopentadienes in the presence of nucleophilic species has been used to obtain a number of tetraphenylcyclopentadienylides[59,86,88,90–99], since diazotetraphenylcyclopentadiene itself is readily obtainable[88]:



With copper bronze powder as catalyst the temperature can be lowered and the reaction conducted in such solvents as benzene, cyclohexane, and ethanol, when the yield of ylides is increased[60].

1-Triphenylphosphonio- and 1-triphenylarsonio-2,3,4-triphenylcyclopentadienylides have been obtained by the catalytic decomposition of 1-diazo-2,3,4-triphenylcyclopentadiene[60], although it had been reported earlier[77] that the decomposition of diazocyclopentadienes could not be used to obtain onium betaines of cyclopentadienes unsubstituted at position 2 or 5.

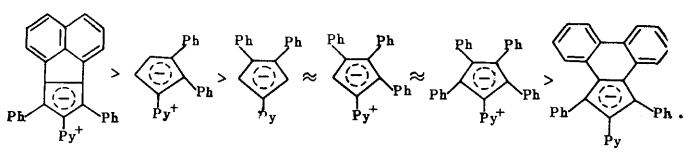
The decomposition of 1-diazo-2,5-diphenylcyclopentadiene in the presence of triphenylphosphine and triphenylarsine yields respectively 1-triphenylphosphonio- and 1-triphenylarsonio-2,4-diphenylcyclopentadienylides. The explanation proffered[60] is that positions 3 and 4 in the intermediate 1-carbene of 2,5-diphenylcyclopentadiene are sterically more favourable than position 1 to nucleophilic attack by triphenylphosphine or triphenylarsine.

Theoretically ylides can be formed from diazo-compounds in two ways. The nucleophile (triphenylphosphine, triphenylarsine, etc.) may add initially to the diazo-compound, and the resulting adduct breaks down to the ylide with the evolution of nitrogen. Alternatively the ylide may be formed via the carbene, which is partly supported by thermogravimetric investigation of these reactions[100].

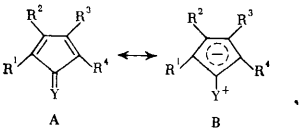
V. PROPERTIES OF ARYLATED CYCLOPENTADIENYLIDES

1. Physical Properties and Structure

Arylated cyclopentadienylides are crystalline, sparingly soluble in water, ethanol, ether, and hexane, and soluble in benzene and chloroform. Phosphonium, arsonium, sulphonium, and selenonium ylides are stable, and decompose only when illuminated. Pyridinium, other *N*-heteronium, and stibonium ylides are stable in the solid state, but decompose in solution. Telluronium and bismuthonium ylides decompose slowly in the solid state, but rapidly in solution[86, 101]. The stability of ylides depends not only on the onium moiety but also on the aryl substituents in the cyclopentadiene ring. For example, known pyridium ylides of arylated cyclopentadienes can be arranged in the stability sequence



The stability of ylides is usually explained[86] by the nature of the bond between the heteroatom and the five-membered ring, which in turn depends on the charge distribution in the molecule (on the "contribution" by the dipolar structure B):



Increase in the volume of the heteroatom enhances the diffuse character of the *d*-orbital, while the efficiency of interaction between the 2*p*-electrons of the carbanion and the vacant *d*-orbitals of the heteroatom diminishes (the contribution by structure A decreases). The stability diminishes also as electrostatic interaction between carbanion and onium heteroatom becomes weaker (with decrease in the electronegativity of the heteroatom, with lengthening of the carbon–heteroatom bond).[86] Arylated cyclopentadienylides are less stable if aryl or onium substituents are "twisted" out of the cyclopentadiene plane owing to the steric hindrance in the molecule.

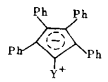
Table 1. Long-wavelength absorption by tetraphenylcyclopentadienylides[85,86].

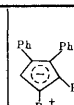
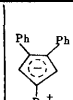
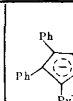
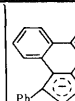
Y	PPh_3	$AsPh_3$	$SbPh_3$	$BiPh_3$	SPh_2
λ_{max}, nm (solvent)	288* (EtOH)	291* (EtOH)	349 ($CHCl_3$)	525 (EtOH); 596 (benzene)	292*; 328*(sh** (EtOH)

Y	$SePh_2$	$TePh_2$		
λ_{max}, nm (solvent	294*; 347* (sh**) (EtOH)	335 (MeOH) 347 (benzene)	538 (EtOH) 595 (benzene)	587 (EtOH) 645 (benzene)

*Absorption maximum independent of solvent (solvatochromism not observed).
**sh = shoulder.

Table 2. Long-wavelength absorption by pyridinium ylides of arylated cyclopentadienes[22].

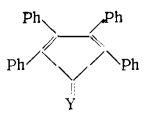


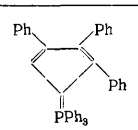
λ_{max} in						
Benzene	572	582	589	590	630	650
Ethanol	530	530	547	535	572	590

The structure of an ylide can best be characterised by X-ray examination, but only a few ylides of unsubstituted cyclopentadiene have been studied in this way[102–104].

All ylides are yellow with the exception of *N*-heteronium and bismuthonium ylides, which in the crystalline form are intensely coloured ($\lambda_{max} \cong 500-800$ nm) [85,87,101] (Table 1). With several ylides (Y = $(C_6H_5)_3P$, $(C_6H_5)_3As$, $(C_6H_5)_3Sb$, $(C_6H_5)_2S$, $(C_6H_5)_2Se$) the longer-wavelength absorption maximum is independent of the solvent, but negative solvatochromism is observed with bismuthonium and telluronium ylides of tetraphenylcyclopentadiene[86] and with all *N*-heteronium ylides of arylated cyclopentadienes[22,77,85,87] (Table 2). Slight solvatochromism has been found in 1-triphenylphosphonio-2,3,5-tri- and -2,4-di-phenylcyclopentadienylides[60]. It is assumed that betaines in which solvatochromism is observed have structure B in the ground state, or that the contribution by this structure is large, and that the longer-wavelength absorption is due to intramolecular charge transfer.

Table 3. Dipole moments of arylated cyclopentadienylides[105].



Y	μ, D	Y	μ, D
SPh_2	6.69		6.99
SPhMe	6.90		
PPh_3	7.75		
$AsPh_3$	8.32		
$SbPh_3$	2.2		

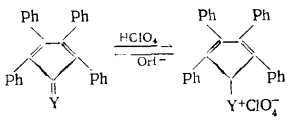
Dipole moments in benzene solution at 25 °C have been determined for several tetra- and 2,3,4-tri-phenylcyclopentadienylides (Table 3)[105]. The results indicate that the contribution by the ionic structure (B) increases in the series of betaines with sulphonio < phosphonio < arsonio. The low dipole moment of triphenylstiboniotetraphenylcyclopentadienylide is explained by association of the betaine with the solvent or with itself[105]. The dipole moment is larger in tetra- than in tri-phenylcyclopentadienylides and ylides of unsubstituted cyclopentadiene[106]; hence substitution by phenyl groups increases the contribution by the ionic structure in the ground state of the molecules.

Ionisation potentials have been determined for several ylides of 7,9-diphenyl-8*H*-cyclopent[*a*]acenaphthylene by spectrophotometric examination of intermolecular charge-transfer complexes[85]. These ylides are found to constitute a novel class of strong electron-donors with ionisation potentials of 6.7–6.75 eV.

2. Reactions of Arylated Cyclopentadienylides

(*a*) Acid-base reactions

Arylated cyclopentadienylides are bases, forming with acids such as perchloric, hydrobromic, etc. salts that are readily hydrolysed to the original ylides:



Y=PPh_3, $AsPh_3$, $SbPh_3$, Py .

This procedure is the only method for purifying ylides that are unstable in solution[86]. However, several cyclopentadienylides of diphenylsulphonium[107], diphenyselenonium, and diphenyltelluronium are too weak bases to be protonated by mineral acids.

Table 4. Acidity constants pK_a of protonated forms of arylated cyclopentadienylides[101,107].

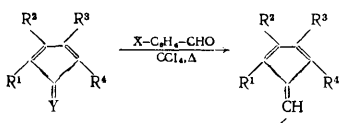
Tetraphenylcyclopentadienylides			2,3,4-Triphenylcyclopentadienylides	
Y=PPh_3	Y=$AsPh_3$	Y=$SbPh_3$	Y=PPh_3	Y=$AsPh_3$
5.3	7.6	7.6	4.2	5.6

Acidity constants of the protonated forms in 95% ethanol have been determined for several tetra- and 2,3,4-triphenylcyclopentadienylides[101,107]. Table 4 shows that the basicity of the ylides is closely related to the polarity of the molecule. The basicity diminishes in the sequence stibonio > arsonio > phosphonio with decrease in the degree of interaction of the 2*p*-electrons of the anion with the vacant orbitals of the heteroatom. Values of pK_a are smaller for tri- than for tetra-phenylcyclopentadienylides, which indicates greater thermodynamic stability of the former[101].

The site of protonation depends on the structure of the ylide. Investigation of the proton magnetic resonance spectra of cyclopentadienylides in trifluoroacetic acid has established[60,101] that the unsubstituted carbon atom is protonated, for example positions 5 and 3 respectively in 2,3,4-tri- and 2,5-di-phenylcyclopentadienylides. On the other hand, 2,3,5-triphenylcyclopentadienylides are not protonated in the vacant position 4, as the n.m.r. spectra do not contain the signal of a methylene group.

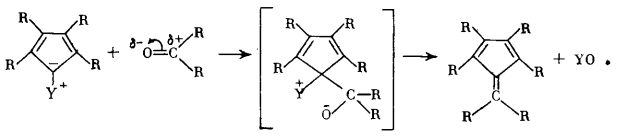
(*b*) Reaction with a polar double bond

Reactions with aldehydes and with *p*-nitrosobenzene have been studied for tri- and tetra-phenylcyclopentadienylides[60,83,86,101]. Only triphenylarsonium, triphenylstibonium, and thiouronium ylides react with benzaldehyde or *p*-nitrobenzaldehyde, forming fulvenes:

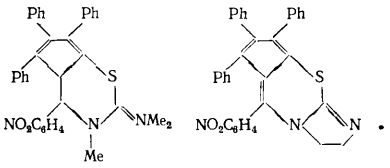


Y=$AsPh_3$, $SbPh_3$, S—CN $(HMe)_2$;
$R^1=R^2=R^3=$Ph, $R^4=$ Ph or H .

Formation of the latter is explained[86] by nucleophilic addition of the ylide to the carbonyl group with further change in the resulting adduct:

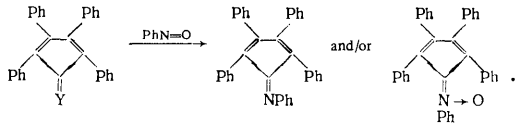


The reaction between 1-thiouronio-2,3,4-triphenylcyclopentadienylide and *p*-nitrobenzaldehyde yields mainly strongly coloured products having the structure[83]



This is attributed[83] to attack by the aldehyde at the unsubstituted position 5 (not position 1) in the cyclopentadiene ring followed by attack on one of the nitrogen atoms. Ylides having Y = $(C_6H_5)_3P$, $(C_6H_5)_2S$, $(C_6H_5)_2Se$, $(C_6H_5)_2Te$ do not react with aldehydes.

Ylides of tetra-arylcyclopentadienes react with nitrosobenzene to form the tetra-arylcyclopentadienone anil, [its *N*-oxide], or a mixture of the two[83,86,101]:



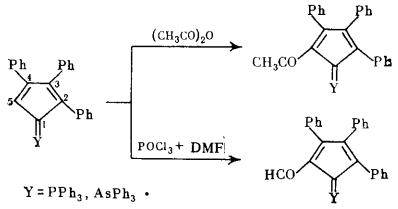
Diphenysulphonio- and -selenonio-tetraphenylcyclopentadienylides, when boiled with nitrosobenzene in tetrachloromethane for 18 h, form the anil *N*-oxides of tetraphenylcyclopentadienone in 5% and 80% yields respectively. Under the same conditions triphenylarsoniotetraphenylcyclopentadienylide forms a mixture of the anil and the anil *N*-oxide (respective yields 35% and 48%), but the corresponding stibonio-ylide forms only the anil *N*-oxide (yield 80%) even with a shorter period of boiling[86].

2,3,4-Triphenylcyclopentadienylides are more reactive than their tetraphenyl analogues towards polar double bonds, although the former are less basic: i.e. the nucleophilicity of the ylides (Sb > As > Se > S > P) does not parallel their basicity (Sb > As > P ≫ S ≅ Se) owing to the great sensitivity of nucleophilic reactions to steric factors[107].

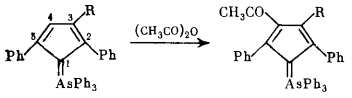
(*c*) Electrophilic substitution

Electrophilic substitution in ylides of unsubstituted cyclopentadiene have been well studied[106,108–110], and arylated cyclopentadienylides are found to follow the same pattern. Substitution occurs more readily at position 2(5), but if this site is occupied, it occurs at position 3(4),[60] which is explained by the more favourable transition state with substitution in position 2(5).[108]

1-Triphenyl-phosphonio- and -arsonio-2,3,4-triphenylcyclopentadienylides are acylated by acetic anhydride[81] and undergo Vilsmeier formylation[101] to the corresponding 5-substituted ylides:



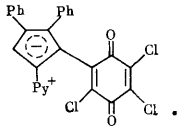
2,5-Di- and 2,3,5-tri-phenylcyclopentadienylides are acylated at position 4:[60]



1-Triphenylphosphonio-2,4-diphenylcyclopentadienylide forms a mixture of 3- and 5-acylated products in which the latter isomer predominates, but Vilsmeier formylation gives the disubstituted 3,5-diformyl-2,4-diphenyl-1-triphenylphosphoniocyclopentadienylide[60].

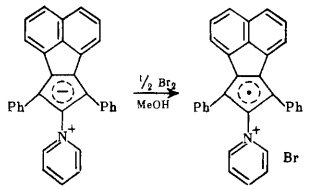
Azo-coupling has been investigated in 1-phosphonio- and 1-arsonio-2,4-di-, -2,5-di-, and -2,3,4-tri-phenylcyclopentadienylides. The products are quite stable red 2(5)-azo-compounds[60].

1-*N*-Pyridinio-3,4-diphenylcyclopentadienylide reacts with *p*-chloranil to form as electrophilic substitution product a stable betaine having two absorption bands in the visible (at 480–520 and 800 nm). The former absorption maximum exhibits negative solvatochromism, but the latter is independent of the solvent. Thus the interesting phenomenon is observed of simultaneous intramolecular charge transfer from the 3,4-diphenylcyclopentadiene anion to the onium substituent (~500 nm) and to the 2-substituent (~800 nm):[22]



(*d*) Oxidation

N-Heteronium, stibonium, telluronium, and bismuthonium ylides of arylated cyclopentadienes are relatively unstable[24,86,101]. Their instability is connected with their ready oxidisability by atmospheric oxygen, since they are more stable in an inert atmosphere. However, the decomposition (atmospheric oxidation) products of ylides have not yet been studied. It has been shown merely[22] that oxidation by bromine of 8-*N*-pyridinio-7,9-diphenyl-8*H*-cyclopent[*a*]-acenaphthylenylide gives a salt of a radical-cation:



In the crystalline state the yellowish-green product is extremely stable, but it decomposes readily in solution.

REFERENCES

1. G.Rio and J.Mion-Coatleven, Bull.Soc.chim.France 3774 (1966).
2. P.Pauson and B.Williams, J.Chem.Soc., 4153 (1961).
3. A.N.Elizarova, "Khimiya Tsiklopentenonov" (The Chemistry of Cyclopentenones), Nauka, Moscow, 1966, p.150.
4. P.Bladon, S.McVey, and P.Pauson, J.Chem.Soc.C, 306 (1966).
5. G.Rio and M.Charifi, Bull.Soc.chim.France, 3585 (1970).
6. R.Riemschneider and R.Nerin, Monatsh., **91**, 829 (1960).
7. W.Borsche and W.Menz, Ber., **41**, 190 (1908).
8. D.Farnum, A.Mostashari, and A.Hagedorn, J.Org. Chem., **36**, 699 (1971).
9. G.Rio and G.Sanz, Bull.Soc.chim.France, 3775 (1966).
10. B.Freeman, J.Gagan, and D.Lloyd, Tetrahedron, **29**, 4307 (1973).
11. N.Drake and J.Adams, J.Amer.Chem.Soc., **61**, 1326 (1939).
12. G.A.Chukhadzhyan, Zh.I.Abramyan, G.M.Tonyan, and V.A.Matosyan, Zhur.Org.Khim., **10**, 1994 (1974).
13. J.Wislicenus and H.Carpenter, Annalen, **302**, 223 (1898).
14. K.Ziegler and B.Schnell, Annalen, **445**, 266 (1925).
15. E.Auerbach, Ber., **36**, 993 (1903).
16. L.Mehr, E.Becker, and P.Spoerri, J.Amer.Chem. Soc., **77**, 984 (1955).
17. M.Rosenblum, W.Howells, A.Banerjee, and C.Bennett, J.Amer.Chem.Soc., **84**, 2726 (1962).
18. P.Pauson, J.Amer.Chem.Soc., **76**, 2187 (1954).
19. F.Newman, Annalen, **302**, 237 (1898).
20. M.Ogliaruso, M.Romanelli, and E.Becker, Chem.Rev., **65**, 261 (1965).
21. N.Sonntag, S.Linder, E.Becker, and P.Spoerri, J.Amer.Chem.Soc., **75**, 2283 (1953).
22. Ya.N.Kreitsberga, Candidate's Thesis, Riga Polytechnic Institute, 1977.
23. M.Cava and K.Narashimhan, J.Org.Chem., **34**, 3641 (1969).
24. H.Czwikla, Dissertation Technische Universität, Hannover, 1971.
25. W.Ried, W.Merkel, and H.Herrmann, Annalen, **750**, 91 (1971).
26. H.Bandara, N.Rajasckera, and S.Sotheeswaren, Tetrahedron, **30**, 2587 (1974).
27. W.Ried and H.Herrmann, Tetrahedron, **769**, 201 (1974).
28. M.Gallagher and I.Jenkins, J.Chem.Soc.C, 2605 (1969).
29. D.Taber, E.Becker, and P.Spoerri, J.Amer.Chem. Soc., **76**, 776 (1954).
30. K.Kun and P.Spoerri, J.Amer.Chem.Soc., **77**, 4676 (1955).
31. A.Bonagura, M.Meyers, S.Storfer, and E.Becker, J.Amer.Chem.Soc., **76**, 6122 (1954).
32. S.Linder, E.Becker, and P.Spoerri, J.Amer.Chem. Soc., **75**, 5972 (1953).
33. R.Fuson and O.York, J.Org.Chem., **18**, 570 (1953).
34. R.Bresloy, H.WonChang, R.Hill, and E.Wasserman, J.Amer.Chem.Soc., **89**, 1112 (1967).
35. H.Volz, Tetrahedron Letters, 1899 (1964).
36. R.Breslow and H.WonChang, J.Amer.Chem.Soc., **83**, 3727 (1961).
37. R.Breslow and H.WonChang, J.Amer.Chem.Soc., **85**, 2033 (1963).
38. G.Rio and A.Ranjon, Compt.rend., **254C**, 2997 (1962).
39. C.Dufraisse, G.Rio, and A.Liberles, Compt.rend., **256**, 1873 (1963).
40. A.Youssef and M.Ogliaruso, J.Org.Chem., **37**, 2601 (1972).
41. F.Leavitt, T.Manuel, and F.Johnson, J.Amer.Chem. Soc., **82**, 5099 (1960).
42. E.Braye, W.Hubel, and Y.Caplier, J.Amer.Chem.Soc., **83**, 4406 (1961).
43. M.Tsutsui, J.Amer.Chem.Soc., **81**, 6090 (1959).
44. A.Nakamura and N.Hagihara, Nyppon Kagaku Zasshi, **84**, 344 (1963).
45. A.Streitwieser and L.Lebenzahl, J.Amer.Chem.Soc., **98**, 2188 (1976).
46. K.Yamamoto, M.Morioka, and I.Murata, Tetrahedron Letters, 3009 (1975).
47. H.Prinzbach, D.Seip, L.Knothe, and W.Faist, Annalen, **698**, 34 (1966).
48. V.Weinmayr, J.Amer.Chem.Soc., **77**, 3012 (1955).
49. S.McVey and P.Pauson, J.Chem.Soc., 4312 (1965).
50. F.Klages and K.Bott, Chem.Ber., **97**, 735 (1964).
51. T.Eicher and A.Loscher, Z.Naturforsch., **21b**, 295 (1966).
52. E.Bergmann and J.Arganat, Chem.Comm., 512 (1965).
53. B.Eistert and J.Arackal, Chem.Ber., **108**, 2397 (1975).
54. A.Lüttringhaus, H.Berger, and H.Prinzbach, Tetrahedron Letters, 2121 (1965).
55. W.Dilthey and P.Huchtemann, J.prakt.Chem., **154**, 238 (1940).
56. P.Pauson and B.Williams, J.Chem.Soc., 4162 (1961).
57. F.Klage, K.Bott, P.Hegenberg, and H.Jung, Chem. Ber., **98**, 3765 (1965).
58. D.Lloyd and F.Wasson, J.Chem.Soc.C, 408 (1966).
59. M.Regitz and A.Liedhegener, Tetrahedron, **23**, 2701 (1967).
60. B.Freeman and D.Lloyd, Tetrahedron, **30**, 2257 (1974).
61. G.Rio and M.Charifi, Compt.rend., **268**, 1960 (1961).
62. K.Leppanen, Ann.Acad.Sci.Fennicae, Ser.A, **11**, 50 (1965).
63. K.Leppanen, Suomen Kem., **B44**, 384 (1971).
64. G.Evrard, P.Piret, G.Germain, and M.Van Meerssche, Acta Cryst., **27B**, 661 (1971).
65. G.Schenck and W.Müller, Naturwiss., **41**, 474 (1954).
66. G.Schenck, Naturwiss., **41**, 452 (1954).
67. C.Dufraisse, G.Rio, and J.Basselier, Compt.rend., **246C**, 1640 (1958).
68. J.Basselier and J.LeRouse, Compt.rend., **286**, 970 (1960).
69. D.Reitz, J.Chem.Phys., **34**, 701 (1961).
70. H.Kurreck and W.Broser, Chem.Ber., **98**, 11 (1965).
71. K.Möbius, Z.Naturforsch., **20a**, 1117 (1965).
72. W.Broser, H.Korreck, and P.Siegle, Chem.Ber., **99**, 2246 (1966).
73. C.Tuzun, Comm.Fac.Sci.Univ.Ankara, Ser.B, **13**, 53 (1966).
74. W.Broser, P.Siegle, and H.Kurreck, Chem.Ber., **101**, 69 (1968).
75. W.Broser, J.Reusch, H.Kurreck, and P.Siegle, Chem. Ber., **102**. 1715 (1969).
76. D.Janzen and H.Kurreck, Tetrahedron Letters, 5231 (1972).
77. D.Lloyd and M.Signer, J.Chem.Soc.C, 2941 (1971).
78. H.Kainer, Annalen, **578**, 232 (1952).

79. S.S.Trach and N.S.Zefirov, Zhur.Org.Khim., **10**, 219 (1974).
80. A.V.Strashnenko and S.V.Zavgorodnyi, Zhur.Org. Khim., **3**, 91 (1967).
81. G.Harris, D.Lloyd, N.Preston, and M.Singer, Chem. and Ind., 1483 (1968).
82. A.W.Johnson, "Ylid Chemistry" (Translated into Russian), Mir, Moscow, 1969, p.58.
83. D.Lloyd, R.Millar, H.Lumbroso, and C.Liegeois, Tetrahedron, **33**, 1379 (1977).
84. D.Lloyd and J.Sneezum, Tetrahedron, 334 (1958).
85. Ya.N.Kreitsberga, V.E.Kampar, and O.Ya.Neiland, Zhur.Org.Khim., **11**, 1508 (1975).
86. B.Freeman, D.Lloyd, and M.Singer, Tetrahedron, **28**, 343 (1972).
87. Ya.N.Kreitsberga, O.Ya.Neiland, and V.E.Kampar, Zhur.Org.Khim., **11**, 1941 (1975).
88. D.Lloyd and M.Singer, J.Chem.Soc.C, 2939 (1971).
89. D.Lloyd, M.Singer, M.Regitz, and A.Liedhegener, Chem. and Ind., 324 (1967).
90. D.Lloyd and M.Singer. Chem. and Ind., 510 (1967).
91. D.Lloyd and M.Singer, Chem. and Ind., 787 (1967).
92. D.Lloyd and M.Singer, Chem.Comm., 1042 (1967).
93. D.Lloyd and M.Singer, Chem. and Ind., 118 (1967).
94. D.Lloyd and M.Singer, Chem.Comm., 390 (1967).
95. B.Freeman and D.Lloyd, Chem.Comm., 924 (1970).
96. I.Band, D.Lloyd, M.Singer, and F.Wasson, Chem. Comm., 544 (1966).
97. D.Lloyd and F.Wasson, Chem. and Ind., 1559 (1963).
98. D.Lloyd and F.Wasson, J.Chem.Soc.C, 1086 (1966).
99. G.Seitz, Angew.Chem., **81**, 518 (1969).
100. B.Freeman, G.Harris, and B.Kennedy, Chem.Comm., 913 (1972).
101. D.Lloyd and M.Singer, Tetrahedron, **28**, 353 (1972).
102. H.Anmon, G.Wheeler, and P.Watts, J.Amer.Chem. Soc., **95**, 6158 (1973).
103. Z.Yoshida, S.Yoneda, T.Yato, and M.Hazawa, Tetrahedron Letters, 873 (1973).
104. V.G.Andrianov and Yu.T.Struchkov, Izv.Akad. Nauk SSSR, Ser.Khim., 687 (1977).
105. H.Lumbroso, D.Lloyd, and G.Harris, Compt.rend., **278C**, 219 (1974).
106. Z.Yoshida, S.Yoneda, and I.Murata, J.Org.Chem., **38**, 3537 (1973).
107. D.Lloyd and M.Singer. Chem. and Ind., 1277 (1968).
108. D.Lloyd and M.Singer, Chem. and Ind., 786 (1971).
109. Z.Yoshida, S.Yoneda, I.Murata, and H.Hashimoto, Tetrahedron Letters, 1523 (1971).
110. Z.Yoshida, S.Yoneda, and M.Hazama, J.Org.Chem., **37**, 1364 (1972).

Riga Polytechnic Institute

Translated from *Uspekhi Khimii*, **49**, 1774-1800 (1980) U.D.C. 547.372

Prop-2-ynyl Ethers

S.F.Karaev and Sh.V.Garaeva

Information on preparation, properties, and practical application is summarised with 306 references.

CONTENTS

I.	Introduction	865
II.	Methods of preparation	865
III.	Physicochemical and spectroscopic properties	868
IV.	Reactivity	869
V.	Practical application	873

I. INTRODUCTION

A prop-2-ynyl (propargyl) ether (the methyl compound) was first obtained by Liebermann in 1865 from glycerol tribromohydrin[1]; its constants were determined by Henry[2]. The next homologue—ethyl prop-2-ynyl ether—was prepared a year later by Bayer[3]. Later the isopentyl[4], phenyl[5], propyl[6], and butyl[7] ethers were obtained. C_{sp}-Halogenated prop-2-ynyl ethers were described as early as 1894.[8] α-Halogeno-ethers of prop-2-ynol were first prepared in 1959.[9] A year later appeared the first paper on propargyl ethers of silanols[10]; those of silylalkanols have not yet been described.

A considerable quantity of information on methods of preparation and chemical behaviour has now accumulated, and indicates that prop-2-ynyl ethers are interesting subjects for investigation. Their peculiar chemical properties are due to the tendency to undergo rearrangements. The prospects for their use in experimental organic chemistry are demonstrated by their employment as starting materials in obtaining the relatively inaccessible allenyl ethers[11], allene hydrocarbons[12], cyclopropane derivatives[13], pyrazoles[14], etc. Prop-2-ynyl ethers are present in several natural materials. According to the patent literature[15] they possess high antibiotic activity.

Propargyl ethers have recently attracted attention in connection with their wide range of useful properties (they have biological activity, help to retard corrosion, aid the flotation of rare metals, and increase the energy content of complicated rocket fuels).

Hitherto, however, hardly any general reviews have appeared on methods of preparation, physical and chemical properties, and applications of this class of heteroatomic acetylenes[16]. The present Review attempts to survey and systematise the information on prop-2-ynyl ethers that has accumulated in the literature.

II. METHODS OF PREPARATION

General methods of preparation of prop-2-ynyl ethers are based on the dehydrohalogenation of halogenoalkyl or halogenoalkenyl ethers[6,17,18] and other elimination reactions[19,20], the action of α-chloroalkyl ethers on metal acetylides[21-24], the alkylation of alkoxides of prop-2-ynols[25-28], the interaction of alkoxides or phenoxides with prop-2-ynyl halides or sulphonates[27,29,30], and the isomerisation of prop-1-ynyl[31] or allenyl[32] ethers.

Alkyl, aryl, and halogenoalkyl prop-2-ynyl ethers have been obtained[17] by the dehydrobromination of 2,3-dibromopropyl ethers in the presence of ethanolic potassium hydroxide:

$$CH_2BrCHBrCH_2OR \xrightarrow[EtOH]{KOH} HC{\equiv}CCH_2OR + KBr \ .$$

This method has no preparative value because of the very low yield (≤10%). The ethyl ether cannot be obtained in this way owing to the difficulty of isolating it from the solvent. The aryl ethers can be obtained by the dehydrohalogenation of 1-aroxy-2,2-dihalogenopropanes in the presence of sodamide in liquid ammonia[33]:

$$\underset{X=Cl,\,Br}{ArOCH_2CX_2CH_3} \xrightarrow{NaNH_2/NH_3} ArOCH_2C{\equiv}CH \ .$$

The propyl ether has been obtained[18] by the dehydrochlorination of 3-chloroallyl propyl ether:

$$PrOCH_2CH{=}CHCl \rightarrow PrOCH_2C{\equiv}CH \ .$$

A method of preparation is provided by the alkylation of prop-2-ynols with alkyl arenesulphonates in alkaline media[25]. A convenient methylating agent is dimethyl sulphate, which is highly reactive and quite cheap:

$$HC{\equiv}CCH_2OH + Me_2SO_4 \rightarrow HC{\equiv}CCH_2OMe \ .$$

The ethyl ether is obtained similarly[34].

A simple and convenient procedure is alkylation with prop-2-ynyl halides. Thus the butyl and phenyl ethers have been obtained[7] by the action of prop-2-ynyl bromide on sodium butoxide and phenoxide respectively in ether, when acetylenic–allenic isomerisation is not observed:

$$HC{\equiv}CCH_2Br + RONa \rightarrow HC{\equiv}CCH_2OR \ .$$

A similar method has been used to obtain the tolyl ether[35], by the action of 3-bromopropyne on *p*-cresol in acetone in the presence of potassium carbonate, as well as the allyl[34] and vinyloxyalkyl[36] ethers. It has been recommended[37] to use metallic sodium in liquid ammonia in the alkylation of certain alkynols with benzyl bromide.

The selective alkylation[26-28] of acetylenic alcohols with alkyl halides, first applied to α-acetylenic alcohols, was extended to substituted α- and β-acetylenic alcohols[38]:

$$HC{\equiv}CCOH \xrightarrow[NH_3]{+MNH_2} HC{\equiv}CCOM \xrightarrow{RX} HC{\equiv}CCOR + MX$$
$$R=Bu,\ Cl(CH_2)_n;\ X=Br;\ M=Na,\ K \ .$$

The reaction is complicated by parallel dehydrohalogenation of the alkyl halide with formation of an alkene. The yield

of the prop-2-ynyl ether is 25–80%. The course of the reaction is affected by the nature of the alkyl halide, the alcohol, and the alkali metal; when lithamide is used, the acetylenic hydrogen atom—not the hydrogen atom of the hydroxy-group—is alkylated. The ethyl and butyl ethers (contaminated with allenic isomers) have been obtained by this method in 30% yield[39], and also the methyl ether in 10% yield[40]. The method has been used to obtain the aryl[37], halogenoalkyl, and higher alkyl[41,42] ethers, as well as prop-2-ynyl ethers of secondary and tertiary prop-2-ynyl alcohols[43].

A method of selective alkylation of acetylenic alcohols in the presence of organomagnesium compounds in Hexametapol has recently been worked out[44]. On reaction between ethylmagnesium bromide, an equivalent quantity of 1-bromobutane, and prop-2-ynol at 80–90 °C the hydroxy-group is 80–90% alkylated. With a molar excess of the organomagnesium bromide at 110 °C partial (15–20%) *C*-alkylation occurs. Under these conditions tertiary propargyl alcohols break down with the formation of ketones. The difference in acidity and reactivity between the hydroxyl and acetylenic hydrogen atoms permits successive alkylation of both functional groups or their simultaneous metallation followed by selective alkylation.

Propargyl ethers are obtained also by alkylating prop-2-ynol with alkyl halides in the presence of potassium hydroxide in dimethyl sulphoxide or cyclohexanone[45]. Benzene can be used as solvent in preparing the benzyl and furfuryl ethers[46,47]. Long-chain ethers have been obtained by alkylating prop-2-ynol in the presence of potassium t-butoxide in n-butanol[48]:

$$HC{\equiv}CCH_2OH + C_{18}H_{37}Br \rightarrow HC{\equiv}CCH_2OC_{18}H_{37} .$$

A patent[49] has described the production of ethers from propargyl alcohols and alkyl chlorides in alcoholic solution at 80–150 °C.

The use of propargyl arenesulphonates under mild conditions enables the prop-2-ynyl group to be introduced into various organic compounds (to give 80–95% yields)[50]. The initial sulphonates are obtained by reaction between the sulphonyl chloride and prop-2-ynol in the presence of powdered potassium hydroxide in absolute ether[51]. Interaction between prop-2-ynyl benzenesulphonate and alkoxides yields the corresponding alkyl ethers[52]:

$$PhSO_2OCH_2C{\equiv}CH + RONa \rightarrow ROCH_2C{\equiv}CH .$$

The reaction can be conducted by adding the alkoxide to an alcoholic solution of the sulphonate or by Claisen's method—addition of potassium hydroxide to a solution of the sulphonate and the alcohol—to give 59–60% yields of the ether[51].

The isomerisation of prop-1-ynyl ethers in several cases leads to prop-2-ynyl ethers[31]. Thus in the alkylation of phenol with 3-bromopropyne in the presence of sodamide the resulting ether isomerises into phenyl prop-2-ynyl ether[53]:

$$PhOC{\equiv}CMe \rightarrow PhOCH_2C{\equiv}CH$$

When allenyl ethers are metallated with lithamide in liquid ammonia, they isomerise into prop-2-ynyl ethers[32]:

$$CH_2{=}C{=}CHOR \rightarrow HC{\equiv}CCH_2OR .$$

Diazoalkynes can be used[19] to obtain prop-2-ynyl ethers. *N*-Nitroso-*N*-propargylureas on methanolysis in alkaline medium are converted into a mixture of allenyl methyl and methyl prop-2-ynyl ethers roughly in the proportions 1 : 10:

$$HC{\equiv}CCH(R)N(NO)CONH_2 \xrightarrow{MeOH} HC{\equiv}CCH(R)OMe + RCH{=}C{=}CHOMe$$

R = H, Alk .

The decomposition of 1,1,1-trichloro-3-ethoxy-2-trimethylsiloxypropane in the presence of butyl-lithium yields ethyl prop-2-ynyl ether[20]:

$$EtOCH_2CH(OSiMe_3)CCl_3 + 3BuLi \xrightarrow{Et_2O/oxolan} EtOCH_2C{\equiv}CH .$$

The phenyl ether can be obtained similarly (in 25% yield). An attempt to obtain this ether from its "structural components" (ethanol, paraform, and acetylene) in the presence of copper(I) chloride under pressure was unsuccessful[39]:

$$EtOH + CH_2O + CH{\equiv}CH \xrightarrow[25-28\ atm]{Cu_2Cl_2} \begin{cases} \rightarrow EtOCH_2OEt \\ \rightarrow EtOCH_2C{\equiv}CH . \end{cases}$$

At 80 °C reaction does not occur, and at 140 °C diethyl formal is produced.

According to patent claims[30] aromatic propargyl ethers are formed by the action of prop-2-ynyl arenesulphonates on phenols in the presence of bases. Prop-2-ynyl ethers of alkylphenols have been prepared[54] by Claisen's method; it was considered that the duration of the reaction greatly influences the yield, which reaches a maximum after 48 h.

A general method for preparing propargyl ethers is the action of alkyl-, aryl-, and aralkyl-magnesium halides on 1-chloroalkyl prop-2-ynyl ethers[55]. A series of studies[56–58] have shown the possibilities of this method for obtaining the ethers of arylalkanols.

C_{sp}-Silylated propargyl ethers of alkanols, phenols, and diols are obtained by the action of Iotsich reagents on trialkylchlorosilanes[55,56,59,60]:

$$ROCH_2C{\equiv}CMgBr + R'_3SiCl \xrightarrow{Et_3N} ROCH_2C{\equiv}CSiR'_3$$
$$R' = Me, Et .$$

4-Alkoxybut-2-ynyl ethers can be prepared from bisbromomagnesioacetylene and α-halogeno-ethers[21]:

$$BrMgC{\equiv}CMgBr + 2\,ClCH_2OR \rightarrow ROCH_2C{\equiv}CCH_2OR .$$

A promising method suitable for industrial application is the addition of prop-2-ynol to substituted alkenes in acid media:

$$HC{\equiv}CCH_2OH + R_2C{=}CR'_2 \rightarrow HC{\equiv}CCH_2OCR_2CHR'_2 .$$

Its possibilities have not yet been completely revealed because of the limited number of alkenes used in this reaction (fluoroalkenes[61], isobutene[62], norbornenes[63,64]).

Prop-2-ynyl ethers containing a halogen atom adjacent to the triple bond can be obtained by the use of hypohalites[65,66]:

$$HC{\equiv}CCH(R)OR' \xrightarrow{+KOCl} ClC{\equiv}CCH(R)OR' .$$

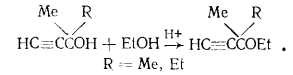
Prop-2-ynyloxyalkyl ethers (formals, acetals) are usually obtained from α-chloroalkyl ethers and prop-2-ynol in the presence of tertiary amines[67,68] or on the contrary from α-chloroalkyl prop-2-ynyl ethers and alcohols[69,70]:

$$\left.\begin{array}{l} HC{\equiv}CCH_2OH + ClCH(R')OR \\ HC{\equiv}CCH_2OCH(R')Cl + ROH \end{array}\right\} \xrightarrow{-HCl} HC{\equiv}CCH_2OCH(R')OR .$$

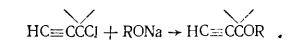
Prop-2-ynyl prop-2-ynyloxyalkyl ethers can also be obtained from prop-2-ynol and aldehydes in the presence of dehydrating agents[71]. Another widely used method for obtaining prop-2-ynyloxyalkyl ethers is the acid-catalysed addition of propargyl alcohols to vinyl ethers[72] and dihydropyran[73]. It is applicable also to the preparation of such ethers of organosilicon alcohols[60].

Tertiary prop-2-ynyl ethers are obtained by different methods from those for the primary ethers. When tertiary propargyl alcohols are heated (at 100 °C for 10 h) with ethanol in the presence of concentrated sulphuric acid, ethyl

tertiary propargyl ethers are obtained[74]:

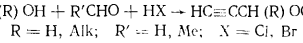


This method can be used also to obtain tertiary homopropargyl ethers[75]. According to patent claims[76] tertiary propargyl ethers are formed by the action of alkoxides on acetylenic tertiary chlorides:

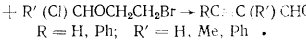


The reaction between acetylenic tertiary alkoxides and alkyl bromides in liquid ammonia gives significantly higher yields[77]. A tertiary benzyl propargyl ether has been obtained similarly; the reaction occurs also in the presence of sodium or sodamide in liquid ammonia[57,58]. Tertiary propargyl ethers are formed also by the alkaline fission of ethers of tetraalkylbutynediols[78] (Favorskii's reaction).

Hologenated ethers are obtained in various ways. Satisfactory yields of 1-chloroalkyl prop-2-ynyl ethers are given by the Henry–Litterscheidt method, by the action of hydrogen chloride or bromide on a mixture of an aldehyde and the alcohol[9]:

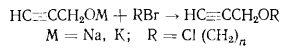


The method can be used to obtain C_{sp}-silylated[79-81] and C_{sp}-chloromethylated[82,83] propargyl ethers. When the chlorinating agent is boron trichloride the yield of 1-chloroethyl prop-2-ynyl ether rises[84] to 71%. Three modifications are proposed[85] for this method of obtaining α-halogenoalkyl ethers of primary and secondary propargyl alcohols. 2-Bromoalkyl prop-2-ynyl ethers can be prepared from Iotsich reagents and 1-chloroalkyl 2-bromoalkyl ethers[86]:



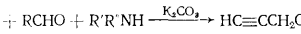
2-Halogenoethyl prop-2-ynyl ethers can be obtained from propargyloxyethanol and a halogenating agent (phosphorus tribromide, thionyl chloride)[87,88]:

2,2,2-Trichloro-1-halogenoethanols are prepared similarly[89,90]. Prop-2-ynyl ethers containing halogen in the γ, δ, and more remote positions are obtained by alkylating prop-2-ynol with alkylene dihalides in the presence of alkali-metal amides in liquid ammonia[28], utilising the greater polarisability of the carbon–bromide than of the carbon–chlorine bond:

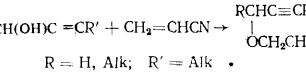


Homopropargyloxyalkyl ethers are formed[91,92] by the action of α-chloroalkyl ethers on terminal β-acetylenic alcohols in the presence of *NN*-dimethylaniline.

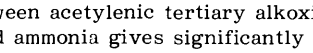
The action of aldehydes and secondary amines on prop-2-ynol forms aminoalkyl ethers[93]:



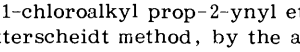
Since aminophenols contain two active centres (amino and hydroxy), their ethers cannot be obtained directly from prop-2-ynyl halides. Aminoaryl ethers are prepared from *N*-acylated aminophenols by the action of 3-bromopropyne in acetone in the presence of potassium carbonate, followed by alkaline hydrolysis[94]. The reaction of propargyl alcohols with acrylonitrile in the presence of sodium methoxide gives 2-cyanoethyl prop-2-ynyl ethers[95]:



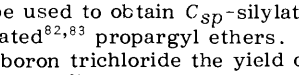
Prop-2-ynyl ethers of silanols (prop-2-ynyloxysilanes) are most often obtained by reaction between trialkylchlorosilanes and propargyl alcohols in the presence of organic bases. The first report[96] that tertiary prop-2-ynyl ethers of trialkylsilanols had been obtained was not confirmed[97,98]. Compounds containing one prop-2-ynyloxy-group attached to the silicon atom were first prepared in 1960 by reaction between prop-2-ynol and monochlorosilanes in the presence of pyridine[10]. Diprop-2-ynyloxysilanes have been obtained from methyldichlorosilane and acetylenic alcohols in the presence of dimethylaniline[99] or triethylamine[100]:



Prop-2-ynyloxysilanes containing aromatic substituents attached to the silicon atom have been prepared similarly[101-103]. 4-Chlorobut-2-ynyloxysilanes have been obtained by reaction between 4-chlorobut-2-ynol and monochlorosilanes[104]:

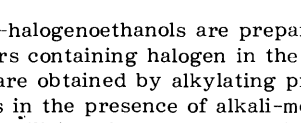


Si-Chloromethylated ethers are formed from chloromethyldimethylchlorosilane and propargyl alcohols[105]. Ethers of methylsilanols have been obtained[106] from the corresponding methylchlorosilanols and prop-2-ynol in the presence of urea (yield 70%):



Tetraprop-2-ynyloxysilane has been obtained by the transesterification of tetramethoxysilane with a considerable excess of prop-2-ynol in the presence of toluene-*p*-sulphonic acid, which enables formation of a difficultly separable mixture of methoxy-prop-2-ynyloxysilanes to be avoided[106]. The prop-2-ynyl ether of triethylsilanol can be obtained in 60–70% yield from triethylsilanethiol and prop-2-ynol[107]:

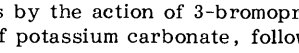
Tertiary propargyl ethers of silanols can be obtained also[108] by the uncatalysed reaction between prop-2-ynols and aminosilanes, which involves fission of the silicon–nitrogen bond, in contrast to the reaction with alkanols:



The dehydrocondensation of propargyl alcohols with alkyl(aryl)silanes also yields ethers of silanols[109]:

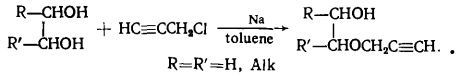
Ethers containing a siloxane group of the type

have been obtained by the dehydrocondensation of prop-2-ynol with tetra-alkyldisiloxanes in the presence of zinc chloride in benzene[110]:

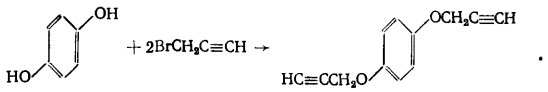


Prop-2-ynyl ethers of glycols can be prepared in various ways. A general method for obtaining partial ethers involves reaction between 3-chloropropyne and monosodio-derivatives

of diols[111]:



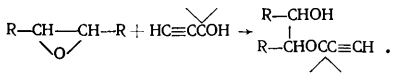
Ethers of polyhydric phenols are obtained by the action of 3-bromopropyne on the phenols[112]:



Mono- and di-ethers of quinol can be obtained by varying the quantities of alkaline component and aryl halide[112]. Prop-2-ynyl ethers containing a vinyl group have been prepared by the reaction[36]

$$CH_2{=}CHO(CH_2)_nONa + BrCH_2C{\equiv}CH \rightarrow CH_2{=}CHO(CH_2)_nOCH_2C{\equiv}CH \quad n=1{-}3 .$$

A convenient route to the monoethers of vicinal glycols is the reaction between propargyl alcohols and symmetrically substituted oxirans in the presence of catalytic quantities of Lewis acids[111,113–119]:



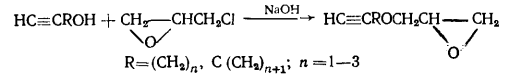
Boron trifluoride etherate[120], a trialkyl phosphite[121], or tin tetrachloride[122–124] can be used as catalyst. The method is restricted to symmetrical oxirans because fission of the epoxide ring is non-selective[125,126]. Furthermore, epichlorohydrin is almost quantitatively and selectively cleaved with the formation of primary monoprop-2-ynyl ethers[122–124,127]. The monoether of ethylene glycol is obtained from prop-2-ynol and 2-chloroethanol in the presence of potassium[120] or sodium[128] hydroxide:

$$ClCH_2CH_2OH + HC{\equiv}CCH_2OH \xrightarrow{-HCl} HOCH_2CH_2OCH_2C{\equiv}CH .$$

It can also be prepared from 3-bromopropyne and ethylene glycol[129]. Monoethers of 2,2,2-trihalogenoethanediols are readily obtained by the reaction of chloral or bromal hydrate with various propargyl alcohols in the presence of hydrochloric acid[89,130]:

$$CH(OH)_2 + HC{\equiv}CCRR'OH \rightarrow CX_3CH(OH)OCRR'C{\equiv}CH$$
$$X=Cl, Br;\ R=R'=H, Alk;\ R=Alk,\ R'=Ar .$$

The cleavage of 2,2-disubstituted 1,3-dioxolans by phenethynyl-, but-3-enynyl-,[131] and prop-2-ynyl-magnesium bromides[132] leads to the formation of γ-substituted tertiary propargyl ethers of ethylene glycol; the reaction of prop-2-ynylmagnesium bromide with 1,3-dioxolans is accompanied by transformation of the terminal triple bond into a disubstituted bond. Propargyl ethers of glycidol are obtained by the action of epichlorohydrin on acetylenic alcohols in the presence of alkali[133] or the ether complex of boron trifluoride[127]:



Phosphorus-containing propargyl ethers are usually obtained from the corresponding phosphorus acid chlorides in the presence of tertiary amines[134,135]:

$$n\,HC{\equiv}CCH_2OH + R_{3-n}PCl \xrightarrow[-n\,HCl]{Et_3N} R_{3-n}P(OCH_2C{\equiv}CH)_n \quad n=1,2 .$$

On standing the ethers are converted into the isomeric allenyl and prop-1-ynyl ethers[136].

C_{sp}-Substituted ethers are prepared by the action of Iotsich reagents obtained from propargyl ethers on alkyl[44], aryl, and hetaryl[137] halides, as well as by the alkylation of prop-2-ynyl ethers with alkyl halides in the presence of sodamide in liquid ammonia[138,139]. A general method for obtaining such substituted ethers is the reaction between acetals and Iotsich reagents based on monosubstituted alkynes[140]:

$$R'R''C(OEt)_2 + RC{\equiv}CMgBr \rightarrow EtOCR'R''C{\equiv}CR .$$

The γ-alkylated ethers can be obtained by the action of alcohols on 1-alkyl-1,3-dichloropropenes in dimethyl sulphoxide at 130–140 °C[141]:

$$ClCH_2CH{=}C(Cl)Me + ROH \xrightarrow[-2HCl]{} ROCH_2C{\equiv}CMe .$$

The action of alkylmagnesium halides on 4-bromobut-2-ynyl ethers also yields 3-alkylated propargyl ethers[142]. A high yield of 3-phenylprop-2-ynyl vinyl ether is formed on the vacuum distillation of bisphenylprop-2-ynyl acetal in the presence of ammonium dihydrogen phosphate[143]:

$$(PhC{\equiv}CCH_2O)_2CHMe \xrightarrow{\Delta} PhC{\equiv}CCH_2OCH{=}CH_2 .$$

1,3-Diphenylprop-2-ynyl ethers can be obtained in good yields[144,145] by heating acetals of aromatic or heterocyclic aldehydes with phenylacetylene in the presence of zinc chloride.

III. PHYSICOCHEMICAL AND SPECTROSCOPIC PROPERTIES

The boiling points of individual branched-chain homologous prop-2-ynyl ethers, in contrast to those of the corresponding alcohols, increase from the primary to the secondary and then to the tertiary ether.

The dipole moments of prop-2-ynyl ethers, unlike those of the corresponding halogeno-derivatives, exceed those of the allyl and propyl ethers, which is explained by a reversal in the direction of the dipole[146]. The inductive constant of the prop-2-ynyloxy-group $\sigma^*(CH{\equiv}CCH_2O) = 2.18$ is almost treble that for the prop-2-ynyl group[147]. Quantum-chemical models of prop-2-ynol and of the prop-2-ynyloxy-anion give a clear idea of the distribution of charges among the atoms and of the strengths of the bonds[148].

Prop-2-ynyl ethers are less basic than the corresponding allyl and propyl ethers because of the decrease in the $+I$ effect in the sequence propyl < allyl < prop-2-ynyl. The centre of maximum basicity in prop-2-ynyl ethers is the oxygen atom. In isostructural ethers $CH{\equiv}CEl(CH_3)_2OCH_3$ the oxygen atom is rather more basic when El = Si than C, which is attributed to $d_\pi-p_\pi$ interaction in the opposite direction to the inductive effect[149]. The oxygen atom is less basic in prop-2-ynyl ethers of silanols than in the saturated analogues, owing to the $-I$ effect of the prop-2-ynyl group and its π-electron-accepting power. 2,2-Dichlorovinyl prop-2-ynyl ether is more basic than the corresponding allyl compound[150].

The presence of intense characteristic absorption bands[151–155] makes it possible to use infrared spectroscopy for the reliable identification of prop-2-ynyl ethers or their detection in a mixture of unsaturated compounds. The spectra of these compounds contain bands characteristic of ≡C–H and C≡C bonds[156,157]. Stretching vibrations of the former bond produce a band in the range 3295–3320 cm^{-1}; the band in the region of 600 cm^{-1}, caused by deformation vibrations (overtone 1200 cm^{-1}), is unsuitable for analytical purposes, since other functional groups are able to absorb in these regions. For the same reasons caution is necessary in the interpretation of structure by means of the band at 1325–1336 cm^{-1},

which is ascribed[158] to angular vibrations of the methylene group in the prop-2-ynyl fragment. Greater importance attaches to the weak band due to the acetylenic bond, which usually appears in the frequency range 2110–2130 cm^{-1}.

A recent study of the infrared spectra of prop-2-ynyl ethers has provided direct evidence of the absence of conjugation through the methylene bridge between the lone electron pair of the oxygen atom and the π electrons of the triple bond[159]. Study of the Raman, ultraviolet, and nuclear magnetic resonance spectra also indicates absence of $p-\pi$ conjugation[160].

The signals from acetylenic protons in the ^1H n.m.r. spectra of alkyl prop-2-ynyl ethers appear down-field relative to those of α-alkoxyacetylenes. The ^1H n.m.r. spectra[161–163] of prop-2-ynyl ethers containing a $CH{:}CCH_2O$ fragment exhibit a triplet in the range $\delta = 1.4–2.2$ ppm (:CH protons) and a doublet at 4.05–4.25 ppm (protons of the $:CCH_2$ group). The characteristic spin–spin coupling constant is 2–3 Hz.[164]

In order to investigate the possibility of hydrogen bonding, chemical shifts of the signal from the acetylenic proton in the n.m.r. spectra of alkyl prop-2-ynyl ethers and their non-oxygen analogues have been measured in concentrated solutions and on dilution with inert or proton-donor solvents[165]. The presence of oxygen causes a considerable shift in the signal, as a consequence of formation of a hydrogen bond with the oxygen atom.

A study has been made of the dependence of the mass-spectrometric fragmentation of substituted phenyl prop-2-ynyl ethers on the nature of the cyclic substituents[166]. In several ethers (e.g. the phenyl ether itself) electron bombardment produces skeletal rearrangements with the loss of carbon monoxide and formation of the $[M-CO]^+$ ion, which has not yet found a theoretical interpretation[167]. In this respect it is interesting that the carbon monoxide molecule is among the stable neutral species most often eliminated in rearrangements of aromatic compounds. The mass spectra of tertiary propargyl ethers of ethanol have been examined[168].

IV. REACTIVITY

Prop-2-ynyl ethers undergo diverse reactions involving the acetylenic hydrogen atom, the triple bond, and also the ethereal oxygen atom. Their reactivity is due not only to the actual nature of the acetylenic bond but also to the presence of the electron-accepting ether group[169,170].

1. Rearrangement

Prop-2-ynyl ethers undergo various rearrangements with the formation of isomeric compounds. Thus the methyl ether isomerises into allenyl methyl ether when heated with solid caustic potash[171]; sodium methoxide in dimethyl sulphoxide has a similar effect[172]:

$$MeOCH_2C{\equiv}CH \rightarrow MeOCH{=}C{=}CH_2 .$$

The n.m.r. spectra show that the mixture does not contain even traces of methyl prop-1-ynyl ether. The latter does not form the allenyl ether under the influence of sodium methoxide in the presence of dimethyl sulphoxide, which implies that it is more stable than the prop-2-ynyl ether[172]. Rearrangement does not take place in the formation of ethers from the corresponding acetylenic chlorides and alcohols in the presence of alkalis[173,174], nor in the replacement of halogen in various prop-2-ynyl halides by means of alkoxides[7].

A method of preparing allenyl ethers[11] was based on the isomerisation of prop-2-ynyl ethers in the presence of potassium t-butoxide:

$$HC{\equiv}CCH_2OR \rightarrow CH_2{=}C{=}CHOR .$$

The allenyl ether is readily metallated by butyl-lithium:

$$CH_2{=}C{=}CHOR + BuLi \rightarrow CH_2{=}C{=}C(Li)OR .$$

When an ether is alkylated with an alkyl halide in liquid ammonia, a mixture of allenyl and prop-2-ynyl ethers is formed, whereas alkylation in an oxolan–ether mixture gives only α-alkylallenyl ethers. The action of organomagnesium compounds on prop-2-ynyl ethers in the presence of cuprous bromide yields allene hydrocarbons[12]:

$$MeOCRR'C{\equiv}CR'' + R'''MgBr \xrightarrow{Cu_2Br_2} RR'C{=}C{=}CR''R''' .$$

Under the influence of aldehydes or ketones in the presence of potassium hydroxide alkyl and aryl prop-2-ynyl ethers give mixtures of acetylenic ether–alcohols and allenyl ethers[172]:

$$PhOCH_2C{\equiv}CH + RCHO \xrightarrow[DMF]{KOH} \begin{cases} \rightarrow PhOCH_2C{\equiv}CCH(R)OH \\ \rightarrow PhOCH{=}C{=}CH_2 \end{cases} .$$

Similar isomerisation of prop-2-ynyl ethers in alkaline medium has been observed by several workers[175,176].

Alkynyl 2-bromoalkyl ethers, on dehydrobromination in the presence of sodamide in a liquid ammonia, undergo partial rearrangement into the corresponding prop-2-ynyl ethers. However, several workers[177] cast doubt on the isomerisation of terminal acetylenic compounds under the influence of this reagent. A tendency to prototropic isomerisation of aryl prop-2-ynyl ethers has been observed also under the influence of alcoholic alkali[33] or potassium t-butoxide[178]. For example, the preparation of prop-2-ynyl ethers from the bromides involves formation of a mixture of prop-2-ynyl, allenyl, and prop-1-ynyl ethers:

$$BrCHR''C{\equiv}CR' + ROM \longrightarrow \begin{cases} \rightarrow ROCHR''C{\equiv}CR' \\ \rightarrow ROCR''{=}C{=}CHR' \\ \rightarrow ROC{\equiv}CCH_2R' \end{cases}$$

R=Alk, Ar; R'=H, Alk, Ar; R''=H, Alk .

Attempts to effect the rearrangement of phenyl and naphthyl prop-2-ynyl ethers under the conditions of the Claisen reaction were unsuccessful[179].

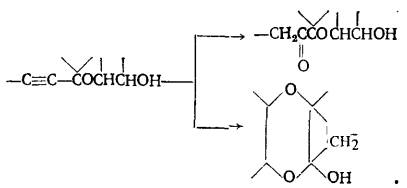
2. Addition

The most characteristic property of prop-2-ynyl ethers is their ready ability to undergo quantitative hydration to ether–ketones. Thus gentle heating of the methyl ether with water in the presence of mercury(II) sulphate forms methoxyacetone[25]:

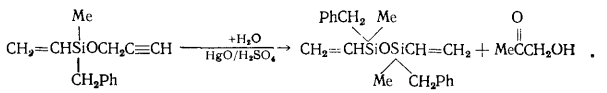
$$HC{\equiv}CCH_2OMe + H_2O \xrightarrow{HgSO_4} MeCOCH_2OMe .$$

A rapid and convenient method has been developed[45] for the catalytic hydration of prop-2-ynyl ethers to the corresponding ethers of hydroxyacetone. Other alkyl prop-2-ynyl ethers have also been subjected to hydration, as well as those containing aromatic, alicyclic, and heterocyclic groups[17,37,139]. The monoethers of α-glycols undergo hydration in two ways determined by the polar and steric effects of substituents,

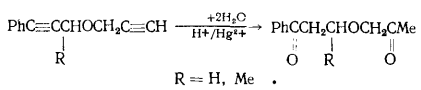
mainly in the prop-2-ynyl fragment[180-182]:



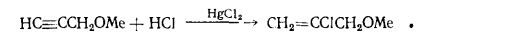
Hydration of the ethers of silanols in the presence of a mixture of mercuric oxide and sulphuric acid is accompanied by rupture of the silicon–oxygen bond, with formation of the corresponding disiloxane and hydroxyacetone[103]:



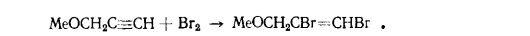
The hydration of prop-2-ynyl ethers of phenylprop-2-ynols gives phenacylalkyl ethers of hydroxyacetone[182]:



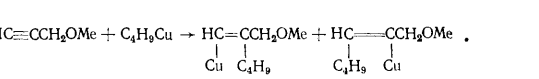
A monoadduct is obtained by the action of concentrated hydrochloric acid on methyl prop-2-ynyl ether in the presence of mercury(II) chloride[183]:



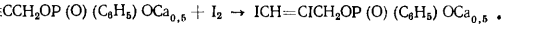
The catalytic effect is due to the formation of complexes with hydrogen chloride, not intermediate organomercury compounds. The kinetics of the addition of elementary bromine to the methyl ether



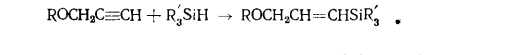
indicates a termolecular process[184]. A kinetic study has been made also of the addition of mercuric chloride to the methyl ether in the presence of lithium chloride[185]. Addition of a copper alkyl to a prop-2-ynyl ether[186] gives a mixture of isomers:



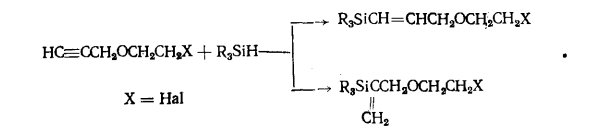
The organophosphorus esters smoothly add iodine[187]:



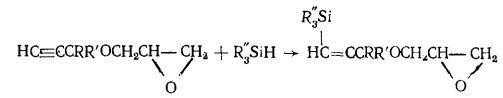
In the presence of a Speier catalyst prop-2-ynyl ethers readily undergo hydrosilylation[188]:



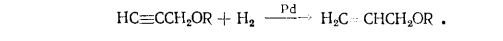
With hydroxylated ethers under these conditions the process is unaccompanied by dehydrocondensation: i.e. the hydroxy-group is unaffected[75]. Halogenated ethers give mixtures of isomeric adducts without involving the halogen atom[189]:



In the hydrosilylation of tertiary prop-2-ynyl ethers of chloral hydrate, however, products of addition at the multiple bond are accompanied by those in which chlorine atoms of the trichloromethyl group have been replaced by a trialkylsilyl radical[190]. The epoxide ring is preserved when prop-2-ynyl ethers of glycidol undergo hydrosilylation[124,127,191-193]:



Prop-2-ynyl ethers are readily hydrogenated in the presence of Raney nickel[137], palladium[139], and also platinum[57] catalysts, whose activity is the main factor determining the reaction velocity. For example, the rate of hydrogenation of the monoether of ethylene glycol on a nickel–molybdenum catalyst exceeds by a factor of 13 the rate when Raney nickel is used under the same conditions[194]. Platinum black can be used[57] for the exhaustive hydrogenation of a tertiary propargyl ether of benzyl alcohol. In the presence of a palladium catalyst deactivated with lead acetate the triple bond is hydrogenated to a double bond[195]:

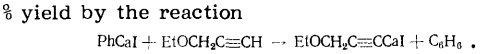


3. Substitution

(a) Reactions with Metals

The tendency of prop-2-ynyl ethers to undergo substitution is evident primarily in their reactions with metals and organometallic compounds. The acetylenic hydrogen atom is readily replaced by a heavy metal. On treatment with ammoniacal silver nitrate white precipitates of silver salts separate. Cuprous chloride solution gives yellow precipitates of copper(I) salts.

Sodium derivatives of the ethers should be prepared by means of sodamide in liquid ammonia[196]. Lithium derivatives are obtained from butyl-lithium and the ether in diethyl ether[197]. Organocalcium derivatives have been obtained[198] in 90% yield by the reaction



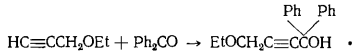
Organomagnesium derivatives of prop-2-ynyl ethers (Iotsich reagents) are smoothly formed in ether or oxolan[199], and will react with almost all the reagents that undergo organomagnesium synthesis[137,197-201]. The reactions of the magnesium derivatives have been studied most thoroughly. Methyl prop-2-ynyl ether in its reactions with organomagnesium compounds is more active than hex-1-yne by a factor of almost 12,[169] which is explained by the ability of the oxygen atom to attract electrons and thereby to increase the mobility of the acetylenic hydrogen atom.

(b) Reactions with Carbonyl Compounds

Organomagnesium derivatives of prop-2-ynyl ethers are widely used for the synthesis of acetylenic ether–alcohols. When aldehydes and ketones are treated with Iotsich reagents obtained from these ethers, the corresponding secondary and tertiary ether–alcohols are formed. Iotsich reagents from alkyl prop-2-ynyl ethers give alcohols in 60–70% yields[199]. The methyl ether with aldehydes forms ether–alcohols in 60% yield[199,202]:

Similarly, 5-phenoxypent-3-yn-2-ol has been obtained (yield 50%) from phenyl prop-2-ynyl ether, iodoethane, and acetaldehyde[201].

Prop-2-ynyl ethers are able to react with aldehydes and ketones also under the conditions of the Favorskii reaction. The ethyl ether condenses with diphenyl ketone in the presence of potassium hydroxide in oxolan even at room temperature[203]:



The propyl and butyl ethers condense smoothly with various ketones[18,39,204,205] and alcoholic ketones[29,206].

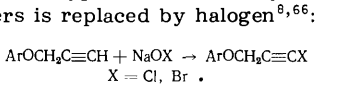
The condensation of prop-2-ynyl ethers with carbonyl compounds takes place also in liquid ammonia[207]. Thus the methyl ether reacts with benzaldehyde to give a 68% yield of 1-phenylbut-2-yne-1,4-diol.

Organomagnesium derivatives of alkyl prop-2-ynyl ethers are carboxylated by means of dialkyl carbonates[208,209] and oxalates[40] in ethereal solvents, being converted into the corresponding alkoxybutynoic esters. With α-chloroalkyl ethers the magnesium derivatives form γ-substituted alkoxyalkyl prop-2-ynyl ethers[197], and with orthoesters acetals are formed[73].

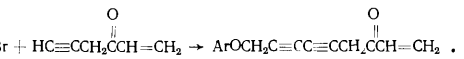
(c) Other Substitutions

In liquid ammonia the Iotsich reagents are readily alkylated by alkyl bromides[137,138].

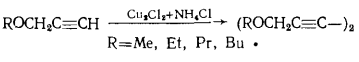
On treatment with hypohalites the acetylenic hydrogen atom in the ethers is replaced by halogen[8,66]:



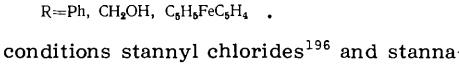
The halogen in the products can easily be substituted[66]:



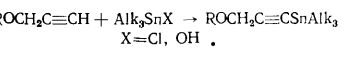
The action of a copper(I) salt and ammonium chloride on the ethers yields diethers of "head to head" type[210]:



Dehydrodimerisation takes place also in the oxidative condensation of *p*-ferrocenylphenyl prop-2-ynyl ether[211] in a mixture of ether, pyridine, and methanol (2 : 2 : 1) in the presence of copper salts[212]:

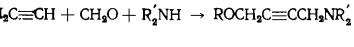


Under certain conditions stannyl chlorides[196] and stannanols[213] react with alkyl prop-2-ynyl ethers with substitution of the acetylenic hydrogen atom by a trialkylstannyl group:



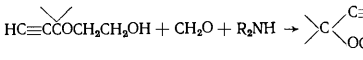
(d) Aminomethylation

Prop-2-ynyl ethers react under the conditions of the Mannich reaction with formaldehyde and secondary amines to form the aminomethylated ethers[25,35,47,55,139,214–216]:



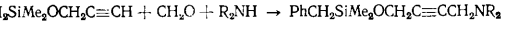
The reaction is usually conducted in the presence of copper(I) chloride in dioxan. Copper acetate has also been proposed as catalyst[139].

The uncatalysed aminomethylation of hydroxylated ethers involves the hydroxyl hydrogen atom[217]:

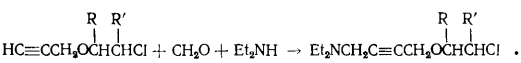


Preliminary chemical protection of the hydroxy-group enables this undesirable process to be suppressed and the desired products to be obtained[218]. Aminomethylation of the monoethers of ethylene glycol in the presence of cuprous chloride involves the ethynyl hydrogen atom without affecting the hydroxyl hydrogen[219].

Results have been published[101] indicating the possibility of obtaining C_{sp}-aminomethylated derivatives of prop-2-ynyl ethers of silanols:

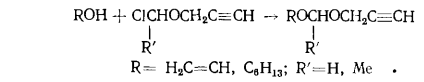


The aminomethylation of the halogenated ethers does not involve the halogen atom[205]:



(e) Reactions of Halogenated Ethers Involving the Halogen Atoms

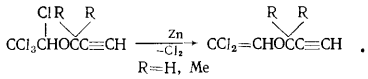
Under certain conditions halogen atoms present in prop-2-ynyl ethers can be replaced by various groups. Thus prop-2-ynyl acetals of aldehydes are formed by reaction of the chloroalkyl ethers with alcohols[220–222]:



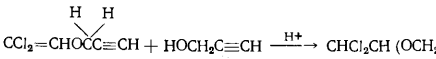
1- and 2-Halogenoalkyl prop-2-ynyl ethers react readily with Iotsich reagents obtained from monosubstituted acetylenes[86] and also with alkali-metal alkoxides[223].

Investigation of the behaviour of mono- and di-halogenated prop-2-ynyl ethers towards various nucleophiles has provided an experimental basis for a suggested activity series of halogen atoms depending on polar and steric factors. This can be used in directed syntheses of technically valuable products[223].

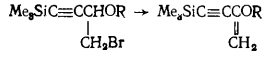
Tertiary propargyl ethers of 1,2,2,2-tetrachloroethanol are dehalogenated in the presence of zinc with the formation of dichlorovinyl prop-2-ynyl ether[224]:



Subsequent addition of prop-2-ynol yields the diprop-2-ynyl acetal of 2,2-dichloroacetaldehyde:



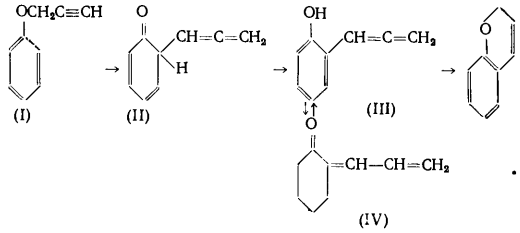
Organosilicon alkoxyalkenynes have been obtained[225] by the dehydrohalogenation of 3-silylated prop-2-ynyl ethers containing a 1-bromomethyl group:



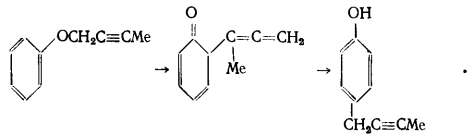
4. Cyclisation

The special synthetic value of prop-2-ynyl ethers consists in the possibility of transforming them into various difficultly accessible carbocyclic and heterocyclic compounds.

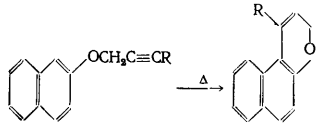
The unique scheme proposed[226] for the cylisation of the aryl ethers involves the formation, from the phenyl ether (I) as example, of the allenyl-dienone (II) (rate-determining stage) followed by rapid enolisation into allenylphenol (III), sigmatropic migration of hydrogen with conversion into (IV), and cyclisation to chromen:



In the case of but-2-ynyl phenyl ether the intermediate methylallenyl-dienone rearranges into but-2′-ynylphenol:

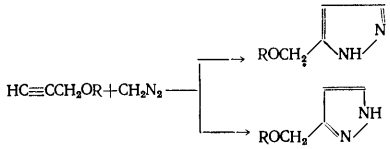


The thermal cyclisation of 4-phenoxybut-2-ynyl phenyl ether forms phenoxymethylbenzopyran[227]. The C_{sp}-substituted naphthyl ethers cyclise in the presence of diethylaniline into the corresponding naphthopyrans[228]:



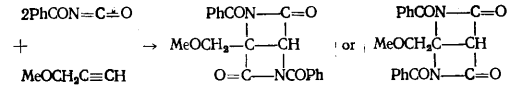
The reaction involves a Claisen rearrangement. Phenyl prop-2-ynyl ethers when heated also undergo a sigmatropic rearrangement with formation of the corresponding chromens[229]. The cyclisation of aliphatic propargyl ethers has been described[230-233].

Examples are known of cyclisation in reactions with various types of dipoles. A method for obtaining alkoxylated pyrazoles is based on interaction with diazoalkanes[14]:

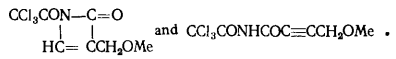


The reaction involves intermediate formation of the zwitterion $^{+}N_2CH_2CH{:}C^{-}R$, the uniform charge separation in which is confirmed by absence of a solvent effect on the proportions of isomers formed.

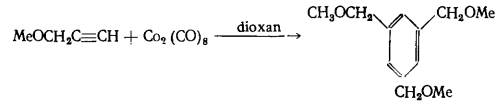
Prop-2-ynyl ethers have been subjected to intermolecular cyclisation with benzoyl and trichloroacetyl isocyanates[170]. The benzoyl compound and the methyl ether in diethyl ether at 0 °C give a product which was regarded as a diadduct:



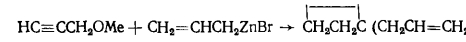
Trichloroacetyl isocyanate reacts far more slowly; under severe conditions a mixture of isomers of cyclic and linear structure is obtained:



Methyl prop-2-ynyl ether undergoes cyclisation to an alkoxymethylquinol under the influence of iron carbonyls[234]. Similarly, trimerisation with formation of a mesitylene derivative occurs on heating in an organic solvent in the presence of a metal carbonyl[235]:

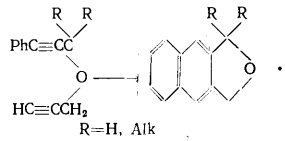


1,1-Diallylcyclopropane has been synthesised by the addition of allylzinc bromide to the methyl ether[13]:



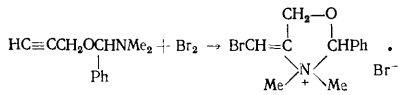
Replacement of methyl by phenyl facilitates cyclisation and increases the yield of the desired product.

Intramolecular cyclisation of phenylprop-2-ynyl prop-2-ynyl ethers in *p*-xylene yields naphtho-oxolans[236]:



The thermal cyclisation of C_{sp}-substituted prop-2-ynyl ethers forms 2*H*-chromens in 60% yield[237].

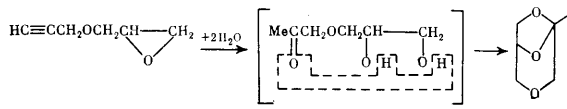
The bromocyclisation of α-dimethylaminobenzyl prop-2-ynyl ether yields 4-bromomethylene-3,3-dimethyl-2-phenyloxazolidinium bromide:



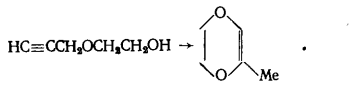
2-Halogenoalkylated prop-2-ynyl ethers are used in the synthesis of difficultly accessible prop-2-ynyated 1,4-dioxans[238].

A cyclobutene derivative is formed in the photochemical addition of methyl prop-2-ynyl ether to vinylene carbonate[239]. The catalytic oligomerisation of butadiene with alkynyl prop-2-ynyl ethers leads to the formation of 4,5-disubstituted cyclodeca-1,4,7-trienes[240].

Cyclisation of the prop-2-ynyl ether of glycidol gives trioxabicyclo-octane[241], presumably with intermediate formation of an acetonyl ether of glycerol, which cyclises by intramolecular acetalisation:



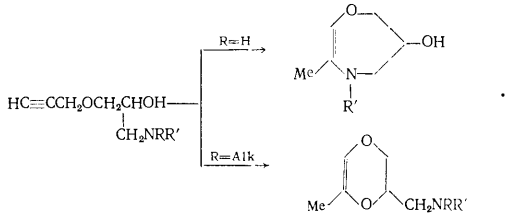
Cyclisation of the ethers of vicinal diols has been studied[111, 120,129]. Prop-2′-ynyloxyethanol in 2-ethoxyethanol in the presence of potassium hydroxide forms 2,3-dihydro-5-methyl-1,4-dioxin[120]:



Cyclisation of the ethers of alkylated ethylene glycols gives mixtures of alkylated dihydro-1,4-dioxins, isomeric heterocycles with an exocyclic double bond, and vinylated 1,3-dioxolans[111,129]. Under these conditions the cyclisation of

prop-2'-ynyloxycyclohexanol yields geometric isomers of dihydrocyclohexanodioxin.

The direction of the base-catalysed intramolecular cyclisation of monoprop-2-ynyl ethers of aminoalkylated α-glycols is determined by the degree of substitution at the nitrogen atom[242]. Cyclisation of the tertiary amines involves the hydroxy-group and gives dihydroaminoalkyl-1,4-dioxins, but that of the secondary amines involves the nitrogen–hydrogen bond and yields oxazepine derivatives:



V. PRACTICAL APPLICATION

Prop-2-ynyl ethers are continually finding new fields of practical application in addition to their use in organic synthesis. They can be applied as stabilisers for cellulose acetate and goods based thereon (acetate rayon, cinematograph film, plastic materials, etc.), which age under the influence of light, temperature, etc. during service, with a consequent deterioration in their physicochemical properties, premature failure, and wear[243]. Benzyl prop-2-ynyl ether has been proposed as stabiliser to increase the resistance of cellulose acetate to light[244]. Stability towards light is also acquired by lower chlorinated hydrocarbons on the addition of propyl, butyl, isobutyl, isopentyl, and phenyl prop-2-ynyl ethers together with a stabiliser[243].

The ethers with aryl and diaryl groups can serve as monomers for the synthesis of heat-resistant polymers[112]. Oligomers of the type $HO[CH_2C{:}CCH_2OCR(OH)]_nR'$ (R, R' = H, Alk) are used as power-consuming additives for rocket fuels, improving the ballistic properties of the compositions[245].

Several hydroxylated prop-2-ynyl ethers have found application in the synthesis of auxiliary agents for the textile and paper industries[246]. Products of the hydrosilylation of prop-2-ynyl ethers of silanols are used as finishes for textile materials[247]. Monoprop-2-ynyl ethers of ethylene and propylene glycols may find application in electroplating as brightening agents[248]. Dibenzocycloheptatrienes obtained from prop-2-ynyl ethers are employed in the pharmaceutical industry with inert carriers[249].

1. Biological Properties

Many prop-2-ynyl ethers possess biological activity and can be used in agriculture both as toxic chemicals and in veterinary practice to destroy parasites and in the fight against gastric diseases in farm animals[250–252].

The use has been proposed of preparations based on these ethers that destroy arachnoid mites, leaf aphids[253], beetles and rats[252], house-flies[254], nematodes and other parasitic worms in the soil[250]. The compound $I_2C{:}CClCH_2OR$, obtained by the interaction of a prop-2-ynyl ether, chloroform, and iodine, stimulates the growth of poultry[255]. The same preparation has been recommended for use in veterinary practice for the treatment of diarrhoea, and its isologue for the treatment of gastric diseases in pigs[252].

Prop-2-ynyl ethers also possess strong bactericidal and herbicidal properties[256]: the ether of 2',4',6'-tri-iodo-2,4-dinitroazophenol is a more active bactericide than is chloramphenicol[257]. 4-Chlorobut-2-ynyl *m*-chlorophenylcarbamate (Barban) is a herbicide for the post-germination treatment of fine-grained cereals against wild oats[258]. Chlorine-containing C_{sp}-silylated prop-2-ynyl ethers of general formula $ClCH_2Si(CH_3)_2C{:}CCH_2OCHRCH_3$ surpass known standard preparations (chloramine, Rivanol, Nitrofungin) in antibacterial activity[259].

There are indications[256] that prop-2-ynyl ethers may serve as starting materials for the synthesis of diverse bifunctional acetylenes and amino-ethers developing fungicidal activity. Several derivatives are pharmacologically active compounds[260]. A tertiary prop-2-ynyl carbamate (Oblivon C) is used as a mild hypno-sedative agent and has an antispasmodic effect[261]. In contrast to prop-2-ynyl ethers[262] homopropargyl aminoacetates possess a strong soporific–anticonvulsant type of psychotropic activity[263–265].

The C_{sp}-iodinated prop-2-ynyl ether of 2,4,5-trichlorophenol is used therapeutically as an antimycotic and antiseptic[266]. The muscarinic action of the prop-2-ynyl ether of choline is double those of the allyl and propyl analogues[266]. C_{sp}-Aminomethylated derivatives of the monoprop-2-ynyl ether of ethylene glycol[264] and diprop-2-ynyl acetal[265] have a mild hypno-sedative action combined with a muscle-relaxant effect and slight antispasmodic properties. Substances having a general hypno-sedative profile include also prop-2-ynyl ethers of silanols[267,268]. The ethers of glycerol possess spasmolytic properties[260], and those of oxan hypnotic properties[266].

1-Alkylprop-2-ynyl ethers of long-chain alcohols $ROCHR'C{:}CH$ ($R = C_6H_{13}$, C_8H_{17}, etc.) have a beneficial effect on blood formation[269]. Prop-2-ynyl ethers of arylated pyranols have been claimed[270] as pesticides. The tertiary prop-2-ynyl ether of the monochlorohydrin of glycerol $HC{:}CC(CH_3)_2OCH_2CH(OH)CH_2Cl$ (an analogue of Mephenesine) is able to relax muscles[122]. The hypothesis that structures having both propargyl and oxiran groups would probably possess antitumour activity was not supported by an investigation of C_{sp}-substituted prop-2-ynyl ethers of glycidol[123]. However, C_{sp}-aminomethylated tertiary ethers of general formula $ROCR'R''C{:}CCH_2N(CH_2CH_2Cl)_2$ do exhibit such activity[271]. Several hydroxylated prop-2-ynyl ethers are perfumes[272].

2. Protection of Metals from Corrosion

The problem of inhibitors of acid corrosion merits close attention, since the rate of corrosion breakdown and the associated material damage are especially large for most metals particularly in contact with acid media[273–280]. In connection with the increasing demand for inhibitors of the high-temperature corrosion of steel in hydrochloric acid recent years have been the concentration of attention on acetylenic compounds, and the preparation of novel functionally substituted compounds of this class has again occupied a primary position in work on fine organic synthesis.

Even mechanical mixtures of known nitrogen-containing inhibitors with certain acetylenic compounds are found to be quite reliable corrosion inhibitors at high temperatures[281,282]. The position of the triple bond has a very strong influence on the protective effect, which is greatest when the bond is terminal[283]. The protective effects of acetylenic compounds fall in the sequence[284] secondary alcohols > primary alcohols > ethers > sulphides > tertiary alcohols > hydrocarbons. Diacetylenic compounds are more promising than vinylacetylene derivatives[285].

Prolonged tests on acetylenic inhibitors in technical 28% hydrochloric acid have demonstrated the stability of prop-2-ynol and its ethers[286,287]. Alkylcycloalkylphosphonic esters of the type $AlkC_6H_{10}PO(OCH_2C{:}CH)_2$ have proved to be effective inhibitors, protecting metals at temperatures up to 100 °C and above[288-290], with the protective effect depending on the size and structure of the radical[284]. Diprop-2-ynyl sulphide, which is comparatively readily available, also has a strong anticorrosive effect[291]. Diprop-2-ynyl ether is a corrosion inhibitor for ferrous metals and nickel in non-oxidising acids[276].

Prop-2-ynyl ethers of phenols also have a protective effect: for example, that of *m*-cresol inhibits the corrosion of steel in hydrochloric acid more effectively than does prop-2-ynol. The protective effect of the *m*-tolyl ether is weakened when the ethynyl hydrogen is replaced by alkyl[292,293]. In the aromatic series the most effective inhibitors of the corrosion of steel and its absorption of hydrogen in hydrochloric acid have been the prop-2-ynyl ethers of 1- and 2-phenylalkanols and of 3-phenylprop-2-ynol[294-296]; the inhibition coefficient increases steadily with temperature. Introduction of a sulpho-group into the benzene (naphthalene) ring weakens the inhibiting properties of the derived ethers[297].

The protective effect of prop-2-ynyl ethers of silanols is determined mainly by the action of products of acid hydrolysis[295]. Among complete and partial prop-2-ynyl and prop-2'-ynyloxyalkyl ethers of glycols the most effective and stable properties are exhibited by diprop-2-ynyl ethers, in particular by that of ethylene glycol[298,299]. Prop-2-ynyl esters of aliphatic acids are less effective corrosion inhibitors than are the corresponding ethers of alcohols and phenols[300]. The introduction of amino-radicals into the ethers considerably diminishes the inhibiting effect[299,300].

Many investigators have been concerned to elucidate the mechanism of the inhibiting effect of acetylenic compounds on acid corrosion[301-306]. An adsorption–polymerisation mechanism is consistent with established laws. Most research workers have shown that the protective action of terminal acetylenes is due to polymerisation by opening of the triple bond, leading to formation of a protective polymer film on the metal surface[301,304]. However, Japanese workers consider[305] that the protective effect of acetylenic compounds is due rather to adsorption than to formation of a polymer film. Acetylenic compounds are adsorbed on iron by means of the triple bonds[278], forming π complexes with the metal, with a consequent positive displacement of the potential on the *I* scale.

Since the mechanism of the protective action of acetylenic compounds in the acid corrosion of metals still remains an open question, further study is required of the influence of their structure on their inhibiting effect.

REFERENCES

1. C.Liebermann, Annalen, **135**, 287 (1865).
2. L.Henry, Ann.Chim., **14**, 81 (1878).
3. A.Bayer, Annalen, **138**, 196 (1866).
4. L.Henry, Ber., **6**, 729 (1873).
5. C.Liebermann and A.Krecshmer, Annalen, **158**, 230 (1871).
6. L.Henry, Compt.rend., **96**, 1235 (1883).
7. M.Gaudemar, Ann.Chim., **1**, 161 (1956).
8. R.Lespieau, Bull.Soc.chim.France, **13**, 629 (1894).
9. M.R.Golse, Bull.Soc.Pharm.(Bordeaux), **98**, 113 (1959).
10. V.F.Mironov and N.G.Maksimova, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 2059 (1960).
11. S.Hoff, L.Brandsma, and J.F.Arens, Rec.Trav. chim., **87**, 916 (1968).
12. J.L.Moreau and M.Gaudemar, J.Organometallic Chem., **108**, 159 (1976).
13. Y.Frangin and M.Gaudemar, Compt.rend., 280C, 1389 (1975).
14. E.Stephan, L.Vo-Quang, and Y.Vo-Quang, Bull. Soc.chim.France, 1793 (1975).
15. US P.2994706 (1961); Chem.Abs., **55**, 8026 (1961).
16. S.F.Karaev, "VI Vsesoyuznaya Konferentsiya po Khimii Atsetilena i ego Proizvodnykh, Tezisy Dokladov" (Sixth All-Union Conference on the Chemistry of Acetylene and its Derivatives—Abstracts of Papers), Baku, 1979, Vol.1, p.12.
17. V.M.Vvedenskii, Ukrain.Khim.Zhur., **25**, 203 (1959).
18. S.A.Vartanyan, A.O.Tosunyan, and L.M.Kostochka, Armyan.Khim.Zhur., **21**, 397 (1968).
19. W.Kirmse and J.Heese, J.Chem.Soc.Chem.Comm., 258 (1971).
20. J.Villieras, C.Bacquet, and J.F.Normant, J.Organometallic Chem., **97**, 355 (1975).
21. G.Gauthier, Ann.Chim., **16**, 334 (1909).
22. G.J.Josiesch and B.P.Orelkin, Bull.Soc.chim.France, **10**, 172 (1911).
23. R.Epsztein, Bull.Soc.chim.France, 158 (1956).
24. H.Normant and P.Montione, Compt.rend., **259C**, 1347 (1964).
25. W.Reppe, Annalen, **596**, 74 (1955).
26. M.Duchon, M.Miocque, and J.Gautier, Compt.rend., **257C**, 2657 (1963).
27. M.Duchon, M.Miocque, and J.Gautier, Bull.Soc. chim.France, 2471 (1964).
28. M.Duchon, Thèse Doct.Sci., phys., Fac.Sci., Univ. Paris, 1964.
29. J.Colonge and R.Gelin, Bull.Soc.chim.France, 797 (1954).
30. US P.2931836 (1960); Chem.Abs., **54**, 15317 (1960).
31. J.J.Van Daalen, A.Kpaak, and J.F.Arens, Rec.Trav. chim., **80**, 810 (1961).
32. S.Hoff, L.Brandsma, and J.F.Arens, Rec.Trav. chim., **87**, 1179 (1968).
33. A.Kh.Filippova, A.I.Borisova, G.S.Lyashenko, N.A.Ivanova, and M.G.Voronkov, Zhur.Org.Khim., **10**, 177 (1974).
34. J.P.Quertmont, Bull.Soc.chim.France, 20, 386 (1953).
35. A.Habich, R.Barner, R.M.Roberts, and H.Schmidt, Helv.Chim.Acta, **45**, 1943 (1962).
36. M.F.Shostakovskii, A.S.Atavin, V.I.Lavrov, and B.A.Trofimov, Dokl.Akad.Nauk SSSR, 171, 1355 (1966).
37. V.P.Fedulov, E.M.Glazunova, and V.I.Nikitin, in "Khimiya v Tadzhikistane" (Chemistry in Tajikistan), Donish, Dushanbe, 1974, p.35.
38. M.Duchon, M.Miocque, and J.Gautier, Bull.Soc. chim.France, 201 (1968).
39. A.S.Atavin, B.A.Trofimov, and V.I.Lavrov, Zhur. Org.Khim., **8**, 1569 (1972).
40. I.I.Lapkin, Yu.S.Andreichikov, Ya.M.Vilenchik, I.V.Krylova, and R.F.Saraeva, Trudy Ural'sk.Univ., Org.Khim., **2**, 121 (1973).
41. V.I.Nikitin, E.M.Glazunova, and I.M.Potapova, Dokl.Akad.Nauk Tadzh.SSR, **13**, 29 (1970).
42. E.M.Glazunova, I.M.Potapova, L.L.Korenskaya, Kh.K.Khafizov, and I.I.Rakitin, Dokl.Akad.Nauk Tadzh.SSR, **21**, 29 (1978).
43. D.Plouin and R.Glenat, Compt.rend., 272C, 89 (1971).

44. J.S.Combret, L.Horaud, and Y.Leroux, Compt. rend., **274C**, 1404 (1972).
45. R.S.Vartanyan, Zh.V.Kazaryan, and V.F.Kucherov, Armyan.Khim.Zhur., **27**, 295 (1974).
46. I.A.Shikhiev, S.F.Karaev, S.Z.Alieva, and G.A.Yur'eva, Zhur.Org.Khim., **11**, 2134 (1975).
47. L.I.Vereshchagin, L.P.Kirillova, A.V.Rechkina, and N.M.Kuimova, Zhur.Org.Khim., **7**, 907 (1971).
48. A.E.Rosenthal, G.M.Kosolapoff, and R.P.Geyer, Rec.Trav.chim., **83**, 1273 (1964).
49. BRD P.804569 (1951); Chem.Abs., **45**, 8027 (1951).
50. O.A.Prib and M.S.Malinovskii, Zhur.Obshch.Khim., **33**, 653 (1963).
51. F.Hahn and H.Walter, Ber., **54**, 1540 (1921).
52. R.V.Vizgert and R.V.Sendega, Zhur.Org.Khim., **5**, 488 (1969).
53. A.Kh.Filippova, A.I.Borisova, and M.F.Shostakovskii, in "Khimiya Atsetilena" (Chemistry of Acetylene), Nauka, Moscow, 1968, p.64.
54. A.B.Kuchkarov, F.K.Kurbanov, K.M.Sadykov, and Kh.Novruzov, Trudy Tashkentsk.Politekh.Inst., **91**, 140 (1973).
55. I.A.Shikhiev, D.S.Dzhafarov, and S.F.Karaev, Zhur.Obshch.Khim., **45**, 1340 (1975).
56. S.F.Karaev, S.T.Kazieva, I.A.Shikhiev, and Ts.M.Naiberg, Zhur.Org.Khim., **14**, 556 (1978).
57. T.A.Favorskaya and O.V.Sergievskaya, Zhur. Obshch.Khim., **28**, 3232 (1958).
58. E.M.Glazunova, V.P.Fedulov, K.Kh.Khaidarov, and M.R.Dzhavadova, "V Vsesoyuznaya Konferentsiya po Khimii Atsetilena, Tezisy Dokladov, Tbilisi" (Fifth All-Union Conference on the Chemistry of Acetylenes, Tiflis—Abstracts of Papers), 1975, p.146.
59. S.F.Karaev, I.A.Shikhiev, A.K.Khabibova, and Sh.V.Garaeva, Zhur.Obshch.Khim., **45**, 346 (1975).
60. S.F.Karaev, Zhur.Obshch.Khim., **47**, 2546 (1977).
61. D.C.England, L.R.Melby, M.A.Dietrich, and R.V.Lindsay, J.Amer.Chem.Soc., **82**, 516 (1960).
62. R.Mantione, Bull.Soc.chim.France, 4523 (1969).
63. O.G.Yashina, L.D.Gavrilov, S.A.Rudnev, and L.I.Vereshchagin, Zhur.Org.Khim., **6**, 971 (1970).
64. A.I.Feoktistov, O.G.Yashina, L.D.Gavrilov, and L.I.Vereshchagin, Zhur.Org.Khim., **8**, 2066 (1972).
65. L.I.Zakharkin, Izv.Akad.Nauk SSSR, Otd.Khim. Nauk, 846 (1958).
66. M.Usmanov, Kh.P.Ibragimov, and A.G.Makhsumov, Uzbek.Khim.Zhur., No.3, 53 (1977).
67. I.A.Shikhiev, S.F.Karaev, S.T.Kazieva, E.A.Akhundov, and Z.M.Tsalikova, Uch.Zap. AzINEFTEKhIM, No.5, 80 (1975).
68. M.M.Movsumzade, S.F.Karaev, and E.M.Guseinzade, Izv.Vys.Ucheb.Zaved., Khim.i Khim.Tekhnol., **17**, 67 (1974).
69. S.N.Mustafaev, I.A.Shikhiev, R.M.Mustafaev, and M.I.Shikhieva, Zhur.Obshch.Khim., **47**, 1812 (1977).
70. M.M.Movsumzade, S.F.Karaev, and M.E.Askerov, Izv.Vys.Ucheb.Zaved., Khim.i Khim.Tekhnol., **16**, 1689 (1973).
71. M.F.Shostakovskii, V.M.Vlasov, and G.G.Balezina, Zhur.Org.Khim., **2**, 2257 (1966).
72. I.A.Shikhiev, S.F.Karaev, and I.T.Ismailova, Azerb.Khim.Zhur., No.3, 69 (1968).
73. R.G.Jones and M.J.Mann, J.Amer.Chem.Soc., **75**, 4048 (1953).
74. Kh.V.Bal'yan and A.S.Solov'eva, Trudy Leningradsk. Tekhnol.Inst., **42**, 5 (1957).
75. S.F.Karaev, M.M.Movsumzade, N.A.Agamirzoev, and M.E.Askerov, Uch.Zap.AzINEFTEKhIM, No.7, 89 (1975).
76. Japanese P.20450 (1964).
77. V.I.Nikitin, E.M.Glazunova, L.A.Kondrat'eva, and I.M.Potapova, Dokl.Akad.Nauk Tadzh.SSR, **14**, 30 (1971).
78. A.P.Chigogidze, Trudy Inst.Khim.Akad.Nauk Gruz.SSR, 13, 207 (1957).
79. I.A.Shikhiev, V.A.Ibragimov, and S.F.Karaev, Zhur.Obshch.Khim., **41**, 622 (1971).
80. I.A.Shikhiev, Sh.V.Garaeva, Sh.O.Guseinov, and S.F.Karaev, Zhur.Obshch.Khim., **48**, 1368 (1978).
81. S.F.Karaev, Ya.A.Dadasheva, and I.A.Shikhiev, Zhur.Obshch.Khim., **48**, 1775 (1978).
82. I.A.Shikhiev, S.S.Abdulragimova, E.A.Akhundov, S.F.Karaev, and Ya.F.Nasirov, Zhur.Org.Khim., **12**, 513 (1976).
83. S.F.Karaev, S.S.Abdulragimova, M.E.Askerov, and E.A.Akhundov, Azerb.Khim.Zhur., No.5, 47 (1978).
84. D.K.Black and S.K.Landor, J.Chem.Soc., 225 (1965).
85. M.F.Shostakovskii, R.G.Mirskov, V.G.Chernova, and V.M.Vlasov, Zhur.Org.Khim., **4**, 1161 (1968).
86. P.Cresson, Compt.rend., 261C, 1707 (1965).
87. I.A.Shikhiev, Z.M.Tsalikova, and S.F.Karaev, Zhur.Obshch.Khim., **42**, 866 (1972).
88. S.F.Karaev, I.A.Shikhiev, and Z.M.Tsalikova, Zhur.Obshch.Khim., **43**, 109 (1973).
89. B.M.Guseinzade, Candidate's Thesis, Institute of the Petrochemical Industry of the Azerbaijan SSR Academy of Sciences, Baku, 1965.
90. A.S.Atavin, A.N.Mirskova, and E.F.Zorina, Zhur. Org.Khim., **3**, 804 (1967).
91. I.A.Shikhiev, S.F.Karaev, and M.G.Mirzakhanova, Izv.Vys.Ucheb.Zaved., Khim.i Khim.Tekhnol., 12, 1537 (1969).
92. I.A.Shikhiev, V.A.Ibragimov, S.F.Karaev, and G.F.Askerov, Zhur.Org.Khim., **6**, 2045 (1970).
93. Yu.V.Melika and V.I.Staninets, Ukrain.Khim.Zhur., **39**, 280 (1973).
94. F.K.Kurbanov, K.D.Ayapbergenov, and A.V.Kuchkarov, Izv.Vys.Ucheb.Zaved., Khim.i Khim.Tekhnol., **19**, 653 (1976).
95. E.S.Laguchevа and K.D.Petrov, Zhur.Obshch.Khim., **23**, 1347 (1953).
96. A.D.Petrov, L.L.Shchukovskaya, and Yu.P.Egorov, Dokl.Akad.Nauk SSSR, **93**, 293 (1953).
97. M.F.Shostakovskii, I.A.Shikhiev, and N.V.Komarov, Dokl.Akad.Nauk SSSR, **109**, 344 (1956).
98. A.D.Petrov, L.L.Shchukovskaya, S.I.Sadykhzade, and Yu.P.Egorov, Dokl.Akad.Nauk SSSR, **115**, 522 (1957).
99. I.A.Shikhiev, Sh.V.Garaeva, and M.I.Shikhieva, Zhur.Obshch.Khim., **37**, 2778 (1967).
100. I.A.Shikhiev, G.A.Abbasova, and R.Yu.Gasanova, Azerb.Khim.Zhur., No.2, 33 (1974).
101. K.A.Andrianov, I.A.Shikhiev, S.Z.Alieva, and S.F.Karaev, Dokl.Akad.Nauk SSSR, **226**, 332 (1976).
102. I.A.Shikhiev, E.M.Movsumzade, D.A.Shabanova, and T.I.Tasulbekova, Zhur.Obshch.Khim., **43**, 614 (1973).
103. K.A.Andrianov, S.F.Karaev, D.S.Dzhafarov, and I.A.Shikhiev, Dokl.Akad.Nauk SSSR, **229**, 1117 (1976).
104. A.D.Petrov, V.F.Mironov, and V.G.Glukhovtsev, Zhur.Obshch.Khim., **27**, 1535 (1957).
105. I.A.Shikhiev, G.A.Abbasova, and R.Yu.Gasanova, "III Respublikanskaya Nauchno-tekhnicheskaya Konferentsiya po Neftekhimii" (Third Republican Scientific and Technical Conference on Petroleum Chemistry), Guryev, 1974, p.20.

106. M.G.Voronkov, Z.I.Dubinskaya, E.O.Tsetlina, S.F.Pavlov, and I.M.Korotaeva, Izv.Akad.Nauk SSSR, Ser.Khim., 2856 (1974).
107. M.M.Danina, A.S.Medvedeva, N.I.Protsuk, and N.S.Vyazankin, Zhur.Obshch.Khim., **47**, 2292 (1977).
108. I.M.Gverdtsiteli, L.V.Baramidze, and M.I.Dzheliya, Zhur.Obshch.Khim., **42**, 2019 (1972).
109. I.A.Shikhiev, R.Yu.Gasanova, G.F.Askerov, and S.A.Rzaeva, Zhur.Obshch.Khim., **40**, 317 (1970).
110. I.A.Shikhiev, G.F.Askerov, and Sh.V.Garaeva, Zhur.Obshch.Khim., **38**, 639 (1968).
111. R.Faure and G.Descotes, Bull.Soc.chim.France, 1569 (1966).
112. A.M.Sladkov, V.V.Korshak, and A.G.Makhsumov, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 1343 (1963).
113. I.A.Shikhiev, S.F.Karaev, and A.K.Khabibova, Zhur.Obshch.Khim., **43**, 612 (1973).
114. M.M.Movsumzade, S.F.Karaev, M.E.Askerov, and N.A.Agamirzoev, Azerb.Khim.Zhur., No.1, 37 (1973).
115. S.F.Karaev, M.M.Movsumzade, and N.A.Agamirzoev, Zhur.Obshch.Khim., **44**, 131 (1974).
116. S.F.Karaev, M.M.Movsumzade, N.A.Agamirzoev, and Z.M.Tsalikova, "II Vsesoyuznaya Konferentsia po Epoksidnym Monomeram i Epoksidnym Smolam, Tezisy Dokladov" (Second All-Union Conference on Epoxy Monomers and Epoxy Resins—Abstracts of Papers), Dnepropetrovsk, 1974, p.130.
117. K.D.Petrov and E.S.Lagucheva, Zhur.Obshch.Khim., **21**, 1247 (1951).
118. E.S.Lagucheva, Zhur.Obshch.Khim., 24, 2207 (1954).
119. K.D.Petrov and E.S.Lagucheva, Zhur.Obshch.Khim., **25**, 111 (1955).
120. US P.3048598 (1962); Chem.Abs., **59**, 2828 (1963).
121. BRD P. 2241157 (1972).
122. V.Petrov, O.Stephenson, and A.Wield, J.Pharm. Pharmacol., 12, 37 (1960).
123. R.B.Fugitt and L.C.Martinelli, J.Pharm.Sci., **62**, 1894 (1953).
124. I.M.Gverdtsiteli, E.S.Gelashvili, E.A.Topchiashvili, and T.M.Gogiashvili, Trudy Tbilissk.Univ., **A9** (57), 107 (1975).
125. S.F.Karaev, M.M.Movsumzade, and N.A.Agamirzoev, Uch.Zap.AzINEFTEKhIM, No.3, 65 (1972).
126. S.F.Karaev, M.M.Movsumzade, N.A.Agamirzoev, and A.S.Kyazimov, Azerb.Khim.Zhur., No.3, 69 (1974).
127. S.F.Karaev, M.M.Movsumzade, M.E.Askerov, and N.A.Agamirzoev, Uch.Zap.AzINEFTEKhIM, No.5, 61 (1976).
128. S.A.Rzaeva, I.A.Shikhiev, M.E.Askerov, and G.F.Askerov, Azerb.Khim.Zhur., No.6, 89 (1971).
129. A.T.Bottini, F.P.Corson, and E.F.Bottner, J.Org. Chem., **30**, 2988 (1965).
130. M.M.Nasirova, Candidate's Thesis, Azerbaijan Institute of Petroleum Chemistry, Baku, 1967.
131. S.E.Korostova, Candidate's Thesis, Irkutsk State University, 1969.
132. S.F.Karaev, I.A.Shikhiev, and A.K.Khabibova, Azerb.Khim.Zhur., No.2, 61 (1977).
133. US P.2986569 (1961).
134. G.Kamai and E.A.Gerasimov, Trudy Kazansk. Khim.-tekhnol.Inst., **23**, 138 (1957).
135. A.N.Pudovik, I.M.Aladzheva, and L.N.Yakovenko, Zhur.Obshch.Khim., **33**, 3443 (1963).
136. A.N.Pudovik and I.M.Aladzheva, Zhur.Obshch. Khim., 33, 707 (1963).
137. O.Riobe and L.Gouin, Compt.rend., **252C**, 1330 (1961).
138. R.Couffind, M.Gaudemar, and P.Perriot, Bull.Soc. chim.France, 3909 (1967).
139. J.A.Gautier, M.Miocque, H.Moskowitz, and M.Loisy, Compt.rend., **270C**, 440 (1970).
140. A.Kranzfelder and R.Vogt, J.Amer.Chem.Soc., **60**, 1714 (1938).
141. A.S.Atavin, A.I.Mikhaleva, E.G.Chebotareva, N.P.Vasil'ev, and B.A.Trofimov, Zhur.Prikl.Khim., **48**, 1826 (1975).
142. C.Troyanowsky and A.Tsamantakis, Compt.rend., **279C**, 175 (1974).
143. E.A.Mirzabaev and K.A.Lutfillin, Uzbek.Khim.Zhur., No.5, 52 (1972).
144. V.B.Mochalin and N.G.Ivanova, Zhur.Obshch.Khim., 32, 1493 (1962).
145. S.V.Vasil'ev, V.B.Mochalin, and V.I.Likhosherstov, Zhur.Obshch.Khim., **34**, 3180 (1964).
146. M.T.Rogers and M.B.Panish, J.Amer.Chem.Soc., 77, 3684 (1955).
147. M.Charlton, J.Org.Chem., **29**, 2122 (1964).
148. A.V.Shchelkunov, K.A.Ayapbergenov, M.G.Finoeva, and M.G.Muldakhmetov, "Spektroskopiya i ee Primenenie, Doklady IX Sibirskogo Soveshchaniya po Spektroskopii" (Spectroscopy and its Application—Paper at the Ninth Siberian Congress on Spectroscopy), Krasnoyarsk, 1974, p.342.
149. M.G.Voronkov, N.I.Shergina, O.G.Yarosh, N.V.Stroshnikova, and Z.G.Ivanova, Zhur.Obshch. Khim., **45**, 2194 (1975).
150. E.F.Zorina, Candidate's Thesis, Irkutsk State University, 1971.
151. S.W.Charles, F.C.Cullen, G.I.Jones, and N.O.Owen, J.Chem.Soc.Faraday Trans., **70**, 758 (1974).
152. J.P.Tollenaere, H.Meeusen, and F.Hoffer, Spectrochim.Acta, **30A**, 193 (1974).
153. A.Bjozseth and J.Gustavsen, J.Mol.Structure, **23**, 301 (1974).
154. S.W.Charles, F.C.Gullen, and N.C.Owen, J.Chem. Soc.Faraday Trans., 72, 351 (1976).
155. S.F.Karaev, Dokl.Akad.Nauk Azerb.SSR, **33**, 43 (1977).
156. N.Sheppard and D.M.Simpson, Quart.Rev., **6**, 1 (1952).
157. R.A.Nyquist and W.Potts, Spectrochim.Acta, **16**, 419 (1960).
158. J.J.Mannion and T.S.Wang, Spectrochim.Acta, **17**, 990 (1961).
159. N.A.Ivanova, Yu.L.Frolov, G.S.Lyashchenko, A.Kh.Filippova, A.A.Borisova, and M.G.Voronkov, Izv.Akad.Nauk SSSR, Ser.Khim., 84 (1974).
160. R.I.Kruglikova, B.K.Berestevich, L.G.Babaeva, A.I.Chernyshev, V.V.Yastrebov, and B.V.Unkovskii, Zhur.Org.Khim., **10**, 2479 (1974).
161. S.F.Karaev, I.A.Shikhiev, Z.M.Tsalikova, A.K.Khabibova, and F.Mukhtarov, Izv.Vys. Ucheb.Zaved., Khim.i Khim.Tekhnol., **17**, 1035 (1974).
162. I.A.Shikhiev, S.F.Karaev, D.S.Dzhafarov, A.I.Nagiev, and E.M.Isaev, Uch.Zap.AzINEFTEKhIM, No.6, 123 (1975).
163. M.Charton, J.Org.Chem., **37**, 3684 (1972).
164. D.H.Williams and I.Fleming, "Spectroscopic Methods in Organic Chemistry", McGraw-Hill, London, 1966.
165. W.E.Benth and L.D.Colebrook, Canad.J.Chem., **47**, 2473 (1969).
166. C.Bogentoft, C.Lindberg, and U.Svensson, Acta. Chem.Scand., **B30**, 85 (1976).

167. V.V.Takhistov, "Prakticheskaya Mass-spektrometriya Organicheskikh Soedinenii" (Practical Mass Spectrometry of Organic Compounds), Leningrad State University, 1977, p.138.
168. P.E.Butler, J.Org.Chem., **29**, 3024 (1964).
169. J.H.Wotiz, C.A.Hollingsworth, and R.Dessy, J.Org.Chem., **20**, 1545 (1955).
170. B.A.Arbuzov, N.I.Zobova, and F.B.Balabanova, Izv.Akad.Nauk SSSR, Ser.Khim., 1570 (1970).
171. F.Montohari, Gazzetta, **86**, 420 (1956).
172. J.Hine, L.G.Mahone, and C.L.Liotta, J.Org.Chem., **32**, 2600 (1967).
173. G.F.Hennion and D.E.Malonay, J.Amer.Chem.Soc., **73**, 4735 (1951).
174. A.N.Pudovik, Zhur.Obshch.Khim., **21**, 1462 (1951).
175. B.Gredy, Ann.Chim., **4**, 5 (1935).
176. J.F.Arens, Adv.Org.Chem., **2**, 117 (1960).
177. T.H.Vought, R.Vogt, and J.A.Nieuwland, J.Amer. Chem.Soc., **86**, 2120 (1964) [sic].
178. G.Pourcelot and P.Cadiot, Bull.Soc.chim.France, 3016 (1966).
179. O.Yakutaro, J.Pharm.Soc.Japan, **80**, 318 (1960).
180. S.F.Karaev, M.M.Movsumzade, and M.E.Askerov, Zhur.Org.Khim., 11, 654 (1975).
181. S.F.Karaev and D.S.Dzhafarov, Zhur.Org.Khim., **14**, 2618 (1978).
182. S.F.Karaev, Dokl.Akad.Nauk Azerb.SSR, **9**, 33 (1976).
183. R.Gelin and D.Pigasse, Bull.Soc.chim.France, 1840 (1971).
184. R.Gelin and D.Pigasse, Bull.Soc.chim.France, 2186 (1971).
185. G.F.Dvorko and E.A.Shilov, Ukrain.Khim.Zhur., **28**, 833 (1962).
186. J.F.Normant, A.Alexakis, and J.Villieras, J.Organometallic Chem., **57**, C99 (1973).
187. E.Cherbuliez, S.Colak-Antie, M.Gowhari, G.Weber, and J.W.Rabinowitz, Helv.Chim.Acta, **47**, 1602 (1964).
188. I.A.Shikhiev, V.A.Ibragimov, and S.F.Karaev, Uch.Zap.Azerb.Inst.Khim., Ser Khim., No.4, 36 (1972).
189. I.A.Shikhiev, S.F.Karaev, S.T.Kazieva, and Z.M.Tsalikova, Azerb.Khim.Zhur., No.6, 43 (1975).
190. I.A.Shikhiev, B.M.Guseinzade, M.I.Aliev, M.S.Salimov, S.A.Rzaeva, and M.M.Nasirova, Zhur.Obshch.Khim., **34**, 1218 (1964).
191. R.A.Sultanov, Sh.A.Tarverdiev, Sh.M.Novruzov, and S.I.Sadykhzade, Zhur.Obshch.Khim., **42**, 1058 (1972).
192. R.A.Sultanov, Sh.A.Tarverdiev, O.V.Askerov, and S.I.Sadykhzade, Zhur.Obshch.Khim., **42**, 2707 (1972).
193. S.I.Sadykhzade, R.A.Sultanov, Ya.M.Israfilov, and I.A.Khudayarov, Zhur.Obshch.Khim., **43**, 2243 (1973).
194. S.F.Karaev, M.E.Askerov, I.A.Shikhiev, and S.S.Dzhienbaev, Uch.Zap.AzINEFTEKhIM, No.2, 52 (1973).
195. V.Prelog, K.Schenker, and H.Gunthard, Helv. Chim.Acta, **35**, 1598 (1952).
196. V.S.Zavgorodnii, E.S.Sivenkov, V.I.Shipkova, and A.A.Petrov, Zhur.Obshch.Khim., **40**, 2257 (1970).
197. R.Mantione, A.Alves, P.P.Montish, G.A.Wildschut, H.J.T.Bos, and L.A.Brandsma, Rec.Trav.chim., **89**, 97 (1970).
198. L.L.Ivanov, V.P.Nepochatykh, and N.A.Smyslova, Zhur.Org.Khim., **7**, 2623 (1971).
199. Y.Tacachasi and T.Matsumato, J.Chem.Soc.Japan, **84**, 145 (1963).
200. M.Gaudemar and P.Perriot, Compt.rend., **264C**, 1492 (1967).
201. G.Frater and H.Schmid, Helv.Chim.Acta, **53**, 269 (1970).
202. P.Perriot and M.Gaudemar, Bull.Soc.chim.France, 3239 (1968).
203. W.Chodkiewiecz, Ann.Chim., 2, 819 (1957).
204. V.I.Lavrov and A.S.Atavin, "IV Vsesoyuznaya Konferentsiya po Khimii Atsetilena, Doklady" (Fourth All-Union Conference on the Chemistry of Acetylene—Lectures), Alma-Ata, 1972, Vol.1, p.168.
205. Z.M.Tsalikova, Candidate's Thesis, Azerbaijan Institute of Petroleum Chemistry, Baku, 1974.
206. L.A.Kondrat'eva, I.M.Potapova, I.N.Grigina, E.M.Glazunova, and V.I.Nikitin, see Ref.204, 1972, Vol.1, p.158.
207. V.Franzen, Chem.Ber., **88**, 717 (1955).
208. J.F.Gillespie and C.C.Price, J.Org.Chem., **22**, 780 (1957).
209. J.T.Harrison, R.J.Taylor, and I.H.Fried, Tetrahedron Letters, 1165 (1975).
210. G.M.Mkryan, N.A.Papazyan, N.S.Arutyunyan, and Sh.P.Mndzhoyan, Armyan.Khim.Zhur., **21**, 295 (1968).
211. H.J.Lorkowski, J.prakt.Chem., **27**, 6 (1965).
212. A.G.Makhsumov and T.Yu.Nasriddinov, Zhur.Org. Khim., 7, 568 (1971).
213. M.F.Shostakovskii, V.M.Vlasov, and R.G.Mirskov, USSR P.173757 (1963); Byull.Izobr., No.16 (1965).
214. A.Gapurov, U.A.Abidov, N.Madikhanov, and A.G.Makhsumov, see Ref.204, 1972, Vol.1, p.145.
215. I.N.Azerbaev, G.N.Kondaurov, and I.A.Poplavskaya, Izv.Akad.Nauk Kazakh.SSR, Ser.Khim., No.3, 48 (1976).
216. R.I.Kruglikova, B.K.Berestavich, L.G.Babaeva, and B.V.Unkovskii, Izv.Vys.Ucheb.Zaved., Khim.i Khim. Tekhnol., 17, 1824 (1974).
217. E.S.Lagucheva, Zhur.Obshch.Khim., 27, 1528 (1957).
218. H.Huggel and J.Rose, J.Chem.Soc., 335 (1950).
219. I.A.Shikhiev, M.E.Askerov, S.F.Karaev, and S.A.Rzaeva, Izv.Vys.Ucheb.Zaved., Khim.i Khim. Tekhnol., **15**, 534 (1972).
220. Sh.M.Mamedov, M.I.Shikhieva, and I.A.Shikhiev, Azerb.Khim.Zhur., No.2, 85 (1968).
221. I.A.Shikhiev, Sh.V.Garaeva, and L.D.Mamedova, Zhur.Obshch.Khim., **47**, 788 (1977).
222. I.A.Shikhiev, Sh.V.Garaeva, L.D.Mamedova, and S.F.Karaev, Zhur.Org.Khim., **13**, 512 (1978).
223. S.F.Karaev, Dokl.Akad.Nauk Azerb.SSR, 1, 61 (1979).
224. M.F.Shostakovskii, A.S.Atavin, A.N.Mirskova, and E.F.Zorina, "Khimiya Atsetilena, Trudy III Vsesoyuznoi Konferentsii po Khimii Atsetilena" (Chemistry of Acetylene—Proceedings of the Third All-Union Conference on Acetylene Chemistry), edited by A.A.Petrov, Nauka, Moscow, 1972, p.29.
225. N.V.Komarov, O.G.Yarosh, and L.P.Vakhrushev, Izv.Akad.Nauk SSSR, Ser.Khim., 2579 (1971).
226. J.Zsindely and H.Schmidt, Helv.Chim.Acta, **51**, 1510 (1968).
227. B.S.Thyagarajan, K.K.Balasubramanian, and R.B.Rao, Tetrahedron, **23**, 1893 (1967).
228. J.Iwai, Chem.and Pharm.Bull.(Japan), **10**, 926 (1962).
229. J.Iwai, Chem.and Pharm.Bull.(Japan), 11, 1742 (1963).

230. R.B.Woodward and R.Hofmann, J.Amer.Chem.Soc., **87**, 2511 (1965).
231. H.J.Hausen, B.Sutter, and H.Schmidt, Helv.Chim. Acta, **51**, 828 (1968).
232. D.K.Black and S.R.Landor, J.Chem.Soc., 3563 (1963).
233. E.R.H.Jones, J.D.Loder, and M.C.Whiting, Proc. Chem.Soc., 180 (1960).
234. W.Reppe and H.Vetter, Annalen, **582**, 133 (1953).
235. W.Hübel and C.Hoogzand, Chem.Ber., **93**, 103 (1960).
236. S.G.Matsoyan, L.A.Akopyan, and A.A.Saakyan, Armyan.Khim.Zhur., **29**, 436 (1976).
237. W.K.Anderson and E.J.La Voie, J.Org.Chem., **38**, 3832 (1973).
238. S.F.Karaev and D.S.Dzhafarov, Zhur.Org.Khim., **13**, 2620 (1977).
239. R.H.Grubbs, T.A.Pancoast, and R.A.Grey, Tetrahedron Letters, 2425 (1974).
240. K.Ploner and P.Heimbach, Annalen, 54 (1976).
241. I.A.Shikhiev, N.A.Agamirzoev, S.F.Karaev, E.A.Akhundov, and M.N.Shintemirova, Zhur.Org. Khim., **13**, 661 (1977).
242. S.F.Karaev, M.N.Shintemirova, and M.E.Askerov, Dokl.Akad.Nauk Azerb.SSR, **11**, 25 (1978).
243. US P.2868851 (1959).
244. K.M.Makanov, Yu.E.Sarkisov, and V.I.Sobolev, see Ref.16, 1979, Vol.2, p.212.
245. US P.2941010 (1960).
246. BRD P.2241155 (1972).
247. M.G.Voronkov and V.M.Makarskaya, "Appretirovanie Tekstil'nykh Materialov Monomerami i Oligomerami" (Textile Finishing with Monomers and Oligomers), Nauka, 1978, p.19.
248. BRD P.2241156 (1972).
249. Swiss P.443281 (1964).
250. US P.2906661 (1959).
251. US P.2865801 (1958).
252. US P.3859362 (1972).
253. BRD P.1063148 (1960).
254. J.Fellig, J.R.Barnes, A.I.Rachlin, J.P.O'Brien, and A.Focella, J.Agric.Food Chem., 18, 78 (1970).
255. US P.3932668 (1974).
256. O.G.Yashina and L.I.Vereshchagin, Uspekhi Khim., 47, 557 (1978) [Russ.Chem.Rev., No.3 (1978)].
257. A.Shukurov and S.I.Aminov, see Ref.16, 1979, Vol.2, p.220.
258. G.Mayer-Bode, "Herbicides and their Residues" (Translated into Russian), Mir, Moscow, 1972, p.209.
259. S.F.Karaev, Ya.A.Dadasheva, and S.N.Guseinova, see Ref.16, 1979, Vol.2, p.150.
260. J.A.Gautier, M.Miocque, C.Fauran, G.Huguet, G.Raynaud, M.Sergant, and C.Gouret, Chim. thérapeut., 2, 189 (1967).
261. F.Svec, "Pharmacodynamics of Drugs", Slovakia, Bratislava, 1963, Vol.1, p.174.
262. S.F.Karaev, Z.M.Tsalikova, K.F.Karaeva, and I.A.Shikhiev, Azerb.Med.Zhur., No.7, 79 (1974).
263. S.F.Karaev, Yu.I.Vikhlyaev, T.A.Klygul', and I.A.Shikhiev, Azerb.Med.Zhur., No.5, 19 (1971).
264. S.F.Karaev, Yu.I.Vikhlyaev, and D.Ya.Guseinov, Azerb.Med.Zhur., No.5, 16 (1973).
265. S.F.Karaev, T.A.Klygul', and D.Ya.Guseinov, Azerb.Med.Zhur., No.7, 69 (1972).
266. K.E.Schulte and G.Rucker, Fortscr.Arzneim., **14**, 387 (1970).
267. S.F.Karaev, G.A.Abbasova, T.A.Klygul', K.F.Karaeva, Yu.I.Vikhlyaev, and I.A.Shikhiev, Azerb.Med.Zhur., No.1, 76 (1976).
268. I.A.Shikhiev, S.F.Karaev, E.A.Akhundov, and M.E.Askerov, "II Vsesoyuznyi Simpozium po Biologicheskoi Aktivnosti Soedinenii Elementov IV Gruppy" (Second All-Union Symposium on the Biological Activity of Compounds of Group IV Elements), Irkutsk, 1977, p.54.
269. V.I.Nikitin, E.M.Glazunova, I.M.Potapova, K.K.Khaidarov, and T.M.Tukhgaev, in "Sbornik po Khimii Atsetilena" (Handbook of Acetylene Chemistry), Nauka, Moscow, 1972, p.73.
270. Swiss P.572406 (1973).
271. M.A.Poplavskaya, G.N.Kondaurov, and K.A.Abdullin, see Ref.16, 1979, Vol.2, p.188.
272. Sh.Mamedov, "Prostye Efiry Glikolei" (Glycol Ethers), Izd.Akad.Nauk Azerb.SSR, Baku, 1961.
273. T.Baba and T.Yoshino, J.Chem.Soc.Japan, Ind. Chem.Sect., **63**, 1373 (1960).
274. J.J.Funkhouser, Corrosion, **17**, 109 (1961).
275. E.J.Duwell, J.Electrochem.Soc., **109**, 1013 (1962).
276. R.M.Hunson and K.J.Riedy, Metal Finish., **62**, 42 (1964).
277. N.I.Podobaev, S.A.Balezin, A.G.Voskresenskii, and G.F.Semikolenov, in "Ingibitory Korrozii Metallov" (Inhibitors of Metal Corrosion), Sudostroenie, Leningrad, 1965, p.103.
278. N.I.Podobaev, S.A.Balezin, I.A.Shikhiev, M.I.Aliev, S.Z.Israfilova, and F.K.Kurbanov, USSR P.179406 (1965); Byull.Izobr., No.5 (1966).
279. V.E.Novikov, Candidate's Thesis, Lenin Moscow State Pedagogic Institute, 1973.
280. E.S.Ivanov, see Ref.16, 1979, Vol.2, p.149.
281. N.I.Podobaev and F.K.Kurbanov, Neft.Khoz., No.7, 33 (1965).
282. S.A.Balezin, F.K.Kurbanov, and N.I.Podobaev, Zashchita Metallov, **1**, 337 (1965).
283. A.S.Sadykov, F.K.Kurbanov, A.N.Denisov, and A.B.Kuchkarov, Dokl.Akad.Nauk SSSR, **201**, 655 (1971).
284. N.I.Podobaev and V.V.Vasil'ev, Uch.Zap.MGPI Lenina, No.3, 30 (1969).
285. N.I.Podobaev and E.D.Gasparyan, Uch.Zap.MGPI Lenina, 47 (1971).
286. A.G.Voskresenskii, N.I.Podobaev, and S.F.Semikolenov, Uch.Zap.MGPI Lenina, 130 (1971).
287. Z.M.Tsalikova, S.F.Karaev, I.A.Shikhiev, and A.F.Asadullaev, Azerb.Khim.Zhur., No.3, 83 (1978).
288. S.A.Balezin, I.A.Shikhiev, and N.I.Podobaev, USSR P.131632 (1966); Byull Izobr., No.3 (1966).
289. S.A.Balezin, I.A.Shikhiev, and N.I.Podobaev, USSR P.131633 (1966); Byull.Izobr., No.8 (1966).
290. S.A.Balezin, I.A.Shikhiev, and I.I.Aliev, USSR P.182826 (1966); Byull.Izobr., No.10 (1966).
291. A.I.Altsybeeva and S.Z.Levin, "Ingibitory Korrozii Metallov" (Inhibitors of Metal Corrosion), Khimiya, Leningrad, 1968, p.54.
292. R.N.Gafurova, F.K.Kurbanov, and A.B.Kuchkarov, Izv.Vys.Ucheb.Zaved., Khim.i Khim.Tekhnol., **19**, 325 (1976).
293. F.K.Kurbanov, K.M.Sadykov, and A.B.Kuchkarov, Korroziya Zashchita Neft.Prom., No.9, 8 (1973).
294. S.F.Karaev, S.T.Kazieva, and I.A.Shikhiev, Korroziya Zashchita Neft.Prom., No.2, 10 (1978).
295. S.F.Karaev, S.A.Balezin, E.S.Ivanov, S.Z.Alieva, and I.A.Shikhiev, Korroziya Zashchita Neft.Prom., No.7, 17 (1976).
296. S.F.Karaev, I.A.Shikhiev, D.S.Dzhafarov, A.K.Khabibova, and N.I.Podobaev, Korroziya Zashchita Neft.Prom., No.7, 1 (1976).

297. F.K.Kurbanov, K.D.Allebergenov, A.B.Kuchkarov, and S.A.Sarankina, Izv.Akad.Nauk Turkmensk.SSR, Ser.Fiz.Tekh.Khim.Geol.Nauk, 121 (1975).
298. S.F.Karaev, N.I.Podobaev, Z.M.Tsalikova, and I.A.Shikhiev, USSR P.487962 (1975); Byull.Izobr., 38 (1975).
299. S.F.Karaev, Z.M.Tsalikova, N.I.Podobaev, and I.A.Shikhiev, Korroziya Zashchita Neft.Prom., No.10, 3 (1974).
300. S.F.Karaev and I.A.Shikhiev, "Nauchno-tekhnicheskoe Soveshchanie 'Ingibitory Korrozii' (V Negreevskie Chteniya), Tezisy Dokladov" (Scientific and Technical Conference on Corrosion Inhibitors (Fifth Negreev Readings)—Abstracts of Papers), Baku, 1977, p.72.
301. A.Fischer, Symp.Europ.sevn.los Inhich de Corrosion, **5**, 31 (1961).
302. I.N.Putilova, N.V.Rudenko, and A.P.Terent'ev, Zhur.Prikl.Khim., **38**, 494 (1964).
303. I.N.Putilova and A.M.Dolua, Zashchita Metallov, No.4, 4 (1968).
304. N.I.Podobaev and V.I.Kotov, Zhur.Prikl.Khim., **42**, 1569 (1969).
305. T.Kato, H.Sakai, and T.Mirakawa, Corrosion Eng., **18**, 307 (1969).
306. I.L.Rozenfel'd, "Ingibitory Korrozii" (Corrosion Inhibitors), Khimiya, Moscow, 1977, p.152.

Azizbekov Azerbaijan Institute of
Petroleum and Chemistry,
Baku

Translated from *Uspekhi Khimii*, **49**, 1801-1828 (1980) U.D.C. 547.341

α,β-Unsaturated Heteroatomic Compounds in 1,3-Dipolar Addition Reactions

V.A.Galishev, V.N.Chistokletov, and A.A.Petrov

The reactions of α,β-unsaturated heteroatomic compounds with an unshared electron pair in the heteroatom, proceeding via the 1,3-dipolar addition mechanism, are examined. The ideas about 1,3-dipolar compounds developed by Huisgen are extended to compounds with elements in the Long Periods (phosphorus and sulphur).
The bibliography includes 231 references.

CONTENTS

I. Introduction 880
II. Oxygen- and nitrogen-containing π-systems 881
III. Phosphorus(III)-containing π-systems 882
IV. Sulphur-containing π-systems 886

I. INTRODUCTION

Among the methods for the synthesis of alicyclic and heterocyclic compounds, which play an exceptional role in modern organic chemistry and industry (mainly in the synthesis of polymers, dyes, pesticides, medicinal preparations, etc.), reactions in which ring formation involves the dissociation of π-bonds only, without the scission of any other fragments, occupy a notable place. Such processes include the reactions of carbenes with unsaturated compounds, the dimerisation of allenes, syntheses involving alkadienes (of the 4 + 1 = 5 type), the diene synthesis (4 + 2 = 6), and 1,3-dipolar cycloaddition (3 + 2 = 5 or 3 + 3 = 6).

The term 1,3-dipolar cycloaddition was proposed by Smith in 1938.[1] The complete classification of 1,3-dipolar systems (1,3-DS) was given by Huisgen[2,3]. According to Huisgen's definition, a 1,3-dipolar system can be any compound a–b–c, in which the atom a has an electron sextet and constitutes a positive centre, the atom c has a free electron pair and carries a negative charge, and the atom b has an unshared electron pair. According to Huisgen, six octet-stabilised 1,3-DS with a double bond and twelve octet-stabilised dipoles without a double bond can be constructed with elements in the Second Period. All the 1,3-DS with a double bond are known. Typical 1,3-DS are nitrile imines, nitrile ylids, nitrile *N*-oxides, diazo-compounds, and azides. Reactions involving addition to double bonds via a 3 + 2 = 5 mechanism and dimerisation reactions proceeding by both 3 + 2 = 5 and 3 + 3 = 6 mechanisms are most characteristic of 1,3-DS.

Huisgen's school investigated widely only the reactions of 1,3-DS incorporating the elements of the Second Period. The authors of the present review attempted to analyse on the basis of literature data the possibility of constructing 1,3-DS with participation of the elements of the Long Periods, in particular phosphorus and sulphur. Attention was turned to α,β-unsaturated compounds of the above elements, which correspond to Huisgen's limiting carbenoid structure of the 1,3-DS.

The reactivity of unsaturated compounds containing a heteroatom with an unshared electron pair ($\ddot{Z}$–X=Y, $\ddot{Z}$–X≡Y) in the α-position is determined by the degree of localisation of the unshared electron pair of the element $\ddot{Z}$ and the presence of vacant *d* orbitals in the latter. According to modern ideas, a heteroatom with an unshared electron pair exhibits as a rule an electron-donating effect in relation to the multiple bond: the unshared electron pair of the heteroatom is delocalised (p,π conjugation)[4]. The capacity of heteroatoms with an unshared electron pair for p,π conjugation is determined, according to Tsvetkov and Kabachnik[5], mainly by the nature of the hybridisation of this pair. Since the capacity of heteroatoms for p,π conjugation increases with increasing *p* character of the unshared electron pair, atoms can be arranged in the following sequence in terms of their capacity for p,π conjugation: N > O > S > P. The validity of this sequence has been confirmed by quantitative data for the ability of aromatic phosphines, sulphides, and amines to form polar complexes with strong acceptors (for example Group III metal halides).[6-10]

Whereas in the case of elements in the Second Period (O, N) the distribution of electron density in the ground state of the molecule gives rise only to a π-donor effect[11,12], for elements of the Third Period (S, P) the effect caused by the involvement in the conjugation of low-lying 3*d* orbitals ($d-p$) π-conjugation can also be manifested. The interaction of 3*d* orbitals with the electrons of the multiple bonds is responsible for the mesomeric electron-accepting properties of the heteroatoms of the elements of the Third Period: the electron density at the heteroatom increases and that in the multiple bond decreases. It has been shown[13] that the symmetry of the 3*d* orbitals permits overlap with a *p* orbital of the type of (p,p)π-bond. The possibility of ($d-p$)π-conjugation has also been confirmed for arylphosphines[14-16]. The degree of conjugation depends on the electronegativity of the substituents: a more electronegative substituent decreases the electron density at the phosphorus atom, promoting the contraction of the 3*d* orbitals and a stronger ($d-p$)π-interaction[13,17,18]. For example, in this connection, the degree of π-binding in acetylenic compounds of phosphorus(III) is greater than in the ethylenic compounds owing to the greater electronegativity of carbon in the *sp*-hybridised state that in the sp^2-state[19,20].

Thus in the Z–X=Y or Z–X≡Y systems, where X is a heteroatom with unshared electron pairs but without vacant *d* orbitals (Z = O or N), the electron density is markedly displaced from the heteroatom towards the multiple bond. By virtue of the delocalisation of the unshared electron pair, the nitrogen and oxygen atoms manifest π-donor properties[21].

If the heteroatom Z = S or P, then, apart from the electron pairs, low-lying vacant *d* orbitals can participate in the distribution of electron density. The negative inductive and weak π-donor effects of the sulphur atom as well as the involvement of the 3*d* orbitals in conjugation lead to the appearance of opposed shifts[21]. In the phosphorus atom the

effect due to p,π-conjugation is either absent or is overlapped by the $(d-p)\pi$-conjugation. As stated above, this is associated with the diminution of the p character of the unshared electron pair at the phosphorus atom and therefore, despite the presence of the electron pair, tervalent phosphorus in α,β-unsaturated compounds exhibits π-acceptor properties in relation to the multiple bonds.

The distribution of electron density in π-systems containing heteroatoms with unshared electron pairs has been studied by various physical methods: with the aid of NMR,[12,21-30] ultraviolet spectroscopy[31-36], infrared spectroscopy[37,38], and the determination of dipole moments[39]. The results of these studies indicate different roles of the effects of the p,π- and $(d-p)\pi$-conjugations in the distribution of electron density and hence a difference in the chemical properties of the compounds investigated.

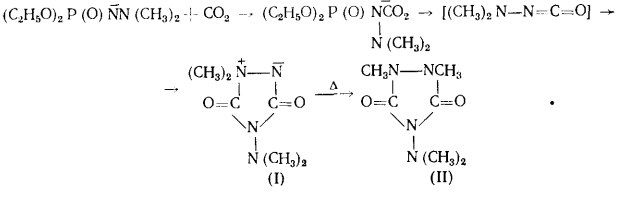
α,β-Unsaturated heteroatomic compounds can enter into 1,3-dipolar addition reactions in two ways. If the unshared electron pair is delocalised over the entire system, then the latter is a dipolarophile and interacts with the 1,3-DS via its multiple bond in accordance with the usual 3 + 2 = 5 cyclisation mechanism with formation of five-membered cyclic compounds. On the other hand, if conditions are created in the initial π-system for the localisation of the unshared electron pair of the heteroatom, two reaction centres are produced (the multiple bond and the heteroatom). Such α,β-unsaturated heteroatomic compounds can undergo cyclisation reactions with participation of the heteroatom both via 3 + 3 = 6 mechanism, i.e. via a mechanism involving the "mixed dimerisation" of the 1,3-DS, and via the 3 + 2 = 5 mechanism, behaving as a 1,3-DS. In the latter case only the electrophilic multiple bonds can behave as dipolarophiles.

II. OXYGEN- AND NITROGEN-CONTAINING π-SYSTEMS

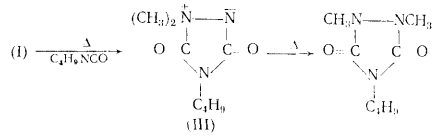
As a rule oxygen- and nitrogen-containing π-systems behave as dipolarophiles in 1,3-dipolar addition reactions. The mode of the reactions of such systems with 1,3-DS does not differ from that of the reactions of unsubstituted olefins and acetylenes: ynamines[40,41], enamines[42-50], and acetylenic [51-59] and vinyl ethers[60-62] form under these conditions five-membered cyclic compounds without the inclusion of the heteroatom in the ring.

The reactions of α,β-unsaturated oxygen-containing compounds, proceeding via a mechanism of the 1,3-dipolar addition type with inclusion of the oxygen atom in the reaction, have not so far been observed.

α,β-Unsaturated nitrogen-containing compounds can react via a 1,3-dipolar cyclisation mechanism with participation of the nitrogen atom only when the system is highly polarised. Thus it has been established[64] that the carboxylation of a phosphoramidate ion[63] (derivative of *N,N*-dimethylhydrazine) leads to the formation of a dimethylaminoisocyanate dimer (I), having the ylid structure. Its pyrolysis leads to the stable 1-dimethylamino-3,4-dimethyl-1,3,4-triazolidine-2,5-dione (II):

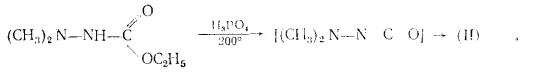


The interaction of the dimer (I) with an excess of butyl isocyanate leads to the formation of a new ylid (III), in which there is also a possibility of the migration of the methyl group:

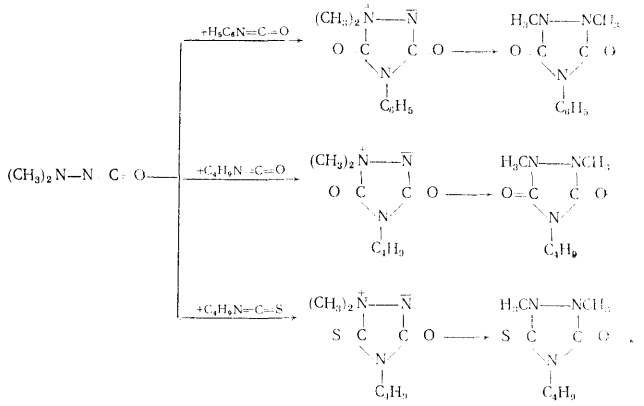


In the case of the t-octyl isocyanate, this type of reaction is reversible and at 90 °C the equilibrium is fully displaced towards the initial reactants, probably owing to steric hindrance.

The ylid structure of compound (I) and its analogues has been demonstrated by the reaction with HCl in benzene and subsequent elimination of methyl chloride. The authors[64] used also another method for synthesising dimethylaminoisocyanate using *N*-dimethylaminourethane:

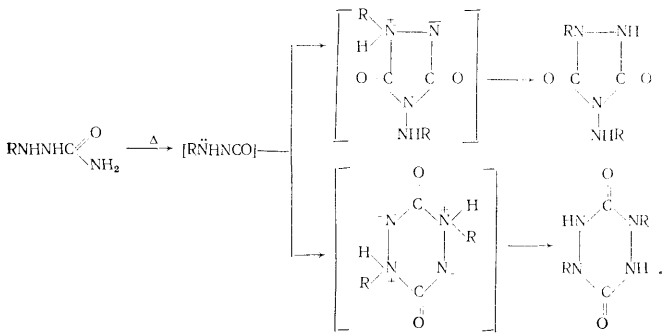


If the reaction is carried out in the presence of isocyanates or isothiocyanates, it is possible to "intercept" the intermediate monomeric dimethylaminoisocyanate:

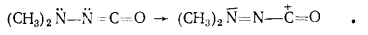


The stable triazolidine derivatives are formed as a result of the migration of the methyl groups. Pyrolysis of *N*-dimethylaminourethane in the presence of isocyanate or isothiocyanate constitutes a convenient method for the synthesis of various methyl-substituted triazolidines.

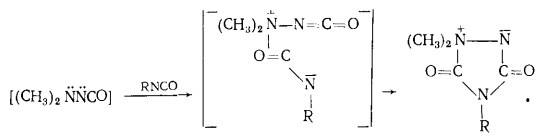
The pyrolysis of methylaminourea likewise leads to the formation of a triazolidinedione[65] and there is also a possibility of dimerisation via a 3 + 3 = 6 mechanism, leading to triazine derivatives:



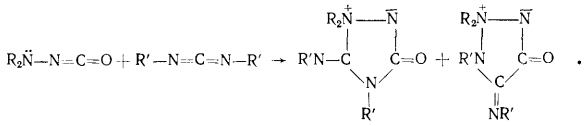
All the reactions described above may be regarded as 1,3-dipolar cycloadditions via the 3 + 2 = 5 mechanism. One molecule of dimethylaminoisocyanate behaves as a 1,3-DS, while another molecule of the same compound or a molecule of iso- or isothio-cyanate behaves as a dipolarophile. The stability of the product is determined by the stability of the ylid linkage. Dimethylaminoisocyanates can be classified as rare nitrogen-containing π-systems in which an electron pair is localised at the nitrogen atom adjoining the multiple bond. The localisation is probably caused by the presence of the adjacent nitrogen atom, which also has an unshared electron pair and this prevents the delocalisation of the charge over the system and enhances sharply the nucleophilic properties of the amino-nitrogen:



The extremely reactive 1,3-DS adds to the multiple bond of the initial molecule or alkyl isocyanate as a result of attack by the nucleophilic nitrogen atom of the dimethyl amino-group on the *sp*-hybridised carbon atom of the isocyanate group. Ring closure occurs when the nitrogen atom of the NCO group interacts with the carbon atom of the aminoisocyanate[64,66]:

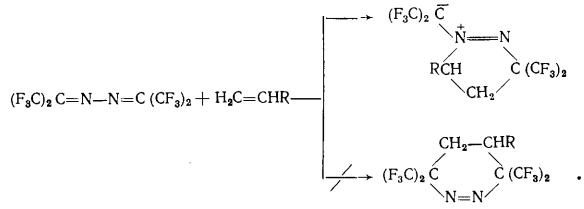


The reactions of dimethylaminoisocyanates with carbodiimides are also known. One of the two reaction products is a structural analogue of compound (I) and the other contains a bond between the amino-nitrogen of the dimethylaminoisocyanate and one of the nitrogen atoms (and not the *sp*-hybridised carbon atom) of the carbodi-imide:



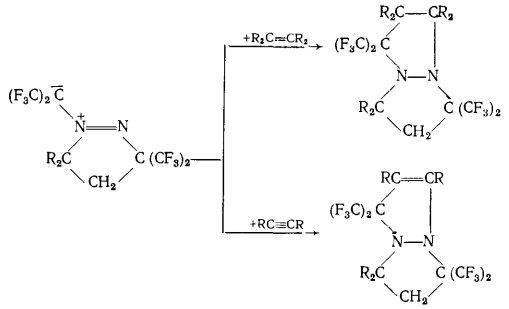
This probably involves nucleophilic attack on the carbodiimide nitrogen with transfer of the negative charge to the *sp*-hybridised carbon atom[67,68].

The interaction of hexafluoroacetone azine[69,70] with terminal olefins or dienes can also serve as an example of the 1,3-dipolar activity of a nitrogen-containing π-system[71-83]. The localisation of the unshared electron pair at the nitrogen atom converts such compounds into 1,3-DS. Hexafluoroacetone azine reacts with olefins of the type $H_2C{=}CHR$ and $H_2C{=}C(CH_3)R$ and with dienes to form, in the first stage, the product of 1,3-dipolar cycloaddition via the 3 + 2 = 5 mechanism and not via the mechanism of diene synthesis (4 + 2 = 6):[74]



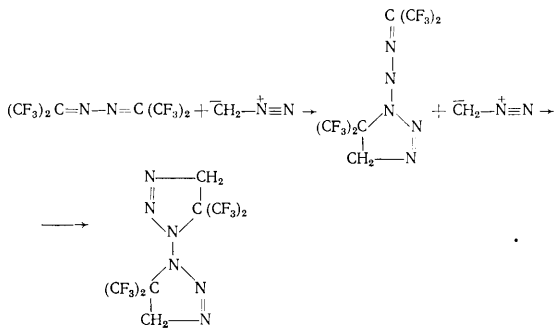
The product is a stable azomethine imine[2,76,81,83-88], If R is a bulky group, subsequent intramolecular deprotonation and reprotonation take place with formation of 3-pyrazolines[74-76,81,89].

The stable azomethine imine is capable of reacting further with systems containing multiple bonds via the usual 1,3-dipolar cycloaddition mechanism[74,75,80,81] to form a bicyclic heterocycle. This product can also be formed immediately if an excess of the olefin relative to the azine is taken:



Such mixed cycloaddition of two differently substituted systems with double bonds (or one system with a double bond and another system with a triple bond) in the 1,3 : 2,4-positions relative to hexafluoroacetone azine with intermediate formation of a stable azomethine imine leads to a new pathway to bicyclic heterocycles of the type of 1,5-diazobicyclo-octenes and 1,5-diazobicyclo-octanes and their heteroanalogues. One should note that the cycloaddition cross-reactions of azines with olefins had also been described earlier[92-97], but due importance had not been attached to them.

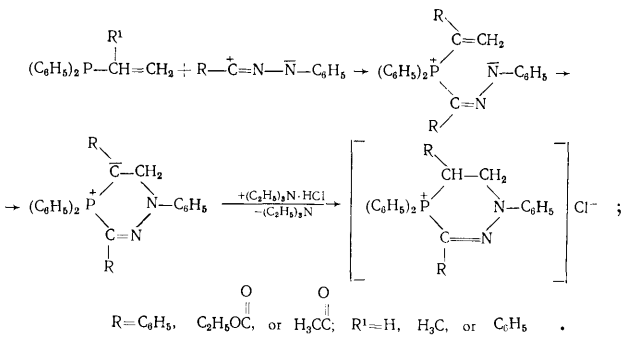
Hexafluoroacetone azine behaves as a dipolarophile in reactions with classical 1,3-DS. Thus the reaction with diazomethane involves one or both C=N bonds of the initial compound[98]:



III. PHOSPHORUS(III)-CONTAINING π-SYSTEMS

The interaction of α,β-unsaturated compounds of tervalent phosphorus and 1,3-DS can proceed via two reaction centres: the heteroatom and the multiple bond. In the general case phosphorus-containing π-systems can be regarded as reactive 1,3-DS with a negative charge on the phosphorus atom and a positive charge on the extreme carbon atom of the multiple bond. The first such reaction of α,β-unsaturated phosphorus(III) compounds with 1,3-DS via the mechanism involving mixed dimerisation of 1,3-DS (3 + 3 = 6) with participation of the phosphorus atom and the multiple bond in the reaction

and the formation of six-membered heterocycles has been described[99]. In this study the interaction of diphenylvinylphosphine with *C,N*-diphenylnitrile imine in the presence of triethylamine hydrochloride yielded a phosphonium salt—a derivative of 1,4,5,6-tetrahydrophosphoniapyridazine:

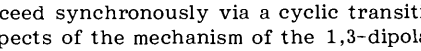


R=C_6H_5, C_2H_5OC, or H_3CC; R^1=H, H_3C, or C_6H_5 .

Alkenylphosphines having a substituent in the α-position relative to the multiple bond or one methyl group in the β-position react with nitrile imines in this way[100-103] regardless of their structure.

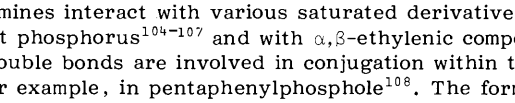
Nucleophilic attack by a tricoordinate phosphorus atom on the carbon atom of the nitrile imine leads apparently to the initial formation of a dipole ion, which, by virtue of the strong polarisation of the multiple bond and the influence of the tetracoordinate phosphorus atom, cyclises to a phosphorane. The cyclic phosphorane, being a stronger base than triethylamine, reacts with triethylamine hydrochloride to form a stable phosphonium salt. The stepwise course of the reaction can probably be regarded as a possible extreme case; one cannot rule out the possibility that such reactions can also proceed synchronously via a cyclic transition state. Different aspects of the mechanism of the 1,3-dipolar cycloaddition reaction are considered in reviews published previously[90,91].

When there are two methyl or phenyl groups in the β-position in alkenylphosphines, the reaction stops in some cases at the stage involving the formation of dipolar ions, the stabilisation of which is promoted by electron-accepting groups at the carbon atom of the nitrile amine. Account should also be taken of the steric hindrance caused by the substituents at the β-carbon atom of the multiple bond[101]:



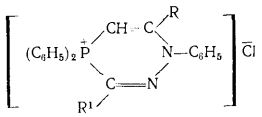
R=C_2H_5OCO, or H_3CCO .

The same azomethylenephosphoranes are formed when nitrile amines interact with various saturated derivatives of tervalent phosphorus[104-107] and with α,β-ethylenic compounds whose double bonds are involved in conjugation within the ring, for example, in pentaphenylphosphole[108]. The formation of these compounds confirms the proposed mechanism of the interaction of α,β-unsaturated derivatives of phosphorus(III) with nitrile amines:



R=Ar, $(Alk)_2N$, or AlkO; R^1=C_2H_5OCO, or H_3CCO; R^2=Ar .

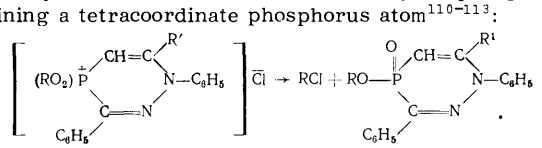
In contrast to alkenylphosphines, alkynylphosphines react with nitrile imines to form cyclic quasi-phosphonium compounds regardless of the degree of substitution at the β-carbon atom of the multiple bond[103,109,110], which indicates a lower sensitivity of acetylenic derivatives of phosphorus(III) to steric hindrance than that of the ethylenic derivatives:



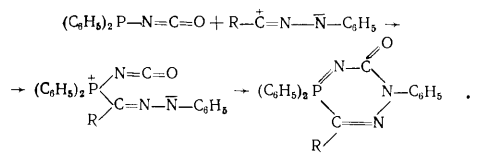
R=H, CH_3, $C(CH_3)_3$, or C_6H_5 .

The degree of conjugation of the 3*d* orbitals of the phosphorus atom with a triple bond is greater than with a double bond[19,20], so that the β-carbon atom should be more activated in the former case. Account should also be taken of the fact that the *sp*-hybridised carbon atom is more reactive in reactions with nucleophiles.

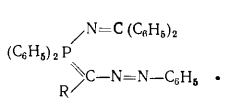
α,β-Unsaturated ethylenic and acetylenic phosphonites react with nitrile amines regardless of the nature of the substitution in the β-position of the multiple bond via the 1,3-DS mixed dimerisation mechanism. The quasi-phosphonium salts obtained undergo the Arbuzov rearrangement with elimination of the alkyl halide and the formation of a cyclic phosphinate containing a tetracoordinate phosphorus atom[110-113]:



The amides of alkenyl- and alkynyl-phosphonous acids form cyclic compounds only with nitrile amines without electron-accepting substituents at the carbon atom. In all the remaining cases the reaction stops at the stage involving the formation of open-chain azomethylenephosphoranes[101,114]. Heteroatomic α,β-unsaturated compounds of tervalent phosphorus such isocyanates of phosphorus acids and methyleneaminophosphines can also enter into Huisgen's 1,3-dipolar addition reactions with 1,3-DS. The reaction with diphenylphosphinyl isocyanate also proceeds via the 1,3-DS "mixed dimerisation" mechanism and stops at the stage involving the formation of a cyclic ketoiminophosphorane[115,116]. The isolation of this product can be regarded as confirmation of the possibility of the formation of cyclic methylenephosphoranes as intermediates also in the other cases described above:



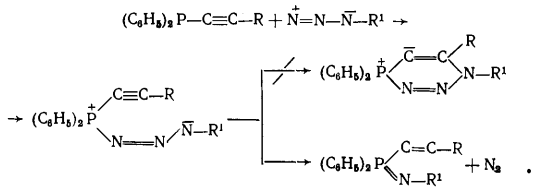
Acyclic azomethylenephosphoranes are products of the interaction of diphenylmethyleneaminophosphines with nitrile imines:



Cyclisation does not take place, apparently owing to the steric hindrance in ring closure caused by the phenyl groups[117].

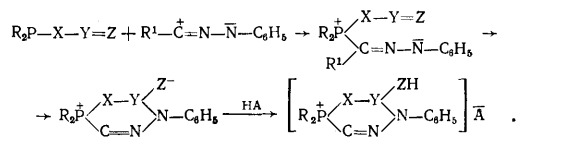
The choice of a 1,3-DS for reactions with α,β-unsaturated phosphorus(III) compounds is limited by the high reducing capacity of the latter. This factor rules out the possibility of using oxygen-containing 1,3-DS such as nitrile oxides, nitrones, etc. Together with nitrile imines, organic azides can serve as 1,3-DS. The interaction of α,β-unsaturated acetylenic phosphines with organic azides does not lead to cyclic products. The initial dipolar ion (phosphatriazene) is unstable and decomposes with liberation of nitrogen and the formation of a phosphine imine with an unsaturated group at

the phosphorus atom[118]:

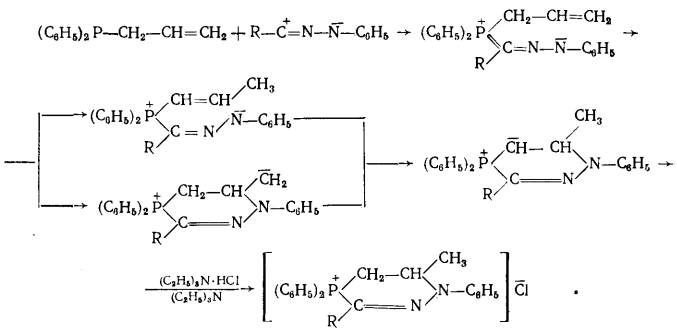


The nucleophilic mechanism of the reaction of unsaturated phosphorus(III) compounds with nitrile imines is also indicated by the relative rate constants for the reactions of different phosphorus-containing compounds with diphenylnitrile imine. For example, $(k_2)_{rel} = 0.56$, 1.00, and 2.72 for $(C_2H_5O)_2P{-}C{\equiv}C{-}C_6H_5$, $(C_6H_5)_2P{-}C{\equiv}CH$, and $[(CH_3)_2N]_2P{-}C{\equiv}C{-}C(CH_3)_3$ respectively[114]. The study of the dipole moments and ^1H NMR spectra of unsaturated phosphorus(III) derivatives is also important for the understanding of the mechanism of this reaction[119,120].

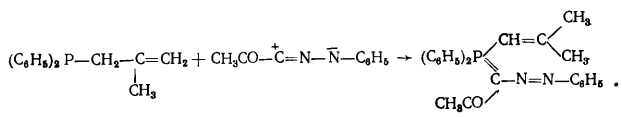
In the case of β,γ-unsaturated phosphorus(III) compounds the manifestation of 1,3-dipolar activity may be expected when an active electrophile is present in the β-position:



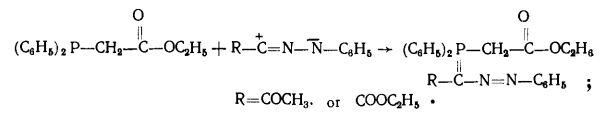
β,γ-Unsaturated phosphines (studied in relation to allyldiphenylphosphine)[102] isomerise in the reaction and the resulting phosphoniapyridazine is identical with the products of the reaction of diphenylpropenylphosphine (an α,β-unsaturated compound of tervalent phosphorus) with nitrile imines:



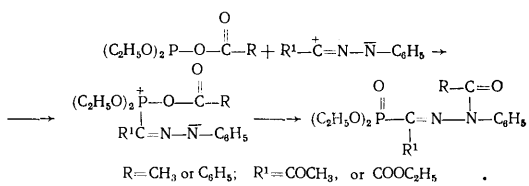
The isomerisation can occur either in the stage involving the formation of the intermediate dipolar ion or in the intermediate formed as a result of the attack by the nitrogen atom on the β-position of the multiple bond; this is followed by the transfer of a proton from the methylene group. The first pathway is apparently preferred, since the positively charged phosphorus atom facilitates the isomerisation of the allyl group[121]. In addition, it has been established that methylallyldiphenylphosphine reacts with *C*-acetyl-*N*-phenylnitrile imine to form azomethylenephosphorane as the product of the isomerisation of the phosphorane formed in the first stage[102]:



When nitrile imines react with ethoxycarbonylmethyldiphenylphosphine, the ethoxycarbonyl group is not involved in the reaction. Evidently the abstraction of a methylene proton and the substitution of the ethoxy-group, without which a stable product cannot be formed, is impossible in this case. The reaction stops at the stage involving the formation of azomethylenephosphorane[122]:

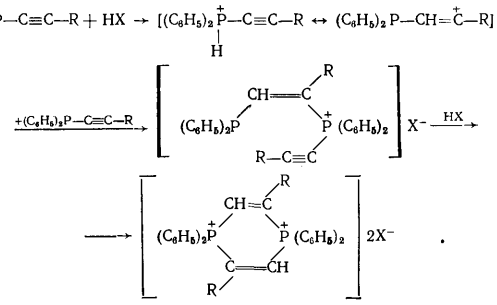


Only mixed anhydrides of dialkylphosphorus and carboxylic acids (diethyl acetyl phosphite and diethyl benzoyl phosphite) react with nitrile imines, where the carbon atom of the carbonyl group is involved in the reaction in addition to the phosphorus atom. As a result of the rearrangement, the final reaction products are acyclic phosphonates



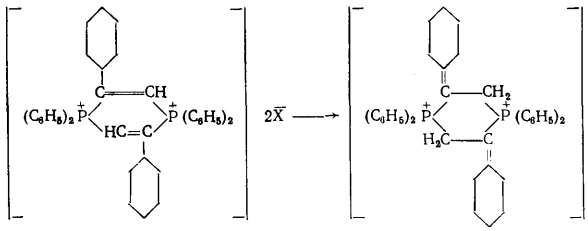
Mixed anhydrides of dialkylphosphorous and carboxylic acids react via a similar mechanism with methyl iodide[123], aldehydes, and ketones[124-126].

α,β-Acetylenic phosphines can also participate in simple dimerisation reactions via the 3 + 3 = 6 mechanism. Derivatives of 1,1,4,4-tetraphenyl-1,4-diphosphiniacyclohexa-2,5-diene are formed from alkynyldiphenylphosphines in glacial acetic acid in the presence of HBr.[127,129] According to the authors, the initial phosphine is protonated at the phosphorus atom in the first stage of the reaction, as a result of which the β-carbon atom of the multiple bond becomes more electrophilic owing to the strong conjugation of the 3*d* orbitals of phosphorus with the π-electrons of the triple bond. A second phosphine molecule with a localised unshared electron pair attacks the β-carbon atom of the first phosphine molecule with subsequent cyclisation and formation of a diphosphonium salt[130,131]:



The mode of this reaction, which proceeds in a protic solvent, can depend on the nature of the halide involved in it. The strongest nucleophile (the iodide ion) prevents cyclisation and the competing reaction involving the formation of β-iodovinylphosphine takes place; in the presence of the bromide ion, which is less nucleophilic than the iodide ion, cyclisation proceeds more readily. It is facilitated still further in the presence of the chloride ion. If the substituents in the β-position of the multiple bond are alkyl, cyclopentyl,

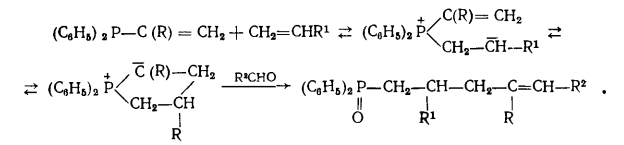
or cyclohexyl, then heating of the cyclic salts can lead to irreversible isomerisation, showing that the degree of stabilisation of the system as a result of the π-electronic interaction with the phosphorus atom is low[129,131]. For example, with R = cyclohexyl, the isomerisation proceeds as follows:



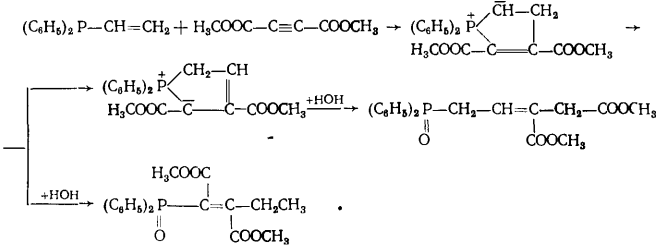
It is noteworthy that the study of the electrochemistry of derivatives of 1,4-diphosphophoniacyclohexa-2,5-diene led to the discovery of a new class of radical-cations[132,133].

Phosphorus-containing π-systems, like the classical 1,3-DS, can react with compounds containing activated multiple bonds (dipolarophiles) via the 3 + 2 = 5 mechanism. The five-membered heterocycles formed in these reactions are unstable. in some cases. For this reason, the products of their interaction with other substances have been isolated.

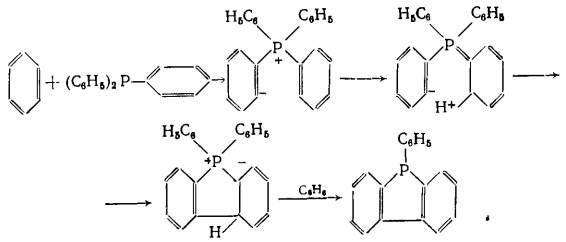
The interaction of vinylphosphines with activated olefins leads to the formation of five-membered ylids, apparently with the intermediate formation of dipolar ions[134]. When the reaction is carried out in the presence of aldehydes, the five-membered ylid undergoes the Wittig reaction with formation of the corresponding phosphine oxide[135]:



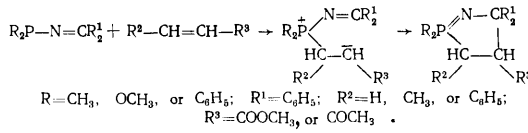
Diphenylphosphine reacts with the dimethyl ester of acetylenedicarboxylic acid to form a cyclic compound which can rearrange to a tautomer having the ylid structure: on interaction with water, both ylids decompose with formation of phosphine oxides[136]:



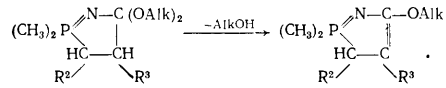
When triphenylphosphine interacts with dehydrobenzene, biphenylenephenylphosphine is formed as one of the products. A betaine is apparently formed as an intermediate with subsequent cyclisation and elimination of benzene[137]:



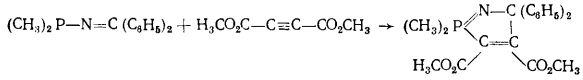
Phosphorus-containing dipolar π-systems with multiple heterobonds can also undergo the 3 + 2 = 5 cycloaddition reactions. Methyleneaminophosphines[138] react with derivatives of acrylic, crotonic, and cinnamic acids and α,β-unsaturated ketones to form five-membered addition products via the 2 + 3 = 5 mechanism[139,140] and the intermediate formation of the betaine is also postulated:



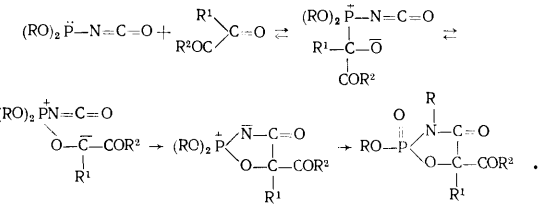
If R^1 = OAlk, then the cyclic product is converted with elimination of the alcohol, forming a more stable product[140]:



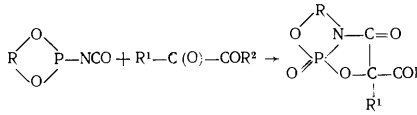
The dimethyl ester of acetylenedicarboxylic acid reacts with methyleneaminophosphines to form a cyclic iminophosphorane:



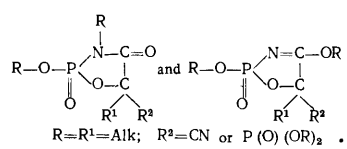
Dialkyl and alkylene phosphoromonoisocyanatidites also react via the 3 + 2 = 5 1,3-dipolar cycloaddition mechanism with carbonyl compounds activated by electron-accepting substituents α,β-unsaturated phosphorus(III) compounds with an unshared electron pair at the phosphorus atom functioning as the 1,3-DS. In cases where the dipolarophiles are the esters of α-ketocarboxylic acids and α,β-diketocarboxylic acids or α-diketones, the reaction begins with nucleophilic attack by the phosphorus atom on the carbon atom of the carbonyl group with formation of a dipolar ion, which rapidly isomerises to the thermodynamically more stable ion with P–O–C bonds. The latter is stabilised with formation of a five-membered ring as a result of the attack by the carbanion on the carbon atom of the isocyanate group. The final reaction product is obtained after subsequent *N*-alkylation[141–143]:



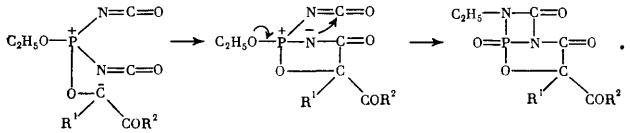
Alkylene phosphoroisocyanatidites form bicyclic addition products[143,144]:



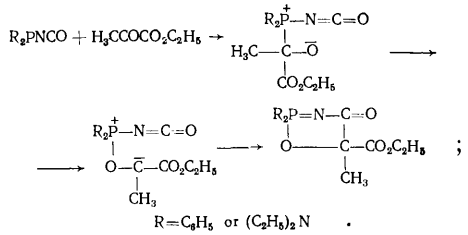
If the dipolarophiles are the nitriles of α-ketocarboxylic acids, the final stage of the reaction is not only *N*-alkylation, but also *O*-alkylation and a mixture of two products is formed[145,146]:



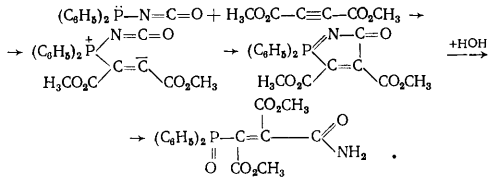
The ethyl ester of a phosphorodi-isocyanatidic acid reacts with carbonyl-containing compounds via a mechanism common to such reactions, but the second isocyanate group also participates in the stabilisation process[147]:



The intermediate dipolar ions can be stabilised not only via transalkylation but also via a pathway involving the formation of cyclic phosphine imines. The reaction between diethyl phosphoroisocyanatidite and aldehydes[148] and between isocyanatodiphenylphosphine and the bis-(*N*,*N*-diethylamide)-of phosphoroisocyanatidic acid, on the one hand, and ethyl pyruvate, on the other, also proceeds via this pathway[149]:



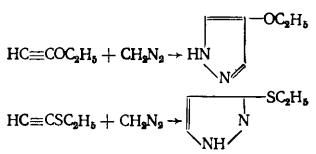
Isocyanatodiphenylphosphine reacts as a 1,3-DS with a dipolarophile such as dimethyl acetylenedicarboxylate with formation of a five-membered heterocycle, which being unstable, decomposes with formation of phosphine oxide. The reaction apparently proceeds via a stage involving the formation of a dipolar ion[150]:



The data presented show that formally α,β-unsaturated compounds of phosphorus(III) do not differ in type of reactivity from classical 1,3-DS.

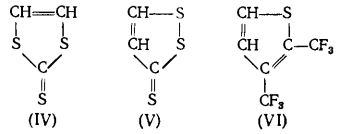
IV. SULPHUR-CONTAINING π-SYSTEMS

In many cases ethylenic and acetylenic compounds of sulphur and its analogues (selenium and tellurium) combine with 1,3-DS as dipolarophiles via the multiple bond[151], although the presence of vacant 3*d* orbitals in the sulphur atom influences the mode of the 1,3-dipolar cycloaddition[59]. For example, the interaction of diazomethane with ethoxyacetylene and ethylthioacetylene leads to products of different structure, which makes it possible to postulate the possibility of the stabilisation of the carbanion formed initially by (*d*-*p*) π-conjugation, which determines the mode of addition in the case of a sulphur-containing compound:

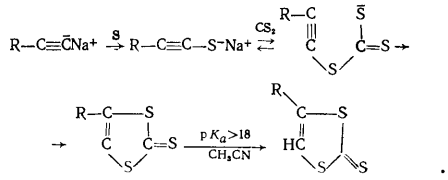


However, the multiple bond nevertheless remains the reaction centre.

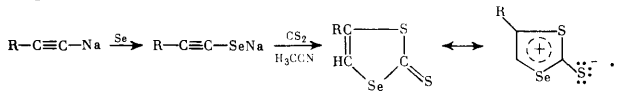
The reactions of compounds containing sulphur next to a multiple bond, which proceed via the 1,3-dipolar addition mechanism, have been described in recent years. The reaction of acetylene with sulphur and carbon disulphides, yields, together with other compounds, the isomeric 1,3-dithiole-2-thione (IV) and 1,2-dithiole-3-thione (V).[152] The analogous reaction in the presence of perfluoro-2-yne yields 1,3-bis-(trifluoromethyl)thiophen (VI):[153,154]



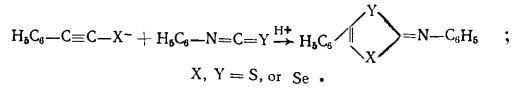
The reaction apparently proceeds with formation of a primary thiolation product. The interaction of acetylenes with sulphur and carbon disulphide in polar solvents probably proceeds via the same mechanism with formation of 1,3-dithiole-2-thiones[155-157]. If one begins with sodium acetylide, sulphur, and carbon disulphide, then derivatives of 1,3-dithiole-2-thiones are formed in the presence of a proton-donating solvent even at room temperature[156-158]. The formation of the product of the thiolation of sodium acetylide is most probably an intermediate stage[159]:



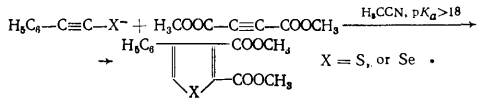
Products of analogous structure are formed also by selenium and tellurium which are sulphur analogues[160-162]. In the presence of carbon disulphide in a proton-donating solvent, when the product obtained by treating sodium acetylide with selenium is acted upon by carbon disulphide in a proton-donating solvent, 1-thia-3-selenole-2-thione is formed[163] and is stabilised by resonance, like its sulphur analogue:



The use of phenyl isothiocyanate and phenyl isoselenocyanate as heterocumulenes in this type of reaction does not alter its mechanism[164]:

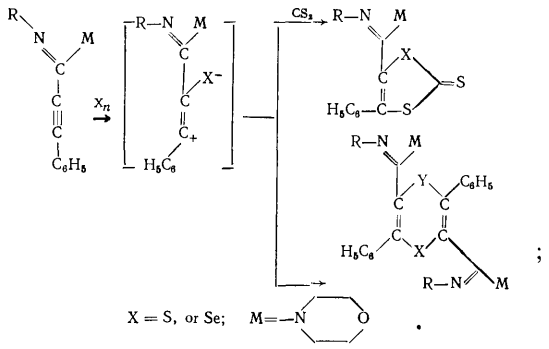


Acetylenic thiolates and selenolates also react with dimethylacetylenedicarboxylate via the 1,3-dipolar cycloaddition mechanism with formation of derivatives of thiophen- or selenophen-dicarboxylic acids[165-166]:



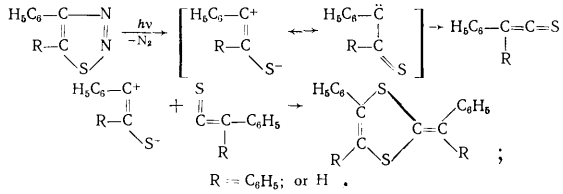
1,3-Dithiole-2-thiones have been obtained not only from terminal acetylenes with intermediate formation of thiolates but also from compounds having a doubly substituted triple bond. When the amidines of phenylpropiolic acid interact with sulphur or selenium in the presence of a tertiary amine, derivatives of 1,3-dithiole-2-thiones are produced[167]. A

sulphur-containing 1,3-DS is apparently formed in the first stage and then reacts with the dipolarophile (carbon disulphide):

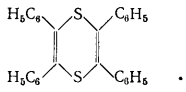


If phenyl isocyanate or phenyl isothiocyanate is introduced into the reaction mixture instead of carbon disulphide, the sulphur-containing 1,3-DS dimerises, apparently owing to the lower reactivity of the multiple bond of the heterocumulene.

Extremely reactive compounds are formed on decomposition of 1,2,3-thiadiazoles. Photolysis of derivatives of 1,2,3-thiadiazoles proceeds with evolution of nitrogen and the formation of dithiafulvenes[168]. It has been suggested[169] that, when a nitrogen molecule is split off, a thioketocarbene is formed as an intermediate and can then be converted into a thioketen as a result of a rearrangement analogous to the Wolff rearrangement. The reaction probably proceeds subsequently via the 1,3-dipolar cycloaddition mechanism: the thioketocarbene (1,3-DS) reacts with the thioketen (dipolarophile) via the 3 + 2 = 5 mechanism:

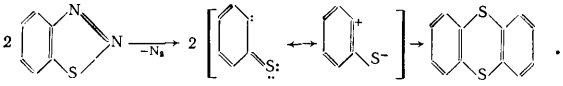


If R = C_6H_5, the competing dimerisation reaction of the 1,3-DS (thioketocarbene) can proceed via the 3 + 3 = 6 mechanism with formation of dithiacyclohexadiene[168]:

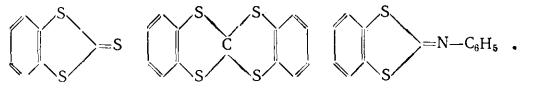


It is noteworthy that the products of cycloaddition via the 3 + 2 = 5 mechanism (the dithiafulvenes) are also obtained from acetylenic thiolates and selenolates[157,165,166] and the lower the pK_a of the solvent the higher the yield of the dithiafulvenes.

The aromatic thioketocarbenes formed on thermolysis of benzothiazoles dimerise with formation of thianthrene[170]:

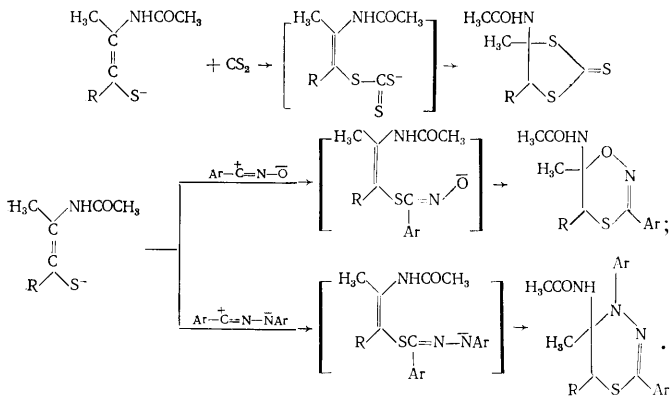


Thioketocarbenes dimerise so readily that, even when the reaction is carried out in dipolarophiles (used as solvents) such as diethyl fumarate, α-naphthyl isocyanate, or benzonitrile, the products of addition via the 2 + 3 = 5 mechanism are not obtained; the product of the 3 + 3 = 6 reaction is formed exclusively[2,171]. Only certain compounds containing the C=S double bond combine with thioketocarbene relatively smoothly. Carbon disulphide reacts via both one and two multiple bonds, while phenyl isothiocyanate forms 2-phenylimino-1,3-benzodithiole[171]:

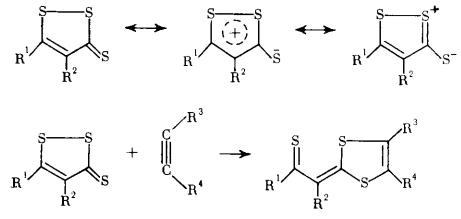


The decomposition of unsubstituted 1,2,3-thiadiazole in carbon disulphide at 200 °C yields only 0.2% of 1,3-dithiole-2-thione[171], while the reaction with perfluorobut-2-yne leads to the formation of 2,3-bis(trifluoromethyl)thiophen; the reaction involving 5-methyl-1,2,3-thiadiazole proceeds analogously[153].

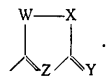
It has been shown recently that alkenethiolates[172,173] are also capable of behaving as 1,3-DS and of reacting with dipolarophiles (carbon disulphide) via the 3 + 2 = 5 cyclisation mechanism[174] and with other 1,3-DS (nitrile oxides, nitrile imines) via the 3 + 3 = 6 cyclisation mechanism[175]:



Numerous studies published recently have been devoted to yet another form of sulphur-containing π-systems capable of undergoing 1,3-dipolar cycloaddition reactions. It has been shown[176,177] that 1,2-dithiole-3-thiones react with activated acetylenes via the 3 + 2 = 5 cyclisation mechanism[176,177]. The nucleophilic properties of the exocyclic sulphur atom in such compounds are based on the stability of the quasi-aromatic dithiole ring system, by virtue of which the unshared electron pair is localised at the thione sulphur atom and the system as a whole is a kind of 1,3-DS:



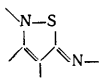
Apart from 1,2-dithiole-3-thiones, their isoelectronic analogues can enter into similar reactions and all these compounds can be represented by the general formula



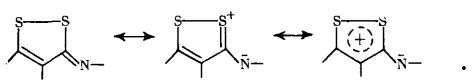
The examples investigated are summarised in Table 1.

Table 1 shows that the ring system can include both sulphur and nitrogen and in the latter case the electron density in the ring increases, which enhances the nucleophilic properties of the exocyclic atom and hence the 1,3-dipolar activity. 1,2,4-Dithiazole-3-thiones react more vigorously with activated acetylenes than 1,2-dithiole-3-thiones.

Table 1. Sulphur-containing 1,3-DS.

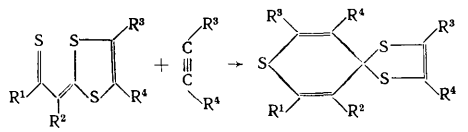
Compound	References	Compound	References
 1,2-Diothiole-3-thione	176—200	 3-Imino-1,2-dithiole	184, 189
 1,2,4-Dithiazole-3-thione	180; 184—186, 189, 195, 199, 201—205	 3-Imino-1,2,4-dithiazole	180, 209
 Isothiazole-5-thione	206—208	 5-Iminoisothiazole	206
 Isothiazole-3-thione	208		

The reaction proceeds in some cases with dissociation of the S–S bond and in others with rupture of the S–N bond, which, incidentally, does not alter its essential features. Instead of the exocyclic sulphur atom, the system may contain an exocyclic nitrogen atom; such a system is also a 1,3-DS and a partly ionised structure can be formulated for it as well:



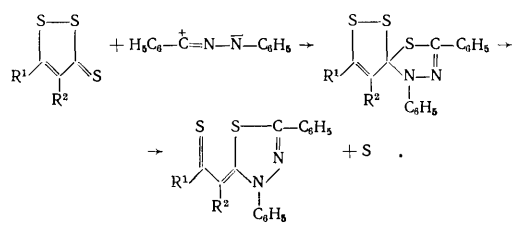
Such systems could be considered in the section devoted to nitrogen-containing π-systems, but, relative to the thiolethione systems, the 1,3-dipolar activity of iminothioles is particularly clear-cut.

The initial 1 : 1 product of the 1,3-dipolar cycloaddition can react in many instances with yet another molecule of the dipolarophile with formation of spirans (1,4-addition):



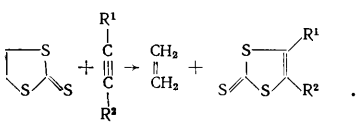
Such spirans can be obtained with almost all the systems investigated[177,184,185,187,191,204], but in some cases the 1,3-dipolar cycloaddition products could not be isolated, since the subsequent reaction was rapid[184,208].

1,2-Dithiole-3-thiones and their analogues participate only via their C=S double bond in reactions with classical 1,3-DS (benzonitrile oxide and diphenylnitrile imines); in other words, sulphur-containing heterocycles behave in this reaction as dipolarophiles[203,210–213]. The products formed initially react subsequently in a way which depends on the nature of the initial substances. For example, the reaction involving 1,2-dithiole-3-thione and diphenylnitrile imine proceeds via the following mechanism[212,213]:



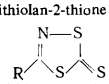
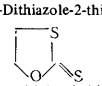
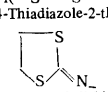
Sometimes the reaction involving addition to the C=S bond (1,2-addition) takes place also with substituted acetylenes[178–181,204], tetracyanoethylene[214], and diphenylketen[215]; likewise one should note that, under the influence of certain reagents, the 1,3-cycloaddition products can rearrange to 1,2-addition products[178,193,220].

Apart from 1,2-dithiole-3-thiones and their analogues, 1,3-dithiolan-2-thione systems and other compounds isoelectronic with them can undergo reactions via the 1,3-dipolar cycloaddition mechanism. During the reaction, ethylenic hydrocarbons or other unsaturated compounds are split off. For example, the reaction of 1,3-dithiolan-2-thiones proceeds as follows:

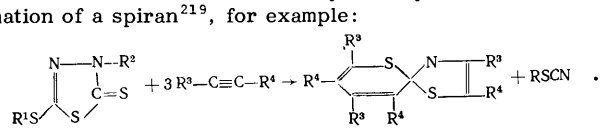


The compounds investigated are listed in Table 2.

Table 2. Nitrogen- and sulphur-containing 1,3-DS.

Compound	Compounds split off	References
 1,3-Dithiolan-2-thione		177, 180, 191, 201, 217, 218
 1,3,4-Dithiazole-2-thione		181, 201, 203
 1,3-Oxathiolan-2-thione		217
 1,3,4-Thiadiazole-2-thione		199, 219
 2-Imino-1,3-dithiolan		199, 219

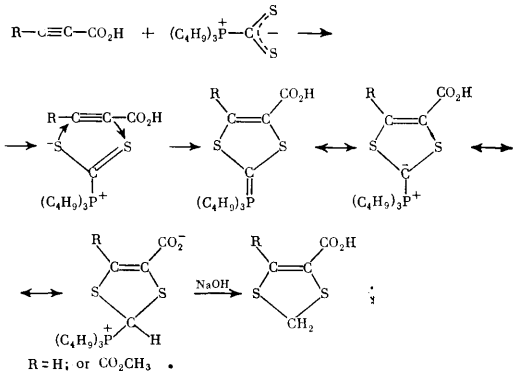
In some cases the product formed initially can combine with a further two molecules of the acetylenic hydrocarbon with formation of a spiran[219], for example:



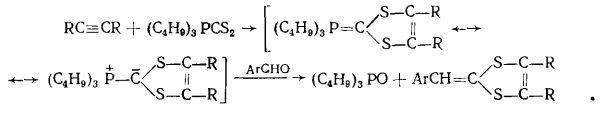
There exist also other examples of the 1,3-dipolar activity of sulphur-contaning π-systems. Complexes of phosphines with carbon disulphide, which have been known for a very long time, can react with acetylenic hydrocarbons via a mechanism which can be regarded as 1,3-dipolar cycloaddition.

Propiolic and acetylenedicarboxylic acids react with the complex $(C_4H_9)_3 \rightarrow CS_2$ to form a dipolar ion[221,222]. The authors suggest that the reaction proceeds via a concerted single-stage addition and that a dipolar complex with a positive charge on the phosphorus atom and a negative charge on the CS_2 group can be regarded as the 1,3-DS in the given reaction; in the limiting case one can postulate the presence of the C=S double bond and a negative charge on the second sulphur atom.

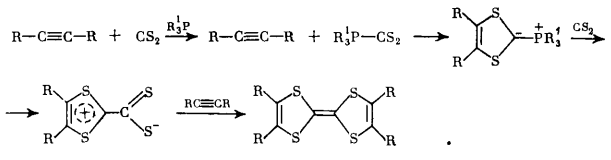
The reaction between $(C_4H_9)_3P \rightarrow CS_2$ and substituted acetylenes in the presence of aldehydes[223,224], leading to the formation of dithiafulvene derivatives, proceeds via an analogous mechanism:



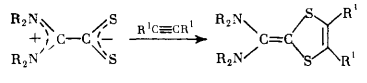
The authors suggest that the intermediate reacts with the aldehyde to form the product of the Wittig reaction:



It is known that acetylenic hydrocarbons react with carbon disulphide to form tetrathiafulvenes[222,223,225-230]. As a rule, this type of reaction takes place in the presence of tertiary phosphines. The formation of fulvenes can be accounted for if one postulates the existence of an intermediate phosphorane, which reacts with carbon disulphide to form a 1,3-dipolar compound[226,229]. The subsequent interaction with a second acetylene molecule gives rise to the final product:



The following reaction probably proceeds via a similar mechanism[193,220]:



The study of reactions in which unsaturated systems containing a heteroatom with an unshared electron pair in the α-position, which are capable of reacting as 1,3-DS, made it possible to formulate new principles for the structure of 1,3-DS.[231] Apparently any system $\ddot{Z}-X=Y$ and $\ddot{Z}-X\equiv Y$, where $\ddot{Z}$ is an element having an unshared electron pair and X and Y are elements capable of forming π-bonds, can behave as a 1,3-DS.[231] The 1,3-dipolar activity of compounds of this type is determined in each individual case by the nature of the elements Z, X, and Y.

Anions of the type $\bar{Z}-X=Y$ or $\bar{Z}-X\equiv Y$ should be more active 1,3-DS, although it is then necessary to add a proton donor to the reaction mass in order to stabilise the anion formed as a result of cyclisation.

The proposed principle for the construction of 1,3-DS can be extended also to the usual Huisgen 1,3-DS. The analogy is particularly clear when the formulae of these 1,3-DS are written as those of carbenoid structures[231].

REFERENCES

1. L.J.Smith, Chem.Rev., **23**, 193 (1938).
2. R.Huisgen, Angew.Chem., **75**, 604 (1963).
3. R.Huisgen, R.Greschy, and J.Sawyer, in "The Chemistry of Alkenes" (Translated into Russian), Izd. Khimiya, Leningrad, 1969, p.181.
4. C.K.Ingold, "Theoretical Principles of Organic Chemistry" ["Structure and Mechanism in Organic Chemistry?"] (Translated into Russian), Izd.Mir, Moscow, 1973.
5. E.N.Tsvetkov and M.I.Kabachnik, Uspekhi Khim., **40**, 177 (1971) [Russ.Chem.Rev., No.1 (1971)].
6. I.P.Romm, E.N.Guryanova, and K.A.Kocheshkov, Tetrahedron, **25**, 2455 (1969).
7. I.P.Romm and E.I.Gur'yanova, Zhur.Obshch.Khim., **38**, 1927 (1968).
8. I.P.Romm, E.M.Sadykova, E.I.Gur'yanova, I.D.Kolme, and K.A.Kocheshkov, Dokl.Akad.Nauk SSSR, **195**, 372 (1970).
9. I.P.Romm, V.V.Kopylov, and E.I.Gur'yanova, Zhur. Strukt.Khim., **11**, 672 (1970).
10. I.P.Gol'dshtein, E.N.Kharlamova, and E.I.Gur'yanova, Zhur.Obshch.Khim., **38**, 1984 (1968).
11. T.Yonezawa, J.Synth.Org.Chem.Japan, **28**, 1197 (1970).
12. D.Rosenberg, J.W.De Haan, and W.Drenth, Rec.Trav. chim., **87**, 1387 (1968).
13. D.P.Craig, A.Maccol, R.S.Nyholm, L.E.Orgel, and L.E.Sutton, J.Chem.Soc., 332 (1954).
14. M.I.Kabachnik, Dokl.Akad.Nauk SSSR, **110**, 395 (1956).
15. M.J.Kabachnik, T.A.Mastrjukowa, T.A.Melentyewa, and A.E.Shipow, Tetrahedron, **9**, 10 (1960).
16. M.I.Kabachnik, T.A.Melentyewa, and T.A.Mastrjukowa, Tetrahedron, **17**, 239 (1962).
17. B.I.Ionin, Doctoral Thesis, Lensovet Leningrad Technological Institute, 1970.
18. R.F.Hudson, "Structure and Mechanism in Organophosphorus Chemistry" (Academic Press, New York, 1965) (Translated into Russian), Izd.Mir, Moscow, 1967.
19. G.V.Bykov, "Elektronnye Zaryady Svyazei v Organicheskikh Soedineniyakh" (The Electronic Bond Charges in Organic Compounds), Izd.Akad.Nauk SSSR, Moscow, 1960.
20. S.S.Batsanov, "Elektrootritsatel'nost' Elementov i Khimicheskaya Svyaz'" (The Electronegativities of Elements and the Chemical Bond), Izd.Sibir.Otd.Akad. Nauk SSSR, 1962.

21. W.Drenth and A.Loewenstein, Rec.Trav.chim., **91**, 635 (1962).
22. W.Drenth and O.Rosenberg, Rec.Trav.chim., **86**, 27 (1967).
23. C.Charrier, W.Chodkiewicz, and P.Cadiot, Bull.Soc. chim.France, 1002 (1966).
24. M.P.Simonnin, Bull.Soc.chim.France, 1774 (1966).
25. M.P.Simonnin, J.Organomet.Chem., **5**, 155 (1966).
26. B.P.Dailey and J.N.Shooley, J.Amer.Chem.Soc., **77**, 3977 (1955).
27. J.R.Cavanaugh and B.P.Dailey, J.Chem.Phys., **34**, 1099 (1961).
28. J.Ficini and C.Barbara, Bull.Soc.chim.France, 871 (1964).
29. W.Drenth, Colloq.int.CNRS, No.182, 91 (1970); Ref.Zhur.Khim., 6B496 (1971).
30. A.Saika and C.P.Slichter, J.Chem.Phys., 22, 26 (1954).
31. I.P.Gol'dshtein, E.N.Gur'yanova, and K.A.Kocheskov, Dokl.Akad.Nauk SSSR, **138**, 1099 (1961).
32. I.P.Romm and E.N.Gur'yanova, Dokl.Akad.Nauk SSSR, **171**, 877 (1966).
33. H.Saot, K.Hirota, and S.Nagatura, Bull.Chem.Soc. Japan, **38**, 962 (1965).
34. H.H.Jaffé and L.D.Freedman, J.Amer.Chem.Soc., **74**, 1069 (1952).
35. C.N.R.Rao, J.Ramachandran, S.Somasekhara, and T.V.Kajakumar, Nature, **183**, 1476 (1959).
36. G.Shaw, J.K.Becconsall, R.M.Canadine, and R.Murray, Chem.Comm., 425 (1966).
37. B.I.Ionin, A.A.Petrov, and G.M.Bogolyubov, Uspekhi Khim., **36**, 587 (1967).
38. M.I.Kabachnik, Tetrahedron, **20**, 655 (1964).
39. W.Drenth, G.L.Hekkert, and B.Z.Zwanenberg, Rec. Trav.chim., **81**, 313 (1962).
40. R.Fuks, R.Buijle, and H.G.Viehe, Angew.Chem., **78**, 594 (1966).
41. H.G.Viehe, R.Fuks, and M.Roinsteinn, Angew.Chem., **76**, 571 (1964).
42. R.Fusko, G.Bianchetti, and D.Pocar, Gazzetta, **91**, 1233 (1961).
43. M.E.Kuchne and S.J.Wegver, J.Org.Chem., **29**, 1582 (1964).
44. G.Bianchetti, D.Pocar, and D.C.Piero, Gazzetta, **93**, 1714 (1963).
45. G.Bianchetti, D.Pocar, and D.C.Piero, Gazzetta, **93**, 1726 (1963).
46. P.Caramella and P.Bianchessi, Tetrahedron, **26**, 5773 (1970).
47. N.Yujuro, F.Fumio, and T.Yoshita, Bull.Chem.Soc. Japan, **40**, 1740 (1967).
48. N.Yujuro, F.Fumio, and T.Yoshita, Bull.Chem.Soc. Japan, **43**, 3001 (1970).
49. O.Fsuje, M.Tashiro, and Y.Nishihara, Tetrahedron Letters, 3769 (1967).
50. D.F.Bettenetti, A.Codoli, and S.A.Omodoi, Ricerca Sci., **38**, 806 (1968).
51. R.Huisgen, R.Knorr, L.Mobius, and G.Sreimies, Chem.Ber., **98**, 4014 (1965).
52. P.Grünanger, P.V.Finzi, and E.Falbori, Gazzetta, **90**, 413 (1960).
53. P.V.Finzi, C.Skotti, and A.Quilico, Atti Accad.naz. Lincei Rend.Classe Sci.fis.mat.nat., **41**, 204 (1966).
54. P.Grünanger and M.P.Langella, Gazzetta, **89**, 1784 (1959).
55. P.Bravo, G.Gaudiano, A.Quilico, and A.Ricco, Gazzetta, **91**, 47 (1961).
56. G.Gaudiano, A.Ricco, and R.Merlin, Gazzetta, **89**, 2466 (1959).
57. P.Grünanger, Atti Accad.naz.Lincei Rend.Classe Sci. fis.mat.nat., **24**, 163 (1958).
58. P.Grünanger and P.V.Finzi, Atti Accad.naz.Lincei Rend.Classe Sci.fis.mat.nat., **31**, 128 (1961).
59. S.W.Groen and J.F.Arens, Rec.Trav.chim., **80**, 879 (1961).
60. P.Paul and S.Schiltchoff, Bull.Soc.chim.France, 4179 (1967).
61. R.Huisgen, R.Sustmann, G.Wallbillich, Chem.Ber., **100**, 1786 (1967).
62. R.Huisgen, R.Groshey, H.Seidl, and H.Hanck, Chem. Ber., **100**, 2559 (1967).
63. W.S.Wadsworth and W.D.Emmons, J.Amer.Chem.Soc., **84**, 1316 (1962).
64. W.S.Wadsworth and W.D.Emmons, J.Org.Chem., **32**, 1279 (1967).
65. M.Busch, Ber., **34**, 2311 (1901).
66. W.Lwowski, R.A.De Maurac, R.A.Murray, and L.Lunow, Tetrahedron Letters, 425 (1971).
67. R.Huisgen, H.Seidl, and J.Bruhning, Chem.Ber., **102**, 1102 (1969).
68. R.Huisgen, J.Org.Chem., **33**, 2291 (1968).
69. W.J.Middleton and C.G.Krespan, J.Org.Chem., **30**, 1398 (1965).
70. K.Burger, J.Fehn, and W.Thenn, Angew.Chem., **85**, 541 (1973).
71. T.P.Forshaw and A.E.Tipping, Chem.Comm., 816 (1969).
72. T.P.Forshaw and A.E.Tipping, J.Chem.Soc.C, 2404 (1971).
73. T.P.Forshaw and A.E.Tipping, J.Chem.Soc., Perkin Trans.I, 1059 (1972).
74. S.E.Armstrong and A.E.Tipping, J.Fluor.Chem., **3**, 119 (1973).
75. S.E.Armstrong and A.E.Tipping, J.Chem.Soc., Perkin Trans.I, 538 (1975).
76. S.E.Armstrong and A.E.Tipping, J.Chem.Soc., Perkin Trans.I, 1411 (1975).
77. K.Burger, W.Thenn, and A.Gieren, Angew.Chem., **86**, 481 (1974).
78. A.Gieren, P.Narayanan, K.Burger, and W.Thenn, Angew.Chem., **86**, 482 (1974).
79. K.Burger, W.Thenn, H.Schickaneder, and H.Peuker, Angew.Chem., **86**, 483 (1974).
80. K.Burger, W.Thenn, R.Rauch, and H.Schickaneder, Angew.Chem., **86**, 484 (1974).
81. K.Burger, W.Thenn, R.Rauch, H.Schickaneder, and A.Gieren, Chem.Ber., **108**, 1460 (1975).
82. K.Burger, H.Schickaneder, and W.Thenn, Tetrahedron Letters, 1125 (1975).
83. K.Burger and H.Schickaneder, Tetrahedron Letters, 2911 (1975).
84. K.Burger, W.Thenn, and H.Schickaneder, Chem.Ber., **108**, 1468 (1975).
85. K.Burger, H.Schickaneder, and M.Pinzel, Annalen, 30 (1976).
86. R.Huisgen, R.Fleischmann, and A.Eckell, Tetrahedron Letters, 1 (1960).
87. R.Huisgen and A.Eckel, Tetrahedron Letters, 5 (1960).
88. H.Dorn and A.Otto, Chem.Ber., **101**, 3287 (1968).
89. S.E.Armstrong, T.P.Forshaw, and A.E.Tipping, J.Chem.Soc., Perkin Trans.I, 1902 (1975).
90. K.Houk, Acc.Chem.Res., **8**, 361 (1975).
91. V.A.Tartakovskii and I.E.Chlenov, Zhur.Vses.Khim. Obshch.im.Mendeleeva, **22**, 252 (1977).
92. T.Wagner-Jauregg, Ber., **63**, 3219 (1930).
93. J.Van Alphen, Rec.Trav.chim., **61**, 892 (1942).

94. D.B.Dutt and P.C.Guha, J.Indian Chem.Soc., **27**, 151 (1950).
95. J.Kovacs, V.Bruckner, and J.Kandel, Acta Chim.Acad. Sci.Hung., **1**, 230 (1951).
96. M.Haring and T.Wagner-Jauregg, Helv.Chim.Acta, **40**, 852 (1957).
97. H.Günther and S.W.Tam, Helv.Chim.Acta, **52**, 1672 (1969).
98. K.Burger, S.Tremmel, and H.Schickaneder, J.Fluor. Chem., 7, 471 (1976).
99. I.G.Kolokol'tseva, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **38**, 2819 (1968).
100. V.V.Kosovtsev, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **40**, 2570 (1970).
101. V.V.Kosovtsev, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **41**, 2463 (1971).
102. I.A.Stepanov, V.I.Zakharov, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **46**, 2463 (1976).
103. I.G.Kolokol'tseva, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **40**, 574 (1970).
104. V.V.Kosovtsev, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., 40, 2132 (1970).
105. S.P.Konotopova, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **41**, 235 (1971).
106. S.P.Konotopova, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **42**, 2412 (1971).
107. S.P.Konotopova, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **43**, 987 (1973).
108. N.P.Ivanova, V.N.Chistokletov, L.A.Tamm, and A.A.Petrov, Zhur.Obshch.Khim., 47, 763 (1977).
109. L.A.Tamm, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **42**, 1926 (1972).
110. V.V.Kosovtsev, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **39**, 223 (1969).
111. V.V.Kosovtsev, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **41**, 2649 (1971).
112. L.A.Tamm, V.N.Chistokletov, and A.A.Petrov, Zhur. Obshch.Khim., **42**, 1864 (1972).
113. L.A.Tamm, V.N.Chistokletov, and A.A.Petrov, Zhur. Obshch.Khim., **43**, 2178 (1973).
114. L.A.Tamm, V.N.Chistokletov, E.S.Turbanova, and A.A.Petrov, Zhur.Obshch.Khim., **44**, 1468 (1974).
115. V.A.Galishev, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **42**, 1876 (1972).
116. V.A.Galishev, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **43**, 1473 (1973).
117. V.A.Galishev, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **45**, 1695 (1975).
118. V.A.Galishev, V.N.Chistokletov, A.A.Petrov, and L.A.Tamm, Zhur.Obshch.Khim., **43**, 1470 (1973).
119. K.S.Mingaleva, V.N.Chistokletov, V.V.Kosovtsev, and A.A.Petrov, Zhur.Obshch.Khim., **41**, 862 (1971).
120. V.V.Kosovtsev, T.N.Timofeeva, B.I.Ionin, and V.N.Chistokletov, Zhur.Obshch.Khim., **41**, 2638 (1971).
121. L.Horner, I.Ertel, H.D.Ruprecht, and O.Belovsky, Chem.Ber., **103**, 1582 (1970).
122. I.A.Stepanov, V.N.Chistokletov, and A.A.Petrov, Dokl.Akad.Nauk SSSR, **220**, 127 (1975).
123. A.N.Pudovik, T.Kh.Gazizov, and A.M.Pashinkin, Zhur.Obshch.Khim., Symposium, "Khimiya Organicheskikh Soedinenii Fosfora" (The Chemistry of Organic Phosphorus Compounds), 1967.
124. P.I.Alimov and L.V.Cheplanova, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 939 (1956).
125. A.N.Pudovik and T.Kh.Gazizov, Zhur.Obshch.Khim., **37**, 706 (1967).
126. L.V.Nesterov, R.A.Sabirova, and I.E.Krepysheva, Zhur.Obshch.Khim., **39**, 1943 (1969).
127. A.M.Aguiar, K.C.Hansen, and G.S.Reddy, J.Amer. Chem.Soc., **89**, 3067 (1967).
128. A.M.Aguiar and K.C.Hansen, J.Amer.Chem.Soc., **89**, 4235 (1967).
129. M.S.Chatta and A.M.Aguiar, J.Org.Chem., **38**, 1611 (1973).
130. A.M.Aguiar, J.R.S.Irelan, G.W.Prejean, J.P.John, and C.J.Morrow, J.Org.Chem., **34**, 2681 (1936).
131. A.M.Aguiar, G.W.Prejean, J.R.S.Irelan, and G.J.Morrow, J.Org.Chem., **34**, 4024 (1969).
132. R.D.Rieke, R.A.Copenhafer, A.M.Aguiar, M.S.Chatta, and J.C.Williams, Chem.Comm., 1130 (1972).
133. R.D.Rieke, R.A.Copenhafer, A.M.Aguiar, M.S.Chatta, and J.C.Williams, J.Electroanal.Chem., **42**, 309 (1973).
134. E.E.Schweizer and L.D.Smucker, J.Org.Chem., **31**, 3146 (1966).
135. M.E.Savage and S.Trippett, J.Chem.Soc.C, 591 (1968).
136. A.N.Hughes and M.Davies, Chem.Ind.(London), 138 (1969).
137. G.Witting and E.Benz, Chem.Ber., **92**, 1999 (1959).
138. A.Schmidpeter and W.Zeiss, Chem.Ber., **104**, 1199 (1971).
139. A.Schmidpeter and W.Zeiss, Angew.Chem., **83**, 397 (1971).
140. A.Schmidpeter, W.Zeiss, and H.Eckert, Z.Naturforsch., **B27**, 769 (1972).
141. A.N.Pudovik, I.V.Gur'yanova, and V.P.Kakurina, Zhur.Obshch.Khim., **41**, 1976 (1971).
142. A.N.Pudovik, I.V.Konovalova, V.P.Kakurina, L.A.Burnaeva, and T.A.Komissarova, Zhur.Obshch. Khim., **43**, 256 (1973).
143. I.V.Konovalova, L.A.Burnaeva, and A.N.Pudovik, Zhur.Obshch.Khim., **44**, 261 (1974).
144. A.N.Pudovik, I.V.Konovalova, V.P.Kakurina, and L.A.Burnaeva, Zhur.Obshch.Khim., **43**, 553 (1973).
145. I.V.Konovalova, L.A.Burnaeva, G.S.Temnikova, and A.N.Pudovik, Zhur.Obshch.Khim., **45**, 1003 (1975).
146. I.V.Konovalova, L.A.Burnaeva, L.S.Yuldasheva, and A.N.Pudovik, Zhur.Obshch.Khim., **44**, 2408 (1974).
147. I.V.Konovalova, L.A.Burnaeva, and A.N.Pudovik, Zhur.Obshch.Khim., **45**, 2558 (1975).
148. R.I.Tarasova, N.M.Kislitsina, and A.N.Pudovik, Zhur.Obshch.Khim., **41**, 1972 (1971).
149. I.V.Konovalova, L.A.Burnaeva, and A.N.Pudovik, Zhur.Obshch.Khim., **44**, 743 (1974).
150. L.S.Rodionova, V.A.Galishev, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **45**, 1652 (1975).
151. S.I.Radchenko, V.N.Chistokletov, and A.A.Petrov, Zhur.Org.Khim., **1**, 51 (1965).
152. F.Challenger, E.A.Mason, E.C.Holdsworth, and R.Emmett, J.Chem.Soc., 292 (1953).
153. O.P.Strausz, J.Fout, E.L.Dedio, P.Kebarle, and U.E.Gummig, J.Amer.Chem.Soc., **89**, 4805 (1967).
154. C.G.Krespan and D.C.England, J.Org.Chem., **33**, 1850 (1968).
155. R.Mayer and K.Gewald, Angew.Chem., **79**, 298 (1967).
156. R.Mayer, B.Gebhardt, J.Fabian, and A.K.Müller, Angew.Chem., **76**, 143 (1964).
157. R.Mayer, B.Hunger, R.Prousa, and A.K.Müller, J.prakt.Chem., **35**, 294 (1967).
158. R.Mayer and B.Gebhardt, Chem.Ber., **97**, 1298 (1964).
159. M.Schmidt and V.Potschka, Naturwiss., **50**, 302 (1963).
160. L.Brandsma, H.Wijers, and J.E.Arens, Rec.Trav. chim., **81**, 583 (1962).
161. L.Brandsma, H.Wijers, and C.Jonker, Rec.Trav.chim., **83**, 208 (1964).
162. L.Bransma, Rec.Trav.chim., **83**, 307 (1964).

163. R.Mayer and A.K.Muller, Z.Chem., **4**, 384 (1964).
164. H.Spies, K.Gewald, and R.Mayer, J.prakt.Chem., **313**, 804 (1971).
165. M.L.Petrov, V.N.Chistokletov, and A.A.Petrov, Zhur. Org.Khim., **12**, 2035 (1976).
166. M.L.Petrov, L.S.Rodionova, and A.A.Petrov, Zhur. Org.Khim., **13**, 1564 (1977).
167. W.Ried and M.Wegwitz, Annalen, 89 (1975).
168. O.Kirmse and L.Horner, Annalen, **614**, 4 (1958).
169. V.Franzen, Annalen, **602**, 199 (1957).
170. P.Jacobson and H.Janssen, Annalen, **277**, 209 (1893).
171. R.Huisgen and V.Weberndorfer, Experientia, 17, 566 (1961).
172. S.Hoff, A.P.Blok, and E.Zwanenberg, Rec.Trav.chim., 92, 879 (1973).
173. S.Hoff, A.P.Blok, and E.Zwanenberg, Rec.Trav.chim., **92**, 890 (1973).
174. S.Hoff and A.P.Blok, Rec.Trav.chim., **93**, 75 (1974).
175. S.Hoff and E.Zwanenberg, Rec.Trav.chim., **92**, 929 (1973).
176. H.Behringer and R.Wiedenmann, Tetrahedron Letters, 3705 (1965).
177. D.B.J.Easton and D.Leaver, Chem.Comm., 585 (1965).
178. H.Davy, M.Demuynck, D.Paquer, A.Rouessag, and J.Vialle, Bull.Soc.chim.France, 1150 (1966).
179. C.Portail and J.Vialle, Bull.Soc.chim.France, 3187 (1966).
180. H.Behringer, D.Bender, J.Falkenberg, and R.Wiedenmann, Chem.Ber., 101, 1428 (1968).
181. H.Davy, M.Demyunck, D.Paquer, A.Rouessag, and J.Vialle, Bull.Soc.chim.France, 2057 (1968).
182. M.Stavaux and N.Lozac'h, Bull.Soc.chim.France, 4273 (1968).
183. M.Stavaux and N.Lozac'h, Bull.Soc.chim.France, 4184 (1969).
184. J.M.Buchshriber, D.M.McKinnon, and M.Ahmed, Canad. J.Chem., **47**, 2039 (1969).
185. M.Ahmed, J.M.Buchshriber, and D.M.McKinnon, Canad. J.Chem., **48**, 1991 (1970).
186. N.Lozac'h, Adv.Heterocycl.Chem., **13**, 161 (1971).
187. D.M.McKinnon and J.M.Buchshriber, Canad.J.Chem., **49**, 3299 (1971).
188. G.Hervien, P.Rioult, and J.Vialle, Bull.Soc.chim. France, 4375 (1971).
189. G.Hervien, P.Rioult, and J.Vialle, Bull.Soc.chim. France, 4380 (1971).
190. M.Stavaux, Bull.Soc.chim.France, 4426 (1971).
191. D.B.J.Easton, D.Leaver, and T.J.Rawlings, J.Chem. Soc., Perkin Trans.I, 41 (1972).
192. K.T.Pedersen, N.L.Huaman, and J.Moeller, Acta Chem.Scand., **26**, 565 (1972).
193. H.Davy and J.Vialle, Compt.rend., C, **275**, 625 (1972).
194. C.T.Pedersen, Acta Chem.Scand., **B28**, 367 (1974).
195. J.-M.Decrouen, D.Paquer, and R.Pou, Compt.rend., C, **279**, 259 (1974).
196. K.T.Pedersen, H.Davy, J.Moeller, and J.Vialle, Acta Chem.Scand., **B28**, 964 (1974).
197. H.Davy and J.Vialle, Bull.Soc.chim.France, 1435 (1975).
198. H.Davy and J.-M.Decrouen, Bull.Soc.chim.France, 115 (1976).
199. D.Paquer and R.Pou, Bull.Soc.chim.France, 120 (1976).
200. K.T.Pedersen, H.Davy, E.Wolff-Jensen, J.Moeller, and J.Vialle, Acta Chem.Scand., **B30**, 471 (1976).
201. H.Behringer and D.Deichmann, Tetrahedron Letters, 1013 (1967).
202. A.Grandin and J.Vialle, Bull.Soc.chim.France, 1851 (1967).
203. D.Noel and J.Vialle, Bull.Soc.chim.France, 2239 (1967).
204. G.Long and J.Vialle, Bull.Soc.chim.France, 2865 (1967).
205. J.W.McDonald and D.M.McKinnon, Canad.J.Chem., **45**, 1225 (1967).
206. H.Behringer, J.Kilger, and R.Wiedenmann, Tetrahedron Letters, 1185 (1968).
207. G.F.Bachers, D.M.McKinna, and J.M.Buchshriber, Canad.J.Chem., **50**, 2568 (1972).
208. N.S.Chauhan, M.E.Hassan, and D.M.McKinnon, Canad. J.Chem., **52**, 1738 (1974).
209. H.Behringer and D.Weber, Chem.Ber., **97**, 2567 (1964).
210. F.Boberg and J.Knoop, Annalen, **708**, 148 (1967).
211. G.Le Coustumer and J.Moeller, Compt.rend., C, **270**, 433 (1970).
212. J.Poirier, Bull.Soc.chim.France, 1203 (1968).
213. M.Maquet, J.Poirier, and J.Teste, Bull.Soc.chim. France, 1503 (1970).
214. A.Rouessac and J.Vialle, Bull.Soc.chim.France, 2054 (1968).
215. P.Rioult and J.Vialle, Bull.Soc.chim.France, 2883 (1967).
216. S.Davidson and D.Leaver, Chem.Comm., 540 (1972).
217. B.R.O'Connor and F.N.Jones, J.Org.Chem., **35**, 2002 (1970).
218. C.M.Pittman, M.Narita, and J.E.Liang, J.Org.Chem., **41**, 2855 (1976).
219. C.Gueden and J.Vialle, Bull.Soc.chim.France, 270 (1973).
220. H.Behringer and J.Falkenberg, Tetrahedron Letters, 1865 (1967).
221. C.U.Pittman and M.Narita, Chem.Comm., 960 (1975).
222. C.U.Pittman and M.Narita, Bull.Chem.Soc.Japan, **49**, 1996 (1976).
223. H.D.Hartzler, J.Amer.Chem.Soc., **93**, 4961 (1971).
224. H.D.Hartzler, US P.3 781 281 (1973); Chem.Abs., **80**, 70 796 (1974).
225. H.D.Hartzler, J.Amer.Chem.Soc., **92**, 1412 (1970).
226. H.D.Hartzler, J.Amer.Chem.Soc., **92**, 1413 (1970).
227. A.Krebs and H.Kimling, Angew.Chem., Int.Ed., **10**, 509 (1971).
228. H.D.Hartzler, J.Amer.Chem.Soc., **95**, 4379 (1973).
229. L.R.Melby, H.D.Hartzler, and W.A.Sheppard, J.Org. Chem., **39**, 2456 (1974).
230. H.D.Hartzler, US P.3 876 662 (1974); Chem.Abs., **83**, 58 890 (1975).
231. V.N.Chistokletov and A.A.Petrov, Zhur.Obshch.Khim., 42, 1865 (1972).

Lensovet Leningrad
Technological Institute

Leningrad Technological Institute
of the Cellulose and Paper Industry

Translated from *Uspekhi Khimii*, **49**, 1829-1854 (1980) U.D.C. 547.113:547.024

Organometallic (Non-transition Metals) Free Radicals

A.G.Milaev and O.Yu.Okhlobystin

The available information about the free radicals and radical-ions formed by "true" organometallic compounds of non-transition metals is surveyed and described systematically. The methods of synthesis and the properties of radicals with the free valence located at the metal or in a ligand and the synthesis and structure of organometallic radical-ions are considered.
The bibliography includes 185 references.

CONTENTS

I. Introduction 893
II. Organometallic radical-ions 893
III. Element-centred radicals 897
IV. Organoelemental compounds with paramagnetic ligands 899

I. INTRODUCTION

The study of organoelemental free radicals and radical-ions constitutes a new branch of physical organic chemistry, which has arisen at the boundary between classical organoelemental chemistry and the physical chemistry of free radicals. For a long time, the intermediate formation of species of this kind was merely postulated in the study of various organometallic reactions and only in recent years they became the object of direct investigation. The first advances in this field led to a flood of hypotheses and postulates, many of which lack experimental justification and are purely speculative. However, progress in outwardly varied fields, such as reaction mechanisms, biochemical electron transport, catalysis, and organic synthesis, depends significantly on the prospects for the development of the chemistry of organoelemental radicals. The aim of the present study was to select and describe systematically the reliable relevant information and to outline the most fruitful pathways to be followed in future research.

The field under consideration can be clearly divided into three main branches: organoelemental radical-ions; element-centred free radicals; organometallic compounds with the unpaired electron localised preferentially in the ligand†.

II. ORGANOMETALLIC RADICAL-IONS

Many organometallic reactions can be usefully regarded as a consequence of electron transfer[1-3]. In this approach one postulates two main types of dissociation of the metal–carbon bond, which are in general unrelated to its homolytic or heterolytic dissociation under the influence of a reactant or the solvent[4]. Electron capture by the organometallic molecule leads to the splitting off of a carbanion with formation of a reduced form of the metal:

$$R{-}m \underset{-e}{\overset{+e}{\rightleftarrows}} [R{-}m]^{\cdot-} \rightarrow R^- + m^{\cdot} \quad .$$

In the one-electron oxidation of the substrate a free radical is produced:

$$R{-}m \underset{+e}{\overset{-e}{\rightleftarrows}} [R{-}m]^{\cdot+} \rightarrow R^{\cdot} + m^+ \quad .$$

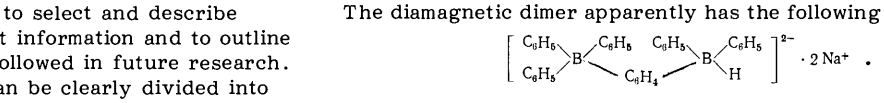
†The free radicals of phosphorus compounds, information about which can be found in a recent review by V.V.Pen'kovskii in Uspekhi Khimii, **44**, **969 (1975)**, **have been** excluded from consideration.

The radical-ion states $R{-}m^{\cdot-}$ and $R{-}m^{\cdot+}$ are then formed either as elements of the activated complex or as more or less stable intermediates whose energy corresponds to dips in the energy curve; in the latter case they can be identified directly and investigated. There are as yet few examples of this kind, but it is already evident that the stability of organoelemental radical-ions varies within very wide limits.

Organoboron radical-anions were discovered first. As early as the 1930's, the formation of coloured adducts of alkali metals with triarylboron derivatives was noted[5,6]. Subsequent studies showed that solutions of these compounds contain equilibrium mixtures of the triarylboron radical-anion $Ar_3B^{\cdot-}M^+$ (M is an alkali metal) and the diamagnetic dimeric form[7,8]:

$$2\,Ar_3B^{\cdot-}M^+ \rightleftarrows (Ar_6B_2)^{2-} \cdot 2\,M^+ \quad .$$

The diamagnetic dimer apparently has the following structure[9]:



The ratio of the two forms depends on the nature of the aryl group and the solvent. Thus, whereas the trimesitylboron radical-anion is monomeric in ether, the triphenylboron radical-anion is fully dimerised in this solvent; tri-α-naphthylboron-sodium exists as a dimer in ether but in tetrahydrofuran (THF) it is fully monomeric and paramagnetic[10].

It follows from the EPR spectra of triarylboron radical-anions that the unpaired electron is delocalised over all the aryl groups; in other words, the boron atom does not behave as an isolating bridge. The form of the spectra is determined by the interaction of the unpaired electron with the ^{11}B nucleus ($I = 3/2$), which is responsible for the appearance of the four main lines, each being split owing to the interaction with the protons of the aryl groups[11-13]. The following hyperfine interaction (HFI) constants have been obtained for the triphenylboron radical-anion in dimethoxyethane: $a_B = 7.84$ G, $a_H^{para} = 2.73$ G, $a_H^{ortho} = 1.99$ G, and $a_H^{meta} = 0.67$ G. The assignments were made on the basis of a study of the EPR spectra of deuterated triphenylboron radical-anions[11]. The reduction of alkyl derivatives of boron does not lead to stable radical-anions; only in the case of tribenzylboron is the solution coloured dark-green and the EPR spectrum shows a single line with a width of 30 G.[11]

Being powerful reductants, triarylboron radical-anions are instantly decolorised by iodine and reduce the triphenylmethyl radical to the anion:

$$2\,Ar_3B^{\cdot-} + I_2 \rightarrow 2\,Ar_3B + 2\,I^- \quad ,$$
$$Ar_3B^{\cdot-} + Ph_3C^{\cdot} \rightarrow Ar_3B + Ph_3C^- \quad .$$

An interesting reaction of triphenylboron-sodium with methanol leads to the formation of sodium triphenylborohydride[14]:

$$2\,(C_6H_5)_3\,B^{\cdot-}Na^+ + CH_3OH \rightarrow Na\,[(C_6H_5)_3\,BOCH_3] + Na\,[(C_6H_5)_3\,BH]\ .$$

Triarylboron radical-anions are capable of combining with a further electron to form a diamagnetic dianion[7,8,15]:

$$Ar_3B^{\cdot-} \underset{-e}{\overset{+e}{\rightleftarrows}} Ar_3B^{2-}\ .$$

The triarylboron radical-anions are fully stable in solution in dimethoxyethane (DME), but, after prolonged contact with the metal, the EPR spectrum of the radical-anion disappears and is replaced by that of the decomposition products. Depending on the nature of the aryl group, the following processes are observed:

$$Ar_3B^{\cdot-} \xrightarrow{K,DME} ArH^{\cdot-}\ , \qquad (1)$$

$$Ar_3B^{\cdot-} \xrightarrow{K,DME} (Ar{-}Ar)^{\cdot-}\ . \qquad (2)$$

If Ar = 2,4,6-trimethyl-3,5-dinitrophenyl, the decomposition takes place in accordance with Eqn.(1), while in the case of Ar = Ph or MeC_6H_4, it follows Eqn.(2). When Ar = 2,4,6-Me_3.C_6H_2 or 2,4-$Me_2C_6H_3$, the corresponding organoboron radical-anions do not decompose at all. It is important to note that reaction (2) is an intramolecular process, which has been demonstrated by the formation of only symmetrical biphenyls from an equimolar mixture of their radical-anions $(p\text{-}DC_6H_4)_3B^{\cdot-}$ and $(3,5\text{-}D_2C_6H_3)_3B^{\cdot-}$. The elimination of biaryl is accompanied by the formation of the arylboron[11]:

$$n\,Ar_3B^{\cdot-} \xrightarrow{K,DME} n/2\,(Ar{-}Ar)^{\cdot-} + (ArB)_n\ .$$

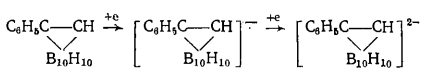
The latter is obtained also in the reduction of phenylboron dichloride by sodium in toluene[16]:

$$n\,C_6H_5BCl_2 \xrightarrow{Na} (C_6H_5B)_n\ .$$

Its hydrolysis leads to phenylboronic acid:

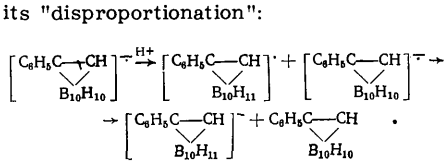
$$(C_6H_5B)_n \xrightarrow{H_2O} n\,C_6H_5B\,(OH)_2 + H_2\ .$$

When phenyl-*o*-carbaborane is acted upon by alkali metals in THF or dimethylformamide (DMF), a coloured paramagnetic solution, whose EPR spectrum shows a single broad signal (11 G) without a hyperfine structure, is readily formed[17,18]. When it is acted upon further by the reductant, a diamagnetic dianion, obtained previously[19–21] in liquid ammonia, is formed:



The absence of a hyperfine structure in the spectrum of the radical-anion indicates a high degree of delocalisation of the unpaired electron over the entire carbaborane system. It is of interest to note that, despite the presence of acidic hydrogen atoms in the phenylcarbaborane molecule, the reaction with alkali metals is not accompanied by the evolution of hydrogen and the formation of a carbanion. On formation of the radical-anion no changes in the skeleton take place, since oxidation of the radical-anion with mercury(II) chloride results in a quantitative regeneration of the initial phenylcarbaborane[18].

The acid hydrolysis of the phenylcarbaborane radical-anion results in its "disproportionation":



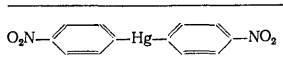
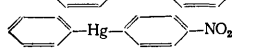
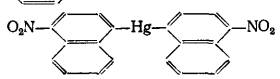
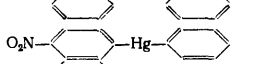
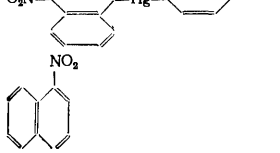
Organoaluminium radical-anions have been generated in the low-temperature γ-radiolysis (^{60}Co) of trialkylaluminium compounds[22]. Analysis of the EPR spectra indicates a pyramidal structure of such radical-anions in which the angle of deviation from the plane is ~21°. This agreed well with the large splitting constants for the ^{27}Al nuclei (324–390 G) due to the appreciable s character of the unpaired electron orbital[28]. The reduction of triphenylaluminium with sodium in ether leads to a dimeric product whose structure is apparently similar to that of its boron analogue[23].

Organogallium radical-anions have not been detected by EPR. It is only known that, when trimethylgallium is reduced with alkali metals in dimethoxyethane, a dimer is formed[24]:

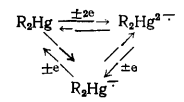
$$2\,K^+\,[(CH_3)_3\,Ga{-}Ga\,(CH_3)_3]^{2-}\ .$$

The existence of organomercury radical-anions of the type $R_2Hg^{\cdot-}$ has been demonstrated in relation to nitroaryl derivatives obtained both in electrochemical reduction[25] and on treatment with sodionaphthalene[26]. Analysis of the HFI constants shows that the mercury atom has hardly any influence on the spin density distribution (cf. the constants for $R_2Hg^{\cdot-}$ and $RH^{\cdot-}$ in Table 1).

Table 1. The nature of the EPR spectra of the radical-anions of certain organomercury compounds R_2Hg and the corresponding hydrocarbons[25,26].

Compound	a_H^{ortho}, G	a_H^{meta}, G	a_H^{para}, G	a_N, G	a_{Hg}, G
	3.25	1.00	—	9.29	42.3
	3.25	1.10	—	9.29	39.2
	3.20	—	4.00	9.50	—
	5.20	—	—	7.35	58.0
	5.08	—	—	7.30	52.3
	5.24	—	5.24	7.43	—

The stepwise nature of the electrochemical reduction of diarylmercury is noteworthy. Thus di-(*p*-nitrophenylmercury) is reduced in DME at a potential of −1.58 V to the radical-anion $R_2Hg^{\cdot-}$, which is also formed on oxidation of the corresponding triplet dianion $R_2Hg^{2\cdot-}$. The latter is a result of the two-electron reduction of di-(*p*-nitrophenyl)mercury at −1.84 V:



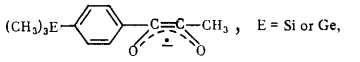
The fact that the ultraviolet spectra of $R_2Hg^{\cdot-}$ and $R_2Hg^{2\cdot-}$ are entirely identical indicates the lack of interaction between the unpaired electrons of the two nitrophenyl groups separated by the mercury atom (i.e. mercury behaves as a non-conducting bridge). The relatively high stability of the radical-anions of the nitrophenyl derivatives of mercury is due to the electron-accepting effect of the nitro-groups,

which prevents the accumulation of excess spin density in the mercury–carbon bond. In the general case radical-anions of the type $R_2Hg^{\cdot-}$ (R = phenyl, benzyl, or phenyl-*o*-carbaboranyl), formed on reduction of substrates with sodionaphthalene or lithium in DME, are unstable and decompose with liberation of metallic mercury and the formation of reactive carbanions, which undergo various transformations[26,27]:

$$R_2Hg + C_{10}H_8^{\cdot-} \rightarrow R_2Hg^{\cdot-} + C_{10}H_8 \rightarrow R^- + {}^1/_2R_2Hg + {}^1/_2Hg \quad .$$

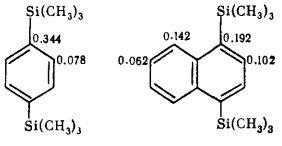
Numerous studies have been devoted to the radical-anions of Group IVA elements. It was of interest to elucidate the possibility of the involvement of the vacant *d* orbitals of these elements in the delocalisation of the unpaired electron. The radical-anions of trimethylsilyl- or trimethylgermyl-substituted benzenes and naphthalenes have EPR spectra with a hyperfine structure due to the methyl protons of the Me_3M groups[28–33]. The splitting of the signal by the methyl protons of the trimethylsilyl and trimethylgermyl groups is observed also in the radical-anions obtained by the reduction of phenylethynyltrimethylsilane and phenylethynyltrimethylgermane by alkali metals THF ($a_H^{SiMe_3} = 0.28$ G, $a_{Si} = 4.4$ G, $a_H^{GeMe_3} = 0.15$ G, and $a_{Ge} = 1.67$ G).[34,35] The chemical and electrochemical reduction of cyclic permethylpolysilane $(Me_2Si)_n$ ($n = 5$, 6, or 7) leads to the corresponding radical-anions, in which the unpaired electron interacts with all the methyl protons[37,38]. The spectrum of the radical-anion of di-(t-butyl)diacetylene is a singlet, while that of the radical-anion of di(trimethylsilyl)diacetylene consists of 19 lines due to the interaction of the unpaired electron with the 18 methyl protons ($a_H^{SiMe_3} = 0.15$ G and $a_{Si} = 5.25$ G).[36]

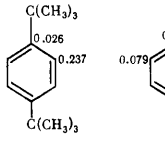
It is noteworthy that the radical-anions containing the trimethylsilyl and trimethylgermyl groups are more stable than their carbon analogues. With increase of the number of these groups, the stability of the radical-anion increases. Thus the *p*-bis-(t-butyl)benzene radical-anion is stable only at −70 °C, the *p*-bis(trimethylsilyl)benzene radical-anion is stable at 0 °C, and the radical-anion derived from 1,3,5-tris-(trimethylsilyl)benzene does not decompose for a long time at 20 °C.[30,39,40] The Hammett constants of the trimethylsilyl and trimethylgermyl groups in radical-anions of the type

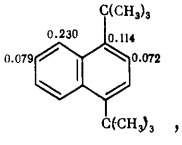


$(CH_3)_3E$, E = Si or Ge,

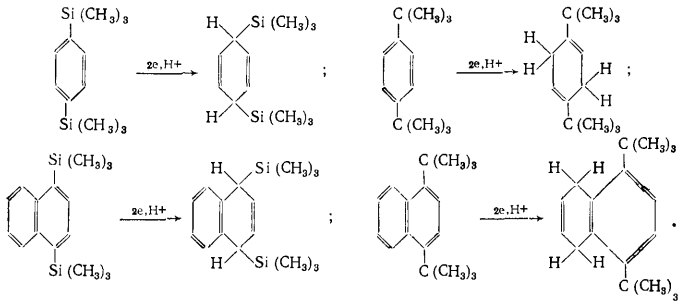
are positive, which shows that they have electron-accepting properties[41,42]. This also follows from a comparison of the HFI constants for the radical-anions containing the trimethylsilyl and t-butyl groups and from the calculation of the spin densities by the MacConnell method[39,43]:





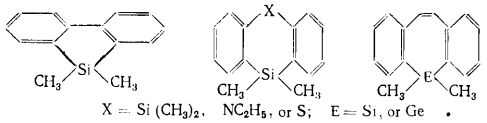


The above difference between the silicon and carbon analogues agrees well with the finding that the reduction of these compounds with sodium in liquid ammonia leads to products of different structure[43]:



In the radical-anions of phenylethyl derivatives of silicon and germanium the hyperfine interaction constants for the *meta*-protons of the benzene rings are higher than those for the *ortho*-protons, which confirms yet again the electron-accepting nature of these groups; the opposite relative values of the constants obtain for the t-butyl group[34,35]. The introduction of the trimethylsilyl group into the *N,N*-dimethylaniline molecule increases its electron affinity to such an extent that, despite the influence of the electron-donating dimethylamino-group, it is possible to obtain the radical-anion[44,45]. In the radical-anion of *p*-trimethylsilyl-*N,N*-dimethylaniline[44] the distribution of spin density is analogous to that for the benzene radical-anion, i.e. the influence of the two substituents cancels out.

The radical-anions formed in the reduction of different cyclic silicon and germanium compounds have been detected[46–49]:



X = $Si(CH_3)_2$, NC_2H_5, or S; E = Si, or Ge .

Their stability varies within fairly wide limits, but in this case the heteroatom has a stabilising influence and exhibits the properties of a π-acceptor[48].

The possibility of the delocalisation of the unpaired electron via the silicon in the radical-anions obtained on reduction (with potassium in DME) of dimethyldiphenylsilane, methyltriphenylsilane, and tetraphenylsilane has been studied[46,50,51]. The EPR spectra of the resulting radical-anions were characterised by the main doublet splitting ($a_H^{para} = 8$ G), which initially led to the conclusion that the unpaired electron is localised solely in the benzene ring. The lack of conductivity of the silicon atom was also noted for the radical-anions in which biphenyl groups are separated by a dimethylsilyl bridge[52,53]. Subsequently it was found that the primary radical-anions are extremely unstable even at a low temperature and decompose as a result of the following rapid reactions[54]:

$$(C_6H_5)_4Si \xrightarrow{e} [(C_6H_5)_4Si]^{\cdot-} \xrightarrow{e} (C_6H_5)_3Si^- + C_6H_5^-$$

$$(C_6H_5)_3Si^- \xrightarrow{CH_3OCH_2CH_2OCH_3} (C_6H_5)_3SiCH_3 \xrightarrow{e} [(C_6H_5)_3SiCH_3]^{\cdot-} \rightarrow$$

$$\xrightarrow{e} (C_6H_5)_2SiCH_3^- + C_6H_5^- \xrightarrow{CH_3OCH_2CH_2OCH_3} \ldots . [C_6H_5Si(CH_3)_3]^{\cdot-} \quad .$$

The trimethylphenylsilyl radical-anion is most stable in this series of radical-anions; its spectrum had apparently been detected in all previous instances.

The radical-anions derived from phenylsilanes are more stable in THF and give rise to resolved EPR spectra, which are identical regardless of whether they are produced chemically or electrochemically. The unpaired electron is delocalised over the entire phenyl groups and the form of the spectra is determined by the principal splitting by the *para*-protons

of the benzene rings with additional splitting of each component by the ring protons and the methyl protons of the silyl groups[54–57] (Table 2). For the dimethyldiphenylsilane radical-anion, the dependence of the distribution of spin density on temperature was demonstrated. In THF at temperatures below −70 °C the unpaired electron is localised in only one benzene ring, while on raising the temperature to −40 °C both phenyl groups are involved in the formation of a single conjugated system incorporating the silicon atom[58].

Table 2. EPR spectroscopic parameters for radical-anions of certain silicon-containing compounds (multiplicity in brakets)[54].

Compound	a_H^{ortho}, G	a_H^{ortho}, G	a_H^{meta}, G	$a_H^{CH_3}$, G
$C_6H_5Si(CH_3)_3$	8.06 (2)	2.61 (3)	1.03 (3)	0.26 (10)
$(C_6H_5)_2Si(CH_3)_2$	4.15 (3)	1.44 (5)	0.34 (5)	0.17 (7)
$(C_6H_5)_3SiCH_3$	2.76 (4)	1.01 (7)	0.19 (7)	0.10 (4)
$(C_6H_5)_4Si$	2.12 (5)	0.80 (9)	0.10 (9)	—

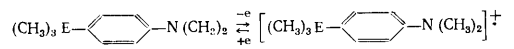
Thus analysis of the EPR data indicates the inclusion of the silicon and germanium atoms in the overall molecular orbital in which the unpaired electron is located. The transfer of spin density apparently takes place via a d_π–p_π interaction, which has been confirmed by the hyperfine structure due to the methyl protons of the trimethylsilyl and trimethylgermyl groups, the π-electron-accepting properties of these groups, and the conductivity of the silicon in the phenylsilane radical-anions.

Organotin and organolead radical-anions are almost unknown. There are data indicating the formation of radical-anions at 77 K by γ-radiolysis (^{60}Co) from tetramethyltin, trimethyltin chloride, and hexaphenyldistannane; the constants for the interaction of the unpaired electron with the $^{117/119}$Sn nuclei and the spin densities in the 5*s* orbitals of these isotopes have been determined. The hexaphenyldistannane radial-anion decomposes in accordance with the equation[59]

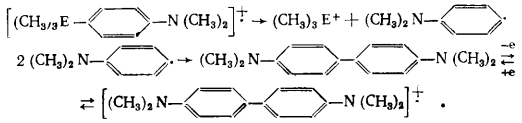
$$[(C_6H_5)_3Sn{-}Sn(C_6H_5)_3]^{\cdot-} \rightarrow (C_6H_5)_3Sn^- + (C_6H_5)_3Sn^{\cdot}\ .$$

Lead-containing radical-anions of the type $R_3PbX^{\cdot-}$ ($R = CH_3$ or C_6H_5; X = Cl or Br),[60,61] characterised by a marked splitting of the EPR signal by the ^{207}Pb nuclei ($a_{Pb} = 2108$–2366 G) and a hyperfine structure due to ^{35}Cl and ^{81}Br, have been generated by the same method.

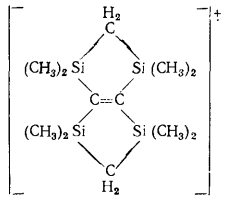
Organoelemental radical-cations were discovered only recently. An unstable radical-cation is formed on electrochemical oxidation of *p*-trimethylsilyl- and *p*-trimethylgermyl-*N*,*N*-dimethylanilines[62,63]:



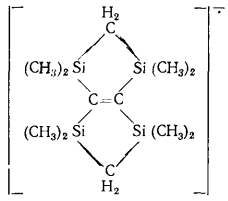
The negligibly small methyl proton hyperfine interaction constants of the organoelemental groups ($a_H < 0.1$ G) indicate only a slight interaction of the silicon and germanium atoms with the π-system of the radical-cation. In the presence of nucleophiles the radical-cations decompose rapidly:



One-electron oxidation of tetrasilylethylenes and tetrasilylhydrazines (by $AlCl_3$, $AgBF_4$, and $SbCl_5$) in CH_2Cl_2 yielded stable silicon-containing radical-cations[64,65]. The splitting constants for the nuclei in the corresponding radical-anions of tetrasilylethylene were much smaller than for the radical-cation[64]:

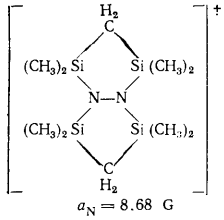


$a_{Si} = 22.716$ G, $a_H^{CH_3} = 0.62$ G, $a_H^{CH_2} = 2.48$ G

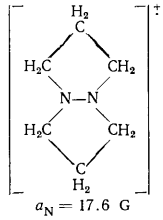


$a_{Si} = 6.72$ G, $a_H^{CH_3} = a_H^{CH_2} = 0.48$ G.

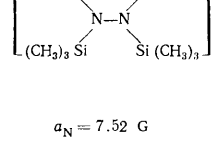
In tetrasilylhydrazine radical-cations the spin density at the >N–N< fragment is reduced compared with the carbon analogues[65,66]:



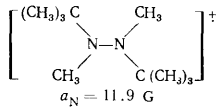
$a_N = 8.68$ G



$a_N = 17.6$ G

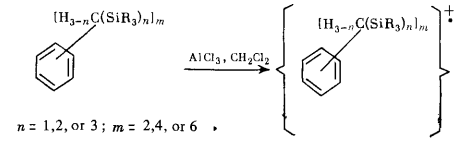


$a_N = 7.52$ G



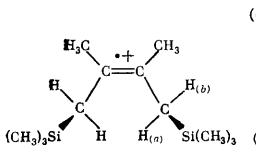
$a_N = 11.9$ G

In the tetrakis(trimethylsilyl)hydrazine radical-cation the trimethylsilyl group has the same influence as the phenyl group in the tetraphenylhydrazine radical-cation ($a_N = 7.52$ G).[67] All this reflects the electron-donating properties of the trimethylsilyl group, which is capable of delocalising the positive charge in the radical-cation[68]. This conclusion was confirmed in a study of a series of radical-cations obtained from derivatives of poly(trimethylsilylalkyl)-substituted benzenes[69]:

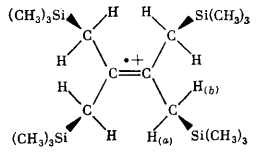


$n = 1,2,$ or 3; $m = 2,4,$ or 6.

Here too a decrease of spin density in the benzene ring was observed with increase of the number of trimethylsilyl substituents. It is noteworthy that the methylene protons in the radical-cations containing trimethylsilylmethyl groups are non-equivalent:



$a_H^a = 1.07$ G, $a_H^b = 0.76$ G



$a_H^a = 0.85$ G, $a_H^b = 0.73$ G.

The difference between the splitting constants ($a_H^a \neq a_H^b$) indicates the absence of free rotation of the $CH_2Si(CH_3)_3$ groups and the conformational stability of these radicals[70,71].

Thus, whereas the trimethylsilyl group in the radical-anions described above behaves as a π-acceptor, in the radical-cations the same group is a powerful electron donor. The transfer of spin density apparently takes place via a mechanism involving hyperconjugation between the silicon–carbon bond and the *p* orbital of the unpaired electron[72].

III. ELEMENT-CENTRED RADICALS

This class of free radicals includes organoelemental radicals in which the unpaired electron is localised preferentially at the atom of the element. The formation of such radicals is frequently an intermediate stage in a whole series of reactions, but there is comparatively little reliable information about them. This is due to the lack of convenient methods for their generation unaccompanied by their rapid subsequent reactions. Being essentially derivatives of elements which do not exhibit their full valence element-centred radicals should behave as active electron donors; in this respect they differ significantly from the majority of "purely" organic free radicals.

The chemistry of organomercury free radicals RHg· has been continuously discussed for more than forty years, but so far it has not been possible to detect them by any of the physical methods. The formation of the free radicals RHg· has been postulated in the classical studies by Razuvaev and coworkers[73–76] on the thermal and photochemical decomposition of organomercury compounds:

$$R_2Hg \rightarrow RHg^{\cdot} + R^{\cdot}; \quad RHgOH \rightarrow RHg^{\cdot} + {}^{\cdot}OH \quad .$$

In halogen-containing media reactions of this kind lead to organomercury halides (formally, this entails the abstraction of the halogen atom):

$$RHg^{\cdot} + R'Cl \rightarrow RHgCl + R'^{\cdot} \quad .$$

However, it is perhaps more correct to treat the last reaction as a one-electron transfer process:

$$RHg^{\cdot} + R'Cl \rightarrow RHg^{+} + R'^{\cdot} + Cl^{-} \quad .$$

The radicals RHg· are clearly incapable of abstracting a hydrogen atom and in solvents without a halogen they decompose, according to Razuvaev, in one of two ways:

$$RHg^{\cdot} \rightarrow R^{\cdot} + Hg, \quad 2\,RHg^{\cdot} \rightarrow R_2Hg + Hg \quad .$$

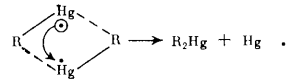
Radicals of the type RHg· are undoubtedly formed in the electrochemical reduction of organomercury solvents[77–79]:

$$RHg^{+} + e \rightleftarrows RHg \quad .$$

However, the electrode reaction, which is in principle reversible, in the present instance becomes in fact irreversible owing to the rapid subsequent reactions of the radical RHg·. The final products are dialkylmercury and mercury[79,80]; the majority of investigators are at present inclined to the idea that an "organic calomel" RHgHgR is formed as an intermediate, but not a single compound of this type has so far been isolated[77–79]. The electrochemical symmetrisation of the stereoisomeric β-chlorovinylmercury chlorides takes place with complete retention of the configuration of the organic group[81], which means that the β-chlorovinyl free radicals are not involved in such symmetrisation and the reaction

$$ClCH{=}CHHg^{\cdot} \rightarrow ClCH{=}CH^{\cdot} + Hg$$

can occur only as a side process (liberation of the radical from the "cage"). The intermediate formation of "organic calomel" is at present only a hypothesis; the available data can be accounted for no less successfully by the disproportionation of two RHg· radicals occurring as a one-electron transfer process in the transition complex:

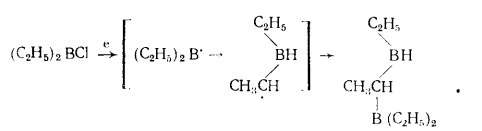


Substances readily conducting electric current and decomposing on heating with formation of dialkylmercury and mercury have been isolated in the electrolysis of solutions of alkylmercury chlorides in liquid ammonia at the cathode[82–84]. However, EPR study of these substances showed that they are diamagnetic[85]. Evidently the compounds obtained have a metallic lattice formed by ions and all the conduction electrons belong to it as a single whole. The view that the homolysis of fully substituted organomercury compounds takes place, like their electrochemical reduction, with the simultaneous abstraction of both organic groups, has been established recently. However, one should bear in mind the meaning attributed to the concept of simultaneity. In their discussion of the mechanism of one-electron transport, Basolo and Pearson correctly note that the "concept of simultaneity is unsatisfactory"[86]. True simultaneity is kinetically indistinguishable from a sequence of two reactions the first of which is rate-limiting:

$$R_2Hg \xrightarrow{\text{slow}} RHg^{\cdot} + R^{\cdot}; \quad RHg^{\cdot} \xrightarrow{\text{fast}} R^{\cdot} + Hg \quad .$$

There is at present no reason to abandon Razuvaev's initial treatment and the reduction of organic halides in the course of photolysis of dialkylmercury can be regarded as important evidence in support of the actual existence of RHg· radicals. The possibility, in principle, of the stepwise electrochemical reduction of diarylmercury also clearly follows from the study of Dessy et al.[25] already quoted.

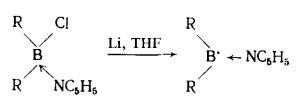
Attempts have been made in a number of investigations to obtain organic derivatives of Group IIIA elements not in their maximum valence state. The reduction of dialkylboron chlorides by alkali metals did not lead to organoboron radicals which could be detected by EPR, owing to their rapid dimerisation[87,88]:



On treatment with potassium in benzene, diphenylboron chloride gives rise to a dimeric product, which is reduced in DME to a radical-anion; the EPR spectrum consists of 7 lines due to the interaction of the unpaired electron with two boron atoms ($a_B = 2.9$ G):[11]

$$(C_6D_5)_2BCl \xrightarrow{\text{K, benzene}} (C_6D_5)_2B{-}B(C_6D_5)_2 \xrightarrow{\text{K, DME}} [(C_6D_5)_2B{-}B(C_6D_5)_2]^{-} \quad .$$

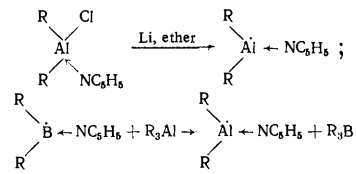
Data apparently indicating the formation of the dimesitylboron radical on reduction of dimesitylboron fluoride proved to be erroneous[89]. The spectrum of the radical obtained proved to be identical with the spectrum of the trimesitylboron radical-anion[11]. However, dialkylboron radicals stabilised by bases (pyridine, quinoline) are fairly stable[87,88]:



(R = C_2H_5 or C_6H_5).

Depending on the base, boron-centred radicals are associated

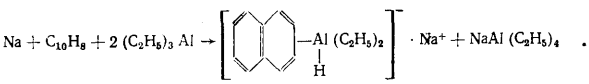
to different extents in solution. Thus the diethylboron radical stabilised with 4-methylquinoline is monomeric. In the case of 4-methylpyridine the analogous radical exists as the trimer; the EPR spectrum exhibits 10 lines due to the splitting of the unpaired electron signal by three boron nuclei ($a_B = 3.83$ G). Aluminium-centred radicals have been obtained similarly[87]:



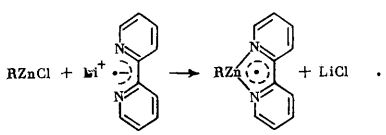
They are also formed on electrochemical reduction or on treatment of trialkylaluminium compounds with sodionaphthalene[90,91]. It is believed that the dialkylaluminium cation, obtained by the reaction[92]

$$[(C_2H_5)_3\,Al]_2 \rightleftarrows (C_2H_5)_2\,Al^+ + (C_2H_5)_4\,Al^-$$

is then reduced. The radicals formed in the reduction process are stabilised in the presence of bases. The following adduct has been obtained with sodionaphthalene[91]:



One must note that the true structure of the boron- and aluminium-centred radicals involves an appreciable transfer of spin density to the stabilised ligand. In the organozinc radicals having a similar structure the unpaired electron is fully localised in the ligand:

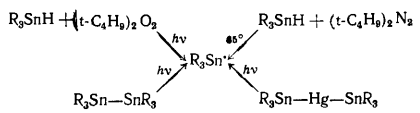


This is indicated by the absence of a hyperfine coupling with ^{67}Zn and the protons of the alkyl substituents[93]. These radicals have in fact the structure of an ion pair.

The greatest successes in the field of element-centred free radicals have been achieved for derivatives of Group IVA elements. A convenient method for the generation of radicals of the type $R_3E^\cdot$ involves the interaction of the hydrides of these elements with t-butyl peroxide under irradiation[94,99]:

$$R_3EH + t\text{-}C_4H_9O^\cdot \rightarrow R_3E^\cdot + t\text{-}C_4H_9OH\ .$$

The tris-(2-phenyl-2-methylpropyl)stannyl radical has been obtained by several methods[100]:



Unusually stable radicals of this type are formed when the dihalides ECl_2 (E = Sn or Ge) interact with bis(trimethylsilyl)methyl-lithium and this is followed by ultraviolet irradiation[101–103]:

$$ECl_2 + RLi \rightarrow R_2E \xrightarrow{h\nu} R_3E^\cdot$$

$$Si_2Cl_6 + RLi \rightarrow (RSiCl_2)_2 + [R_2SiCl{-}SiCl_3] \xrightarrow{-SiCl_4} [R_2Si] \xrightarrow{h\nu} R_2Si\ .$$

The corresponding bivalent derivatives R_2E have been isolated for tin and germanium[104]; therefore the photochemically initiated decomposition actually leads to the formation of stable element-centred radicals. The same radicals can be obtained on ultraviolet irradiation of the trialkyl derivatives of the halides of the elements in the presence of electron-donating olefins[105]:

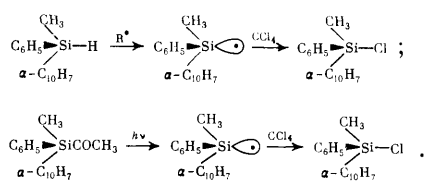
$$2\,R_3ECl + (Me_2N)_2C{=}C(NMe_2)_2 \xrightarrow{h\nu} [R_3ECl]^{\tau} \rightarrow R_3E^\cdot + [(Me_2N)_2C{=}C(NMe_2)_2]^{2+} \cdot 2\,Cl^-\ .$$

The multiplet EPR spectra of element-centred radicals with satellite lines due to the magnetic isotopes ^{29}Si, ^{73}Ge, and $^{117/119}$Sn have been recorded (Table 3).

Table 3. EPR spectroscopic parameters for certain element-centred radicals[100–105].

Radical	a_H, G	a_E, G	g-Factor
$(CH_3)_3Si^\cdot$	6.28	181	2.0032
$(CH_3)_3Ge^\cdot$	5.28	84.7	2.0101
$(CH_3)_3Sn^\cdot$	2.76	1899 and 1986	2.0154
$[(Me_3Si)_2CH]_3Si^\cdot$	4.8	198	2.0027
$[(Me_3Si)_2CH]_3Ge^\cdot$	3.8	92	2.0078
$[(Me_3Si)_2CH]_3Sn^\cdot$	2.1	1698 and 1776	2.0094

The high values of the splitting constants for the nuclei of the central elements indicate significant *s* character of the unpaired electron orbital, as a result of which 80% of the spin density corresponds to the heteroatom[106–109]. This also indicates a pyramidal structure of the radicals, in which the metal–carbon bonds deviate from the plane by 12–14°. This structure has been confirmed by a chemical study of the radicals derived from asymmetric silicon compounds, which react with retention of configuration[110,111]:



The latter factor shows that the large series of old studies on the mechanism of substitution at the silicon atom, where the reaction mechanism was inferred from the retention of optical activity, are evidently incorrect[112].

Element-centred radicals are very reactive and their lifetime is therefore extremely short. However, there exists a group of radicals which are unusually stable: the half-lives of $R_3E^\cdot$ [E = Si, Ge, or Sn; R = bis(trimethylsilyl)methyl] at 30 °C are respectively 10 min, 4 months, and 1 year[102]. This is caused by the steric hindrance due to the bulky alkyl groups, as a result of which the central metal atom cannot assume the tetrahedral configuration and hence the recombination or abstraction of a hydrogen atom from the solvent becomes impossible.

Measurements of the magnetic susceptibilities of solutions of compounds of the type $R_3E{-}ER_3$ ($R = C_6H_5$; E = Ge, Sn, or Pb) showed that they are incapable of dissociating into free radicals[113–115]. Small amounts of trimesityl-lead radicals, detected by EPR, are formed only in highly dilute solutions of hexamesityldiplumbane[116].

Thus the stability of organoelemental radicals R_3E is determined mainly by the size of the organic groups linked to the central metal atom. The radicals are most stable in the presence of bulky substituents.

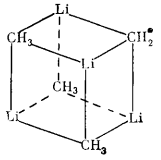
Information about the principal reactions of element-centred radicals can be found in recent monographs[117,118].

IV. ORGANOELEMENTAL COMPOUNDS WITH PARAMAGNETIC LIGANDS

This group of compounds is most varied among those considered. Naturally the classification adopted in the present study is conventional and there are no absolutely clear-cut boundaries between the three groups of paramagnetic species which we have distinguished. Thus in many compounds of the last group a definite proportion of spin density corresponds also to the metal.

Organoelemental free radicals in which the unpaired electron is localised mainly in the ligand include, in particular, α-substituted alkyl radicals of the type $^{\cdot}CR_2ER'_n$, where ER'_n is an organometallic group.

The reaction of methyl-lithium with photochemically generated t-butoxy-radicals in ether yielded a radical containing the CH_2Li fragment[119]. The well-resolved EPR spectrum of this radical consists of a triplet of decets due to the interaction of the unpaired electron with two equivalent protons ($a_H = 18.23$ G) and three equivalent ^7Li nuclei ($a_{Li} = 1.67$ G), which corresponds to the following structure of the radical:



Consequently the structure of tetrameric methyl-lithium[120,121] is not significantly distorted following the abstraction of a hydrogen atom and the system comprising three lithium atoms is non-conducting.

The interaction of t-butoxy-radicals with organomagnesium compounds proceeds in two ways[122]:

$$RCH_2MgX + t\text{-}C_4H_9O^{\cdot} \begin{cases} \longrightarrow R_2\dot{C}H_2 + t\text{-}C_4H_9OMgX \\ \longrightarrow R\dot{C}HMgX + t\text{-}C_4H_9OH \end{cases}$$

The hyperfine interaction constants for the α-protons are almost independent of R for magnesium-containing radicals and are in all cases 18.5 G. The absence of hyperfine structure due to the ^{35}Cl and ^{19}F nuclei in the radicals $^{\cdot}CH_2MgCl$ and $^{\cdot}CH_2MgF$ and the methyl protons in $^{\cdot}CH_2MgCH_3$ shows that the magnesium atom is non-conducting in radicals of this type. Low-temperature γ-radiolysis of trialkylaluminium compounds[123] and methylmercury chloride[124] leads to the corresponding alkyl radicals containing the organometallic group in the α-position. The negative sign of the hyperfine interaction constants for ^{27}Al is evidence for the transfer of spin density via a spin polarisation mechanism.

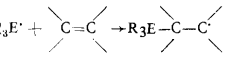
Analogous radicals of Group IVA elements have been obtained via the same general mechanism[125,126]:

$$R_3ECH_3 + t\text{-}C_4H_9O^{\cdot} \rightarrow R_3E\dot{C}H_2 + t\text{-}C_4H_9OH$$

In view of the independence of $a_H^{CH_2}$ and the *g*-factor of the type of element, it was concluded that there is no direct delocalisation of the unpaired electron over the vacant *d* orbitals of these elements[127,128].

Thus the nature of the substituent in the radicals of the type $^{\cdot}CR_2ER'_n$ has little influence on the spin density distribution (the $a_H^{CH_2}$ constant changes only slightly) and the observed splittings by the nuclei of the elements are caused by spin polarisation.

The addition of element-centred radicals to carbon–carbon double bonds leads to radicals in which the organoelemental group is in a β-position with respect to the radical centre[126, 129–132]:



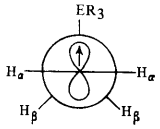
E = Si, Ge, or Sn.

The EPR spectra of these radicals are characterised by an anomalously small splitting by β-protons (Table 4).

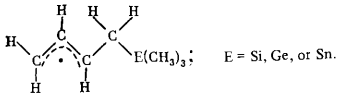
Table 4. EPR spectroscopic parameters for β-substituted ethyl radicals $^{\cdot}CH_2–CH_2–E(CH_3)_3$.[126,129–132]

E	a_H^{α}, G	a_H^{β}, G	$a_H^{CH_3}$, G	a_E, G	*g*-Factor
C	22.06	24.71	0.1	—	2.00268
Si	21.05	17.68	0.10	37.4	2.00265
Ge	20.70	16.57	0.14	488.9	2.00255
Sn	19.69	15.84	0.15	467	2.00255

The temperature dependence of the constant a_H^{β} indicates the presence of a barrier to rotation about the $C_\alpha–C_\beta$ bond. In the most stable configuration the organoelemental group is eclipsed by the *p* orbital, in which the unpaired electron is located:

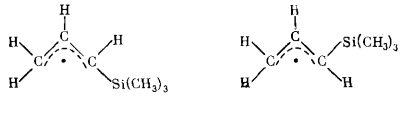


Allyl radicals also exhibit conformational stability[133,134]:



E = Si, Ge, or Sn.

This is confirmed by the non-equivalence of the methylene protons attached to the carbon atom linked to the organoelemental group; here too the organoelemental group is eclipsed by the *p* orbital of the unpaired electron. It is of interest to note the significant difference between the hyperfine interaction constants of the methyl protons in *cis*- and *trans*-trimethylsilylallyl radicals[136]:



$a_H^{CH_3} < 0.05$ G $\qquad$ $a_H^{CH_3} = 0.27$ G

These radicals proved incapable of isomeric interconversion.

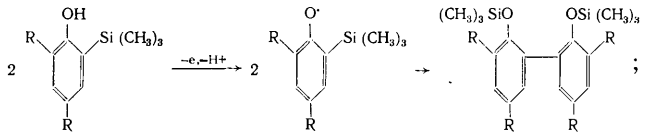
In trimethylsilyl-substituted cyclopentadienyl radicals the trimethylsilyl group in the α-position with respect to the radical centre behaves as an electron acceptor, while the same group in the β-position with respect to the π-system exhibits electron-donating properties. This follows from a comparison of the spin densities in the following radicals[136]:



Thus the conformational stability of β-substituted ethyl radicals $\cdot CH_2CH_2ER_3$ is due to the interaction of the unpaired electron with the organoelemental group, which exhibits the properties of an electron-donating substituent. This interaction apparently takes place via the hyperconjugation of the metal–carbon bond with the *p* orbital of the unpaired electron[137–139].

The radicals obtained by the oxidation of organoelemental derivatives of sterically hindered phenols are convenient objects for the study of the structure and properties of radicals in which the metal atom is involved in conjugation with a paramagnetic fragment. The phenoxy-radicals known hitherto, containing the substituents R_nE (E = Si, Ge, Sn, P, or As), differ sharply in their stability and reactions from their carbon analogues.

When 4,6-di-t-butyl-2-trimethylsilylphenol is oxidised by PbO_2 or an alkaline solution of $K_3Fe(CN)_6$, the phenoxy-radical formed dimerises rapidly with simultaneous migration of the *o*-trimethylsilyl group to the oxygen atom[140,141]:

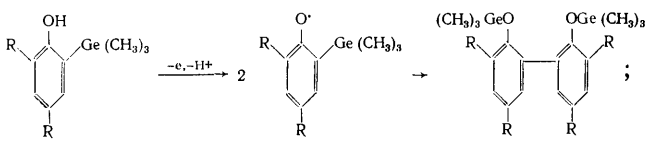


R = C $(CH_3)_3$.

The EPR spectrum of this radical contains four lines due to the interaction of the unpaired electron with the two non-equivalent *meta*-protons (a_H = 1.7 G, a_H = 2.2 G).[142,143] The migration of the *o*-trimethylsilyl group and the formation of a dimer are also possible on oxidation of 4-t-butyl-2,6-bis-(trimethylsilyl)phenol. The spectrum of the intermediate phenoxy-radical consists of a triplet (a_H = 1.8 G) with additional splitting of each component by the protons of the trimethylsilyl group ($a_H^{SiMe_3}$ = 0.4 G).[142]

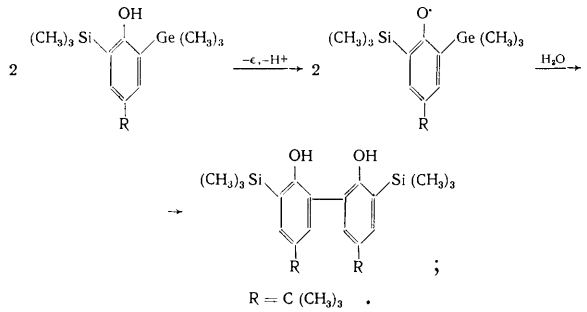
o-Phenyldimethylsilyl and *o*-triphenylsilyl groups are also able to migrate to the oxygen atom of the aryloxy-radical[144,145]. The introduction of the *o*-triphenylsilyl group reduces the capacity of the *o*-trimethylsilyl group for migration, increasing at the same time the stability of the corresponding phenoxy-radical. In the radical formed on oxidation of 4-cyclohexyl-2-trimethylsilyl-6-triphenylsilylphenol the "inhibiting" effect of the triphenylsilyl group makes the trimethylsilyl group altogether incapable of migration, while the 4-t-butyl-2-trimethylsilyl-6-triphenylsilylphenoxy-radical is the most stable silicon-containing phenoxy-radical; its EPR spectrum consists of a triplet (1:2:1) with additional splitting of each component by the protons of the $(CH_3)_3Si$ and $(C_6H_5)_3Si$ groups (a_H^{meta} = 1.8 G, $a_H^{Si(CH_3)_3}$ = 1.5 G).[145] The hyperfine interaction constants for the protons of the t-butyl groups in the *ortho*-positions in the 2,4,6-tri-t-butylphenoxy-radical (a_H = 0.072 G)[146] and the trimethylsilyl groups in the 4-t-butyl-2,6-bis(trimethylsilyl)phenoxy-radical (a_H = 0.4 G) differ by a factor of approximately 6. This shows that the spin conductivity of silicon is much higher than that of carbon[147].

The trimethylgermyl group is also capable of migrating to the oxygen atom of the aryloxy-radical[148–150]:



R = C $(CH_3)_3$.

In order to compare the migratory capacities of R_3Si and R_3Ge, mixed silicon-germanium-containing phenoxy-radicals have been synthesised. The oxidation of 4-t-butyl-6-trimethylgermyl-2-trimethylsilylphenol leads to 5,5′-di-t-butyl-2,2′-dihydroxy-3,3′-bis(trimethylsilyl)biphenyl[149,150]:



R = C $(CH_3)_3$.

This indicates a greater capacity of the trimethylgermyl group for migration. The replacement of the trimethylsilyl group by the triphenylsilyl group increases the stability of the radical[149]. Thus the capacity for migration of the group in the *ortho*-position diminishes in the sequence $(CH_3)_3Ge > (CH_3)_3Si > (C_6H_5)_3Si$.

2,6-Di-t-butylphenoxy-radicals containing an organometallic group in the *para*-position are more common. The EPR spectra contain, apart from the main signal due to the interaction of the unpaired electron with the *meta*-protons, additional lines due to coupling with the magnetic nuclei of the substituents (Table 5).

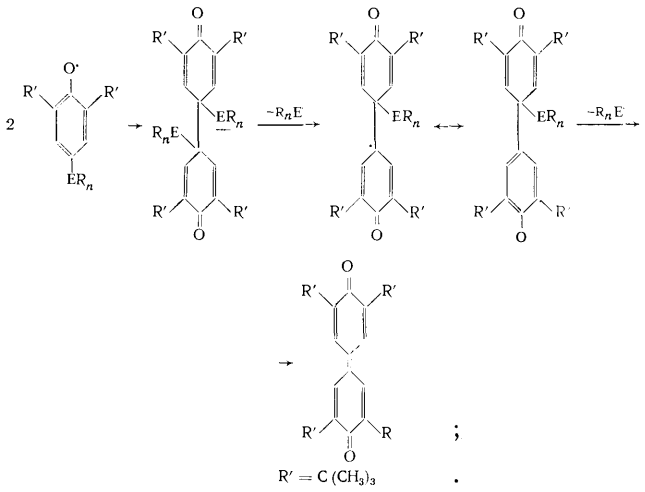
Table 5. EPR spectroscopic parameters for 2,6-di-t-butylphenoxy-radicals containing an organoelemental group R in the *para*-position.

R	a_H^{meta}, G	a_E, G	References
$(CH_3)_3Si$—	1.8	12.4	148
$(CH_3)_3Ge$—	1.7	2.9	148
$(C_6H_5)_3Sn$—	1.82	58.13 и 61.0	151
$(C_6H_5)_2P$—	1.6	6.8	152–154
$(C_6H_5)_2P$ (O)—	2.0	14.7	152–154
$(C_6H_5)_2P$ (S)—	2.0	15.4	152–154
$(C_6H_5)_2As$—	1.83	24.7	153–155
$(C_6H_5)_2As$ (O)—	2.0	14.1	153–155
$(C_6H_5)_2As$ (S)—	2.0	14.5	153–155

It follows from a comparison of a_H^{meta} for the 2,4,6-tri-t-butylphenoxy-radical (a_H = 1.80 G)[157] and the data in Table 5 that the organometallic group has only a weak influence on the spin density distribution in the radical. The splitting constants for Ge and Si in the *para*-position are greater than those for Ge and Si in the *ortho*-position, which shows that, as regards the distribution of spin density, such radicals are analogous to the 2,4,6-tri-t-butylphenoxy-radical[158].

In contrast to the *ortho*-analogues, in *para*-substituted organoelemental phenoxy-radicals the organometallic group proved to be incapable of migrating to the oxygen atom of

the aryloxy-radical. The most common property is elimination of the organometallic group with formation of 3,3',5,5'-tetra-t-butyldiphenoquinone as the final product[152,153]:

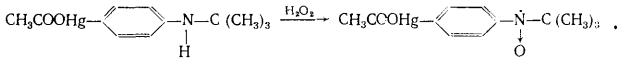


$R' = C(CH_3)_3$.

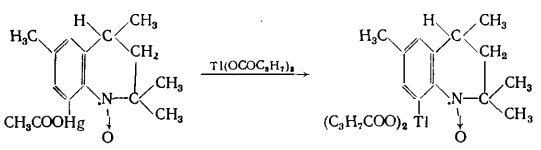
A qualitatively new spin density distribution has been observed for phenoxy-radicals containing electron-accepting carbaboranyl substituents[159]. Analysis of the hyperfine structure of the EPR spectra showed that the unpaired electron hardly interacts with the protons located in the *meta*-positions in the ring. The observed spectra can be interpreted as a result of the splitting of the signal by six boron nuclei ($a_B = 0.9$ G) closest to the carbon–carbon bond in the carbaborane ring. These radicals are distinguished by high stability in solution; in particular, they persist for several hours in acetic acid and hardly interact with atmospheric oxygen. It has been observed[160] that the 2,6-di-t-butyl-4-(2-carbaboranyl)phenoxy-radical readily rearranges to the *ortho*-isomer.

Thus the presence of the unpaired electron in the *m*-carbaborane ring significantly distorts the system of many-centre orbitals linking the boron–carbon skeleton, as a result of which the *meta–ortho* rearrangement, noted previously for the diamagnetic *m*-carbaborane dianions[161,162], is considerably facilitated.

Stable organomercury radicals have been obtained by the oxidation of mercurated phenylamines by hydrogen peroxide in dioxan in the presence of sodium tungstate[163]:



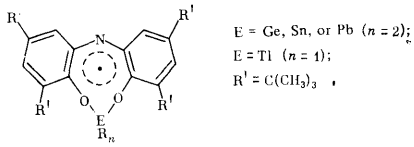
The EPR spectra of these radicals show the main triplet splitting by the ^{14}N nucleus and the additional groups of lines, due to splitting by the magnetic mercury isotopes, reproduce exactly the structure of the "nitrogen" component. A common feature of mercury-containing nitroxy-radicals is increased splitting by nitrogen and the phenyl protons compared with the unsubstituted radicals. An interesting fact was observed in the study of the reaction of 8-acetoxymercuri-2,2,4,6-tetramethyl-1,2,3,4-tetrahydroquinoline nitroxy-radical with thallium tri-isobutyrate[164]:



The exchange of mercury for thallium gives rise to a new thallium-containing radical. The hyperfine structure of its EPR spectrum indicates the interaction of the unpaired electron with two thallium isotopes—^{203}Tl ($I = 1/2$) and ^{205}Tl ($I = 1/2$) ($a_{Tl} \approx 240$ G).

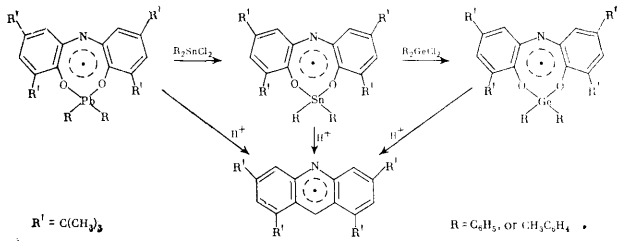
The reduced nitrogen splitting constant ($a_N = 6.5$ G) for the bis(trimethylsilyl)nitroxy-radical $(Me_3Si)_2NO^{\cdot}$ indicates an intense d_π–p_π interaction between the silicon and nitrogen atoms. The trimethylgermyl group is a weaker acceptor; thus the hyperfine interaction constant for nitrogen in $(Me_3Ge)_2NO^{\cdot}$ is 8.8 G.[165]

The interaction of the 2-amino-4,6-t-butylphenoxy-radical with the diaryl derivatives of the halides of Group IVA elements[166–168] and thallium[169] leads to radicals having the following structure:



E = Ge, Sn, or Pb ($n = 2$);
E = Tl ($n = 1$);
$R' = C(CH_3)_3$.

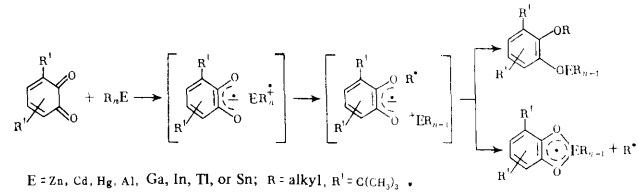
They are stable with respect to the action of atmospheric oxygen and can be isolated in a solid state. Their EPR spectra exhibit lines due to the interaction of the unpaired electron with the nuclei of the elements ^{73}Ge ($a = 3.02$ G), ^{119}Sn ($a = 46.5$ G), ^{117}Sn ($a = 44.5$ G), and ^{207}Pb ($a = 41.68$ G). The hyperfine interaction constants for the protons and the nitrogen atom are virtually the same for all the radicals and are independent of the nature of the substituent R attached to the element. In the series Pb, Sn, Ge each succeeding element can substitute the preceding element in the radical via the mechanism



$R' = C(CH_3)_3$ $R = C_6H_5$, or $CH_3C_6H_4$.

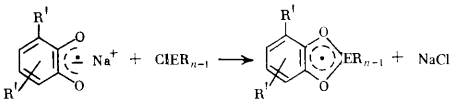
On treatment with acid, the 2,4,6,8-tetra-t-butylphenoxazinyl radical is formed[170].

o-Quinones are effective oxidants for metals capable of one-electron oxidation[171–173]; the reactions of organometallic compounds with substituted *o*-quinones also involve a one-electron transfer stage and lead to the formation of relatively stable intermediates[174–178]:

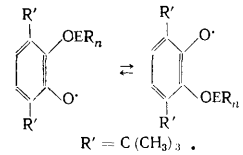


E = Zn, Cd, Hg, Al, Ga, In, Tl, or Sn; R = alkyl, $R' = C(CH_3)_3$.

Paramagnetic semiquinolates containing the organoelemental groups ER_{n-1} have been detected by EPR. The same radicals can be obtained by an exchange reaction:

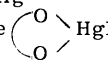


The nature of the metal–carbon bond has a strong influence on the spin density distribution in *o*-semiquinolates and on the hyperfine interaction with the paramagnetic nuclei of the central atom. In the *o*-semiquinolates obtained from 3,6-di-t-butyl-*o*-quinone and organometallic compounds of zinc, cadmium, or tin an intramolecular migration of the organometallic residue between the oxygen atoms at a rate measurable by EPR was observed[175,176]:

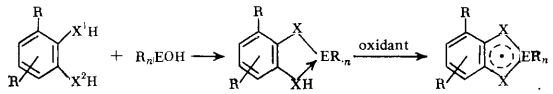


R′ = C(CH$_3$)$_3$.

Thus, owing to the temperature variation of the frequency of the intramolecular migration of the chlorodimethylstannyl group, the EPR spectrum of the radical is transformed from a doublet of doublets with splitting by the ring protons ($a_H = 5.2$ G and $a_H = 2.6$ G) at a low temperature into a triplet ($a_H = 3.6$ G) at a high temperature. The splitting constants for tin change little under these conditions ($a_{^{117}Sn} = 21.5$ G, $a_{^{119}Sn} = 22.5$ G).[176] In paramagnetic chelates formed with central atoms of other elements this effect was not observed, which can be explained either by the rapid migration of the organometallic group or by its localisation on the C_2 symmetry axis or in the symmetry plane of the benzene ring.

A sharp decrease of the *g*-factor has been noted for mercury derivatives compared with other derivatives as well as a dependence of a_{Hg} on the nature of the substituent at the mercury atom[175,177]. With increase of the bulk of the alkyl substituent, a_{Hg} increases from 5.3 G for the methyl group to 10.4 G for the t-butyl group. The nature of the influence of the group at the mercury atom on a_{Hg} has been explained by a change in the configuration of the  fragment as the bulk of the substituent is altered. It is believed that in the complex the mercury atom has a pyramidal structure, but, with increase of the substituent bulk, the fragment is flattened, which leads to an increase of the amount of *s* character of the bonding orbitals of the Hg–O bond. For the most bulky substituent, pure sp^2-hybridisation occurs at the mercury atom, which corresponds to the maximum value of a_{Hg} and this is due to the spin polarisation of the σ-bonds by the unpaired electron in the *p* orbital of the oxygen atom[175]. The increase of splitting by the Al, Ga, Tl, and In nuclei in the alkyl derivatives of the corresponding elements relative to their halides[179,180] has also been attributed to a change in the geometry of the chelate on passing to the more bulky alkyl substituents[174].

Paramagnetic nitrogen-containing thallium and tin chelates have been obtained via the mechanism[181–184]



R = phenyl; E = Sn or Tl; $X^1 = O$, $X^2 = NH$ or $X^1 = X^2 = NH$.

An increase in the splitting constants for the nuclei or the elements on passing to nitrogen-containing chelates has been noted. Whereas $a_{Tl} = 10$ G for the *o*-semiquinolates of diphenylthallium, the constants for the chelates formed by *o*-aminophenol and *o*-phenylenediamine are 40 and 90 G respectively. The dependence of a_{Tl} on the solvating capacity of the solvent increases in the same sequence, which has been explained by the increasing covalence of the metal–ligand bonds for complexes of the latter type[182,183].

The influence of the solvent on the splitting constants due to the interaction with the nuclei of the central elements is apparently associated with a change in the geometry of the chelate under the influence of the solvating solvent, as a result of which the contributions of the *s* and *p* orbitals of the elements to the atomic orbital responsible for the hyperfine structure is changed and the direct appearance of the spin density is caused by the polarisation of these orbitals[185].

Thus there are good prospects for the further development of the chemistry of paramagnetic organic derivatives of non-transition elements established at the present time. The relatively stable radical-ions of the type $R{-}m^{\cdot-}$ and $R{-}m^{\cdot+}$ are convenient models for the determination of the detailed features of the mechanism of the dissociation of the element–carbon bonds. The study of the properties and reactions of element-centred radicals creates the necessary basis for the development of fundamentally new synthetic methods in the field of organoelemental chemistry. Both these fields make it possible in many instances to solve problems of the electronic structure of organoelemental compounds, in particular the problem of the resonance conductivity of the heteroatom. The extensive field of the chemistry of stable radicals will be undoubtedly enriched by data for organoelemental species of this class.

REFERENCES

1. K.A.Bilevich and O.Yu.Okhlobystin, Uspekhi Khim., **37**, 2162 (1968)[Russ.Chem.Rev., No.12 (1968)].
2. O.Yu.Okhlobystin, "Perenos Elektrona v Organicheskikh Reaktsiyakh" (Electron Transfer in Organic Reactions), Izd.Rostov.Univ., Rostov-on-Don, 1974.
3. O.Yu.Okhlobystin, "Tezisy XI Mendeleevskogo S'ezda po Obshchei i Prikladnoi Khimii, Alma-Ata, 1975" (Abstracts of Reports at the XIth Mendeleev Congress on General and Applied Chemistry, Alma-Ata, 1975), p.35.
4. V.Ts.Kampel', K.A.Bilevich, and O.Yu.Okhlobystin, Dokl.Akad.Nauk SSSR, **197**, 95 (1971).
5. E.Krause and H.Polack, Ber., **59**, 777 (1926).
6. H.Bent and M.Dorfman, J.Amer.Chem.Soc., **57**, 1924 (1935).
7. T.L.Shu, J.Amer.Chem.Soc., **75**, 1730 (1953).
8. T.L.Shu and T.J.Weismann, J.Amer.Chem.Soc., **78**, 23 (1956).
9. W.Grimme, K.Reinert, and R.Köster, Tetrahedron Letters, 624 (1961).
10. C.W.Moeller and W.K.Wilmarth, J.Amer.Chem.Soc., **81**, 2638 (1959).
11. J.E.Leffler, G.B.Watts, T.Tanigaki, E.Dolan, and D.S.Miller, J.Amer.Chem.Soc., **92**, 6827 (1970).
12. S.J.Weismann and H.van Willigen, J.Amer.Chem. Soc., **92**, 2285 (1965).
13. R.J.Griffin and H.van Willigen, J.Chem.Phys., **57**, 86 (1972).
14. G.Wittig, Y.Keicher, A.Bückert, and P.Raft, Annalen, **563**, 110 (1949).
15. T.L.Shu and T.J.Weistmann, J.Amer.Chem.Soc., **78**, 3610 (1956).
16. W.Kuchen and R.D.Brinkmann, Angew.Chem., **72**, 564 (1960).
17. K.A.Bilevich, L.I.Zakharkin, and O.Yu.Okhlobystin, Izv.Akad.Nauk SSSR, Ser.Khim., 1914 (1965).

18. K.A.Bilevich, L.I.Zakharkin, and O.Yu.Okhlobystin, Izv.Akad.Nauk SSSR, Ser.Khim., 448 (1967).
19. M.M.Fein, J.Bobinski, N.Mayer, N.N.Schwartz, and M.S.Cohen, Inorg.Chem., 2, 1111 (1963).
20. D.Grafstein and J.Dvorak, Inorg.Chem., 2, 1120 (1963).
21. L.I.Zakharkin and L.S.Podvisotskaya, Zhur.Obshch. Khim., 37, 506 (1967).
22. A.Begum, A.R.Lyons, and M.C.R.Symons, J.Chem. Soc.A, 2290 (1971).
23. E.Krause and H.Polak, Ber., **59**, 1428 (1926).
24. Y.E.Coates and K.Wade, "Organometallic Compounds", Methuen and Co., London, 1969, Vol.1.
25. R.E.Dessy, M.Kleiner, and S.C.Cohen, J.Amer. Chem.Soc., 91, 6800 (1969).
26. V.Ts.Kampel', K.A.Bilevich, V.I.Bregadze, and O.Yu.Okhlobystin, Zhur.Vses.Khim.Obshch.im. Mendeleeva, **19**, 116 (1974).
27. V.I.Bregadze and O.Yu.Okhlobystin, Dokl.Akad. Nauk SSSR, 177, 347 (1967).
28. A.L.Allred and L.W.Bush, J.Amer.Chem.Soc., **90**, 3352 (1968).
29. M.D.Curtis and A.L.Allred, J.Amer.Chem.Soc., **87**, 2554 (1965).
30. F.Yerson, J.Heinzer, H.Bock, H.Alt, and H.Seidl, Helv.Chim.Acta, **51**, 707 (1968).
31. H.J.Sipe, Jr.West, and R.West, J.Organomet.Chem., **70**, 353 (1974).
32. H.J.Sipe and R.West, J.Organomet.Chem., **70**, 367 (1974).
33. A.J.Evans, B.Gerome, and N.H.Rees, J.Chem.Soc., Perkin Trans.II, 2091 (1973).
34. A.J.Evans, J.C.Evans, P.J.Ermes, and T.J.Phelan, J.Chem.Soc.B, 315 (1971).
35. A.J.Evans, J.C.Evans, and T.Y.Phelan, J.Chem. Soc., Perkin Trans.II, 1216 (1974).
36. A.J.Evans, J.C.Evans, and C.Bevan, J.Chem.Soc., Perkin Trans.II, 1220 (1974).
37. E.Carlerry, R.West, and Y.E.Glass, J.Amer.Chem. Soc., **91**, 5446 (1969).
38. R.West and A.Indriksons, J.Amer.Chem.Soc., **94**, 6110 (1972).
39. H.Alt, H.Bock, F.Yerson, and J.Heinze, Angew. Chem., **79**, 933 (1967).
40. N.V.Eliseeva and A.I.Pravednikov, Zhur.Strukt. Khim., **13**, 927 (1972).
41. E.T.Strom, J.Amer.Chem.Soc., **88**, 2065 (1966).
42. E.T.Strom and J.R.Norton, J.Amer.Chem.Soc., **92**, 2327 (1970).
43. H.Alt, E.R.Franke, and H.Bock, Angew.Chem., **81**, 538 (1969).
44. J.N.Jung and R.P.Jones, J.Chem.Soc., Perkin Trans.II, 500 (1975).
45. J.N.Jung and R.P.Jones, J.Orgamomet.Chem., **101**, 35 (1975).
46. V.M.Kazakova, I.K.Makarov, N.G.Komalenkova, L.N.Shamshina, and E.A.Chernyshev, Zhur.Strukt. Khim., **13**, 28 (1972).
47. N.V.Eliseeva, T.L.Krasnova, E.A.Chernyshev, A.I.Pravednikov, and V.L.Rogachevskii, Zhur. Strukt.Khim., **13**, 484 (1972).
48. T.I.Vakul'skaya, L.P.Petukhov, L.I.Larina, V.O.Reisfel'd, Yu.S.Finogenov, V.A.Pestunovich, and N.G.Voronkov, Dokl.Akad.Nauk SSSR, **232**, 77 (1977).
49. H.J.Sipe and J.Y.Corey, J.Organomet.Chem., **120**, 195 (1976).
50. I.G.Makarov, V.M.Kazakova, and Ya.K.Syrkina, Zhur.Strukt.Khim., **8**, 164 (1967).
51. I.G.Makarov and V.M.Kazakova, Zhur.Strukt.Khim., **9**, 996 (1968).
52. F.Correa-Duran, A.L.Allred, and R.J.Loyd, J.Organomet.Chem., **49**, 373 (1973).
53. F.Correa-Duran and A.L.Allred, J.Organomet.Chem., **49**, 365 (1973).
54. Yien-Ping Wan, D.H.O'Brien, and F.J.Smentowski, J.Amer.Chem.Soc., **94**, 7680 (1972).
55. S.R.Solodovnikov and E.L.Chernyshev, Zhur.Strukt. Khim., **3**, 665 (1962).
56. M.J.Townsend, J.Chem.Soc., 51 (1962).
57. A.V.Ilyasov, Y.A.Levin, and J.D.Morosova, J.Mol. Struct., **19**, 671 (1973).
58. E.S.Kean, K.Fisher, and R.West, J.Amer.Chem.Soc., **94**, 3246 (1972).
59. S.A.Fieldhouse, A.R.Lyons, H.C.Starkie, and M.C.R.Symons, J.Chem.Soc., Dalton Trans., 1966 (1974).
60. O.P.Anderson, S.A.Fieldhouse, H.C.Starkie, and M.C.R.Symons, Mol.Phys., **26**, 1561 (1973).
61. J.E.Bennett and J.A.Howard, Chem.Phys.Letters, **15**, 322 (1972).
62. M.J.Drews and R.P.Jones, J.Organomet.Chem., **44**, 253 (1972).
63. M.J.Drews, P.S.Wong, and P.R.Jones, J.Amer. Chem.Soc., **94**, 9122 (1972).
64. H.Bock, G.Brähler, G.Fritz, and E.Matern, Angew. Chem., **88**, 765 (1976).
65. H.Bock, W.Kaim, and J.W.Connolly, Angew.Chem., **88**, 766 (1976).
66. S.F.Nelsen, J.R.Weismann, P.J.Hintz, D.Olp, and M.R.Fahey, J.Amer.Chem.Soc., **96**, 2916 (1974).
67. F.A.Neugebaues and S.Bamberger, Chem.Ber., **101**, 2058 (1972).
68. H.Bock and H.Seid, J.Organomet.Chem., **13**, 87 (1968).
69. H.Bock, W.Kaim, and H.E.Rohwer, J.Organomet. Chem., **135**, C14 (1977).
70. H.Bock and W.Kaim, Tetrahedron Letters, 2343(1977).
71. H.Bock and W.Kaim, Nachr.Chem.Techn.Lab., **25**, 306 (1977).
72. C.J.Pitt, J.Organomet.Chem., **61**, 49 (1973).
73. G.A.Razuvaev and M.M.Koton, Zhur.Obshch.Khim., **1**, 864 (1931).
74. G.A.Razuvaev and M.M.Koton, Zhur.Obshch.Khim., **19**, 361 (1949).
75. G.A.Razuvaev and Yu.A.Ol'dekop, Uch.Zap.Gor'kovsk.Univ., **15**, 85 (1949).
76. G.A.Razuvaev, Yu.A.Ol'dekop, and Z.N.Manchinova, Zhur.Obshch.Khim., **22**, 480 (1952).
77. R.Benesh and R.E.Benesh, J.Amer.Chem.Soc., **73**, 3391 (1951).
78. R.E.Benesh and R.Benesh, J.Phys.Chem., **56**, 648 (1952).
79. K.P.Butin, Doctoral Thesis, Moscow State University, 1974.
80. R.E.Dessy, W.Kitching, T.Psarras, R.Salinger, A.Chen, and T.Chivers, J.Amer.Chem.Soc., **88**, 460 (1966).
81. N.T.Berberova, A.T.Milaev, and O.Yu.Okhlobystin, Zhur.Obshch.Khim., **49**, 621 (1979).
82. C.Kraus, J.Amer.Chem.Soc., **35**, 1749 (1913).
83. H.Erlenmeyr and M.Leb, Helv.Chim.Acta, **15**, 1171 (1932).
84. A.Perret and R.Perret, Helv.Chim.Acta, **16**, 848 (1933).
85. B.Gowenlock, J.P.Jones, and D.W.Ovenak, J.Chem. Soc., 535 (1958).

86. F.Basolo and R.G.Pearson, "The Mechanisms of Inorganic Reactions" (2nd Ed., Wiley, New York, 1967)(Translated into Russian), Izd.Mir, Moscow, 1971.
87. B.Köster and J.Benedikt, Angew.Chem., **76**, 649 (1964).
88. R.Köster, H.Bellut, and E.Ziegler, Angew.Chem., **79**, 243 (1967).
89. J.E.Leffler, E.Dolan, and T.Tanigaki, J.Amer. Chem.Soc., **87**, 927 (1965).
90. H.Lehmkuhl, J.Fuchs, and R.Köster, Tetrehedron Letters, 2511 (1965).
91. H.Lehmkuhl, Tetrahedron Letters, 2811 (1966).
92. H.Lehmkuhl and H.D.Kobs, Tetrahedron Letters, 2505 (1965).
93. J.Boersma, A.Mackor, and J.Y.Noltes, J.Organomet. Chem., **99**, 337 (1975).
94. U.Schmidt, K.Kabitzke, K.Markau, and W.P.Neumann, Chem.Ber., **98**, 3827 (1965).
95. P.J.Krusie and J.K.Kochi, J.Amer.Chem.Soc., **91**, 3938 (1969).
96. S.W.Bennett, C.Eaborn, A.Hudson, R.A.Jackson, and K.D.J.Root, J.Chem.Soc.A, 348 (1970).
97. H.Höpner and J.Lassmann, Z.Naturforsch., **23A**, 1758 (1968).
98. J.B.Watts and K.U.Ingold, J.Amer.Chem.Soc., **94**, 491 (1972).
99. H.Sakurai, K.Mochida, and M.Kira, J.Amer.Chem. Soc., **97**, 929 (1975).
100. H.U.Buschhaus, M.Lehnig, and W.P.Neumann, Chem.Comm., 129 (1977).
101. P.J.Davidson, A.Hudson, M.F.Lappert, and P.W.Lednor, Chem.Comm., 651 (1973).
102. J.D.Cotton, C.S.Cundy, D.U.Harris, A.Hudson, and M.F.Lappert, Chem.Comm., 651 (1974).
103. A.Hudson, M.F.Lappert, and P.W.Lednor, J.Chem. Soc., Dalton Trans., 2369 (1976).
104. P.J.Davidson and M.F.Lappert, Chem.Comm., 317 (1973).
105. M.J.S.Gynake and M.F.Lappert, J.Organomet.Chem., **114**, C4 (1976).
106. R.L.Morehouse, J.J.Christia, and W.Cordy, J.Chem. Phys., **45**, 1751 (1966).
107. R.L.Lloyd and M.T.Rogers, J.Amer.Chem.Soc., **95**, 2459 (1973).
108. M.Geofrey, L.Ginet, and E.A.C.Lucken, Chem. Phys.Letters, **38**, 321 (1976).
109. H.Sakurai, K.Mochida, and M.Kira, J.Organomet. Chem., **124**, 235 (1977).
110. H.Sakurai, M.Muzakami, and M.Kumada, J.Amer. Chem.Soc., **91**, 511 (1969).
111. A.J.Brook and J.M.Duff, J.Amer.Chem.Soc., **91**, 2118 (1969).
112. L.H.Sommer, "Stereochemistry Mechanism and Silicon Compounds" (Translated into Russian), Izd. Mir, Moscow, 1966.
113. P.W.Selwood, J.Amer.Chem.Soc., **61**, 3168 (1939).
114. P.W.Selwood, J.Amer.Chem.Soc., **63**, 2509 (1941).
115. H.Morris, W.Byerly, and P.W.Selwood, J.Amer. Chem.Soc., **64**, 1727 (1942).
116. E.Müller, F.Günter, K.Scheffler, and H.Fettel, Chem.Ber., **91**, 2888 (1958).
117. K.U.Ingold and B.P.Roberts, "Free-Radical Substitution Reactions" (Translated into Russian), Izd. Mir, Moscow, 1974.
118. D.C.Nonhebel and J.C.Walton, "Free-Radical Chemistry: Structure and Mechanism" (Translated into Russian), Izd.Mir, Moscow, 1977, p.289.
119. K.S.Chen, F.Bertini, and J.K.Kochi, J.Amer. Chem.Soc., **95**, 1340 (1973).
120. P.West and B.Waack, J.Amer.Chem.Soc., **89**, 4395 (1967).
121. E.Weiss and G.Henken, J.Organomet.Chem., **21**, 265 (1970).
122. K.Chen, J.P.Battioni, and J.K.Kochi, J.Amer. Chem.Soc., **95**, 4439 (1973).
123. A.Begum, A.R.Lyons, and M.C.R.Symons, J.Chem. Soc.A, 2388 (1971).
124. C.M.L.Kerr, J.A.Wargon, and F.Williams, J.Chem. Soc., Faraday Trans.II, **72**, 552 (1976).
125. A.Hudson and H.A.Hussain, J.Chem.Soc.B, 793 (1969).
126. P.J.Krusie and J.K.Kochi, J.Amer.Chem.Soc., **91**, 6161 (1969).
127. H.J.Mackey and D.B.Wood, Mol.Phys., **18**, 783 (1970).
128. A.R.Lyons, G.W.Neilson, and M.C.R.Symons, J.Chem.Soc., Faraday Trans.II, 807 (1972).
129. P.J.Krusie and J.K.Kochi, J.Amer.Chem.Soc., **93**, 846 (1971).
130. A.R.Lyons and M.C.R.Symons, Chem.Comm., 1068 (1971).
131. T.Kawamura and J.K.Kochi, J.Amer.Chem.Soc., **94**, 648 (1972).
132. D.Gliller and K.U.Ingold, J.Amer.Chem.Soc., **95**, 6459 (1973).
133. T.Kawamura, P.Meakin, and J.K.Kochi, J.Amer. Chem.Soc., **94**, 8065 (1972).
134. T.Kawamura and J.K.Kochi, J.Organomet.Chem., **47**, 79 (1973).
135. D.J.Edge and J.K.Kochi, J.Chem.Soc., Perkin Trans.II, 182 (1973).
136. M.Kira, M.Watanabe, and H.Sakurai, J.Amer.Chem. Soc., **99**, 7780 (1977).
137. A.R.Lyons and M.C.R.Symons, J.Chem.Soc., Faraday Trans.II, **68**, 622 (1972).
138. M.C.R.Symons, J.Amer.Chem.Soc., **94**, 8589 (1972).
139. M.C.R.Symons, Tetrahedron Letters, 793 (1975).
140. G.A.Razuvaev, N.S.Vasileiskaya, and D.V.Muslin, J.Organomet.Chem., **7**, 531 (1967).
141. G.A.Razuvaev, N.S.Vasileiskaya, and D.V.Muslin, Dokl.Akad.Nauk SSSR, **175**, 620 (1967).
142. G.A.Razuvaev, N.S.Vasileiskaya, and N.N.Vavilina, J.Organomet.Chem., **80**, 19 (1974).
143. G.A.Razuvaev, N.S.Vasileiskaya, N.N.Vavilina, and S.N.Uspenskaya, Zhur.Org.Khim., **6**, 980 (1970).
144. G.A.Razuvaev, N.S.Vasileiskaya, and N.N.Vavilina, Zhur.Obshch.Khim., **44**, 135 (1974).
145. G.A.Razuvaev, D.V.Muslin, E.S.Klimov, N.Sh.Lyapina, and N.N.Vasileiskaya, Dokl.Akad. Nauk SSSR, **231**, 897 (1976).
146. K.H.Haussen, H.Brunner, and J.C.Jochims, Mol. Phys., **10**, 253 (1966).
147. A.L.Buchachenko and A.M.Vasserman, "Stabil'nye Radikaly" (Stable Radicals), Izd.Khimiya, Moscow, 1973, p.143.
148. G.A.Razuvaev, N.S.Vasileiskaya, E.P.Oleinik, D.V.Muslin, E.S.Klimov, and N.N.Vavilina, Zhur. Org.Khim., **10**, 2257 (1974).
149. G.A.Razuvaev, N.S.Vasileiskaya, E.P.Oleinik, N.N.Vavilina, and D.V.Muslin, Zhur.Obshch.Khim., **46**, 2720 (1976).
150. E.P.Oleinik, N.L.Khrzhanovskaya, N.P.Makarenko, and N.S.Vasileiskaya, Izv.Akad.Nauk SSSR, Ser. Khim., 936 (1977).

151. H.Stegmann and K.Scheffler, Tetrahedron Letters, 3387 (1964).
152. E.Müller, H.Eggensperger, and K.Scheffler, Annalen, **658**, 103 (1962).
153. E.Müller, H.Eggensperger, A.Rieker, K.Scheffler, H.D.Spanagel, H.Stegmann, and B.Teissier, Tetrahedron, **21**, 227 (1965).
154. E.Müller, A.Ricker, K.Scheffler, and A.Moosmayer, Angew.Chem., **78**, 98 (1966).
155. E.Müller, B.Teissier, H.Eggensperger, A.Ricker, and K.Scheffler, Annalen, **705**, 54 (1967).
156. E.Müller, H.Eggensperger, B.Teissier, and K.Scheffler, Z.Naturforsch., **19b**, 1079 (1964).
157. A.Ricker, Z.Naturforsch., **21b**, 647 (1964).
158. N.M.Altherton, E.J.Land, and G.Porter, Trans. Faraday Soc., **59**, 818 (1963).
159. E.P.Ivakhnenko, V.B.Panov, E.P.Onokolova, and O.Yu.Okhlobystin, Zhur.Obshch.Khim., **47**, 2530 (1977).
160. V.B.Panov, E.P.Ivakhnenko, and O.Yu.Okhlobystin, Zhur.Obshch.Khim., **47**, 2624 (1977).
161. R.Hoffman and W.N.Lipscomb, J.Chem.Phys., **36**, 2179 (1962).
162. L.I.Zakharkin, V.N.Kalinin, and L.S.Podvisotskaya, Izv.Akad.Nauk SSSR, Ser.Khim., 1495 (1966).
163. A.B.Shapiro, A.L.Buchachenko, A.A.Medzhidov, and E.G.Rozantsev, Zhur.Strukt.Khim., 7, 187 (1966).
164. A.B.Shapiro and E.G.Rozantsev, Izv.Akad.Nauk SSSR, Ser.Khim., 1650 (1966).
165. R.West and P.Boudgouk, J.Amer.Chem.Soc., **95**, 3983 (1973).
166. H.B.Stegmann, K.Scheffler, and F.Stöcker, Angew. Chem., **83**, 538 (1971).
167. H.B.Stegmann, K.Scheffler, and F.Stöcker, Chem. Ber., **103**, 1279 (1970).
168. H.B.Stegmann, K.Scheffler, and F.Stöcker, Angew. Chem., **82**, 481 (1970).
169. H.B.Stegmann, K.B.Ulmschneider, and K.Scheffler, J.Organomet.Chem., **78**, 41 (1974).
170. K.Scheffler and H.B.Stegmann, Tetrahedron Letters, 3619 (1968).
171. G.A.Razuvaev, G.A.Abakumov, and E.S.Klimov, Dokl.Akad.Nauk SSSR, **201**, 624 (1971).
172. G.A.Razuvaev, V.A.Muraev, and A.G.Razuvaev, Dokl.Akad.Nauk SSSR, **215**, 1113 (1974).
173. V.A.Muraev, G.A.Razuvaev, and G.A.Abakumov, Izv.Akad.Nauk SSSR, Ser.Khim., 159 (1975).
174. G.A.Razuvaev, T.A.Abakumov, E.S.Klimov, E.N.Gladyshev, and P.Ya.Bayushkin, Izv.Akad. Nauk SSSR, Ser.Khim., 1128 (1977).
175. E.N.Gladyshev, P.Ya.Bayushkin, G.A.Abakumov, and E.S.Klimov, Izv.Akad.Nauk SSSR, Ser.Khim., 176 (1978).
176. S.T.Kukes, A.I.Prokof'ev, N.N.Bubnov, S.P.Solodovnikov, E.D.Korniets, D.N.Kravtsov, and M.I.Kabachnik, Dokl.Akad.Nauk SSSR, **229**, 877 (1976).
177. G.A.Abakumow, E.N.Gladyshev, N.S.Vyasankin, G.A.Razuvaev, P.Ya.Bayashkin, and V.A.Muraev, J.Organomet.Chem., **64**, 327 (1974).
178. G.A.Razuvaev, E.N.Gladyshev, P.Ya.Bayushkin, G.A.Abakumov, and E.S.Klimov, Izv.Akad.Nauk SSSR, Ser.Khim., 2762 (1976).
179. G.A.Abakumov and E.S.Klimov, Dokl.Akad.Nauk SSSR, **202**, 827 (1972).
180. G.A.Abakumov, E.S.Klimov, V.V.Ershov, and I.S.Belostotskaya, Izv.Akad. Nauk SSSR, Ser.Khim., 927 (1975).
181. H.B.Stegmann, K.B.Ulmschneider, and K.Scheffler, J.Organomet.Chem., **101**, 145 (1975).
182. H.B.Stegmann, K.B.Ulmschneider, K.Hicke, and K.Scheffler, J.Organomet.Chem., **118**, 258 (1976).
183. H.B.Stegmann, W.Uber, and K.Scheffler, Tetrahedron Letters, 2697 (1977).
184. W.Uber, H.B.Stegmann, K.Scheffler, and J.Strähle, Z.Naturforsch., **32b**, 355 (1977).
185. G.A.Abakumov and V.A.Muraev, Dokl.Akad.Nauk SSSR, **217**, 1313 (1974).

Institute of Physical and Organic
Chemistry, Rostov State University

Translated from *Uspekhi Khimii*, **49**, 1859 - 1879 (1980) U.D.C. 541(121/123 + 134)

Oxidation-reduction Measurements and Their Applications in the Study of Interactions in Solutions

V.V.Pal'chevskii and Kh.M.Yakubov

The theoretical principles of oxidation-reduction measurements and their applications in the study of chemical processes accompanied by electron transfer are considered. These include complex formation, protolytic reactions, and association in homogeneous and heterogeneous oxidation-reduction systems.
The bibliography includes 168 references.

CONTENTS

I. Introduction 908
II. The oxidation potential 908
III. Theory of oxidation-reduction measurements 909
IV. Measurement of the oxidation potential 909
V. Protolytic equilibria 910
VI. Complex formation 912
VII. Redoxites 914

I. INTRODUCTION

The oxidation potential, which is a thermodynamic characteristic of a reversible oxidation-reduction system or an oxidation-reduction reaction, is used in many studies among which one can distinguish three main fields.

1. Quantitative determination of the content in solution of one or several components. These must react fairly completely and rapidly with the oxidant or reductant introduced into the solution. This field, established for a long time, constitutes a branch of analytical chemistry[1]. The measurement of the oxidation potential in analytical determinations is carried out either potentiometrically or with the aid of oxidation-reduction indicators[2].

2. Determination of the composition and equilibrium constants for the formation of molecular and ionic forms of substances constituting an oxidation-reduction system.

3. The study of the nature of the chemical bond and of the charge distribution in polyatomic compounds capable of oxidation or reduction. The difference between the oxidation potentials of related compounds, in which the nature of the oxidising (reducing) centre remains unchanged, is interpreted quantitatively. The theoretical methods employed (correlations, quantum-chemical methods) are varied and differ significantly in their validity[3,4]. It is noteworthy that the conversion of the oxidation potential to the molecular orbital energy requires assumptions whose justification is difficult to estimate.

The requirements which must be met by the accuracy of the determination of the oxidation potential in each field differ significantly. They are greatest in the second field, whose establishment and development are associated with the studies of Clark and Michaelis[5,6]. Measurements of the oxidation potential in order to discover the nature of the chemical interaction have been made and are being made on a very wide scale. An appreciable development of the second field has been achieved in the studies of Academician B.P.Nikol'skii. This review deals mainly with the studies carried out by Nikol'skii's school.

II. THE OXIDATION POTENTIAL

Oxidation-reduction measurements constitute a branch of physical chemistry which deals with the study of chemical reactions accompanied by electron transfer[7]. This transfer can take place between the components of two oxidation-reduction systems, where the oxidised form of one system removes electrons from the reduced form of the other, oxidising it and being itself reduced. As a result of such oxidation–reduction reaction, new substances are formed. The transfer of n electrons e also occurs between the components of a single oxidation–reduction system:

$$\mathrm{Ox} + ne \rightleftharpoons \mathrm{Red} \ . \qquad (1)$$

Chemical analysis demonstrates the constancy of the concentrations of Ox and Red subject to the condition that the composition of the solution remains unaltered and the influence of any oxidant or reductant is excluded. In order to characterise the oxidation–reduction system (1), it is necessary to introduce another oxidation–reduction system, the role of which is fulfilled by a plate of an indifferent metal. After the attainment of equilibrium, the plate acquires the equilibrium electrical potential, which ensures the equality of the electrochemical potentials of the electrons in the solution and in the metal in the absence of a potential shift of the equilibrium of reaction (1). Hence it follows that

$$\varphi = \psi^{\mathrm{M}} - \psi = \mathrm{const} - \lg a_e = \overline{\varphi}^0 + \frac{\vartheta}{n} \lg \frac{a_o}{a_r} \ , \qquad (2)$$

where ψ^{M} and ψ are the Galvani potentials of the metal and solution, a_e, a_o, and a_r are the activities of the electrons and the oxidised and reduced forms respectively, and $\vartheta = 2.3RT/F$.

The oxidation potential ϕ, which is equal to the difference between the Galvani potentials of the metals and the solution, includes a constant component $\overline{\phi^0}$—the standard oxidation potential. This constant defines the level of the oxidising capacity of the Ox–Red system and depends on the electron affinity of the species constituting the oxidation–reduction

system as well as their free energies of formation and solvation. Since the absolute value of the standard oxidation potential is unknown, it is assumed that $\overline{\phi^0} = 0$ for the standard hydrogen system, where the activity of hydrogen ions $h = 1$ and the partial pressure of hydrogen is 1 atm (1×10^5 Pa). The oxidation potential of the reversible Ox–Red system is then numerically equal to the e.m.f. of the galvanic cell made up of the oxidation–reduction and hydrogen half-cells.

The oxidation potential, referred to the conventional hydrogen zero, is an electrical measure of the free energy of the oxidation–reduction reaction of the Ox–Red system with the standard hydrogen system[8]:

$$\varphi = -\frac{\Delta G}{nF}, \qquad (3)$$

where F is the Faraday.

The oxidation potentials can vary in a specific manner also under conditions where the effect of the oxidant or reductant is excluded, but the concentrations of the other components of the solution vary. Changes in the oxidation potential are induced by the interaction of the substances constituting the reversible oxidation–reduction system with the solvent and other components of the solution. The appearance of a new species as a result of protolytic, complex formation, and association reactions, as well as other processes leads to an alteration of the activity of the electrons in solution and hence to a change of the oxidation potential. Thus the oxidation potential is not only an electrical measure of the free energy of the oxidation–reduction reaction between the given system and the standard hydrogen system, but is also an electrical measure of the free energies $\Delta G'$ of the chemical reactions between the substances in the oxidised and reduced states, on the one hand, and other components of the solution, on the other, i.e.[9]

$$\varphi = -\Delta G/nF - \Delta G'/nF. \qquad (4)$$

If the first term of Eqn.(4) is kept constant (by protecting the system from oxidation or reduction), the oxidation potential will follow the change in the free energy $\Delta G'$ induced by the chemical reactions occurring in solution.

III. THEORY OF OXIDATION–REDUCTION MEASUREMENTS

All the interactions accompanied by the transfer of n electrons between p kinds of species in the reduced state and q kinds of species in the oxidised state can be described by a single equation for the oxidation potential:

$$\varphi = \varphi(P, T, c_0, c_r, x_1, \ldots, x_m) = \overline{\varphi}^0 + \frac{\vartheta}{n}\lg\frac{c_0}{c_r} + \frac{\vartheta}{n}\lg\sum_1 \cdots \sum_q K_i^{(o)} \prod_i x_i^{\nu_i} + \frac{\vartheta}{n}\lg\sum_1 \cdots \sum_p K_j^{(r)} \prod_j x_j^{\nu_j}, \qquad (5)$$

where $\overline{\phi^0}$ is the standard oxidation potential, P the pressure, c_0 and c_r are the overall concentrations of the substances in the oxidised and reduced states respectively, x_1, x_2, ..., x_m are the concentrations of substances of m kinds involved in the reaction, $K_i^{(o)}$ and $K_j^{(r)}$ are the equilibrium constants of these reactions, ν_i and ν_j are stoichiometric coefficients, and the subscripts and superscripts o and r show that the given quantities refer to the oxidised and reduced states.

The first sum in the logarithmic term of Eqn.(5) takes into account the formation of species of any composition in the reactions where the system components in the oxidised state are involved and the second takes into account the corresponding interaction of the components in the reduced state.

It is assumed that the following equation should hold for the chemical potential of species of each ith and jth kind:

$$\mu_k = M_k + RT\ln c_k. \qquad (6)$$

The quantity

$$M_k = \mu_k^0 + RT\ln y_k,$$

where μ_k^0 is the standard chemical potential and y_k the activity coefficient, can be regarded as constant under certain conditions. The number of concentration variables in Eqn.(5) is equal to the sum of the concentrations of all the substances present in solution, i.e. $m + p + q + 2$, while the number of independent variables is $m + 2$.

Eqn.(5) can be regarded as a complete mathematical model of all the interactions associated with the given oxidation–reduction system. Interactions of this kind include the stepwise complex formation reactions, comprising mixed, polynuclear, and heteropolynuclear complex formation, hydrolysis (solvolysis), stepwise protolytic dissociation reactions, and the association of the ions and molecules forming part of the oxidation–reduction system investigated or interacting with the latter.

Eqn.(5) makes it possible to obtain any form of the ϕ surface in the space of states (P, T, c_0, c_r, x_1, ..., x_m) by varying the quantities $K_i^{(o)}$ and $K_i^{(r)}$ from 0 to $+\infty$. The determination of the set of the quantities $\{K_i^{(o)}, K_j^{(r)}\}$ compatible with experimental data constitutes the solution of the problem of the quantitative description of reversible reactions in reversible oxidation–reduction systems. The method involving successive sections through the surface in the $\{c_0, c_r, x_1, \ldots, x_m\}$ space with respect to one of the independent concentration variables while all others are kept constant is widely used. This makes it possible to obtain curves representing the partial relations between the oxidation potential and each independent variable. These curves consist as a rule of linear sections joined by smooth bends. The linear sections correspond to the states of the solution in which compounds with specific stoichiometric coefficients predominate. The compositions of the compounds formed can be found from the slopes of the linear sections, which are proportional to the stoichiometric coefficients. The sets of constants $\{K_i^{(o)}, K_j^{(r)}\}$ are determined in simple cases by graphical or computational methods. In the case of chemical interactions leading to the formation of several compounds of complex composition, which are frequently present simultaneously, the above quantities are found with the aid of computers.

In specific cases Eqn.(5) is simplified, because the number of independent concentration variables is reduced and limitations are imposed on the permissible stoichiometric coefficients.

IV. MEASUREMENT OF THE OXIDATION POTENTIAL

The description of interactions in solutions of oxidation–reduction systems is based on the experimental values of the oxidation potential under the conditions of equilibrium at the indicator electrode–solution interface. The correct formulation of the potentiometric experiment involves the establishment of this equilibrium.

The solution of specific problems may be complicated by the low rates of homogeneous and heterogeneous electron transfer reactions, by the breakdown of the condition of the indifference of the electrode owing to the catalytic effect of the material on the processes in solution, including the decomposition of its components, and other causes[7,10–12].

Thus platinum electrodes cease to be indifferent at low oxidation potentials. On the other hand, certain oxidation–reduction systems, for example Ce(IV)–Ce(III), Ti(IV)–Ti(III), V(III)–V(II), and Eu(III)–Eu(II), which should decompose water on the basis of their standard oxidation potentials, actually form stable aqueous solutions. Their stability is associated with the low rates of the reactions of the components of the above oxidation–reduction systems with water. The possibility of the measurement of the oxidation potential depends on the availability of an electrode material with a high oxygen overvoltage (in the region of low potentials) or a high hydrogen overvoltage (in the region of high potentials). Noble metal electrodes are heterogeneous catalysts of reactions involving the decomposition of water and cannot serve as materials for the indicator electrode[13]. On the other hand, when the rate of the homogeneous electron transfer reaction is low, the electrode must catalyse the electron transfer between the oxidised and reduced forms of the system or must catalyse one of the stages of the overall oxidation–reduction reaction.

By virtue of the above complications, the range of systems susceptible to experimental study and the quality of the information obtained depend largely on the extent to which the material of the indicator electrode and the state of its surface satisfy the requirements arising from specific conditions. These requirements can be justified, because, together with the thermodynamic characteristics of oxidation–reduction systems, there are data on the rates of homogeneous[14] and electrode[15] oxidation–reduction reactions. The following postulates have been formulated concerning oxidation–reduction measurements[7,8,10,11]: (1) there can be no universal electrode in oxidation–reduction measurements; a set of electrodes with a wide range of properties is required; (2) in the absence of equilibrium between the components of the solution which are capable of participating in oxidation–reduction interaction, one chooses an electrode whose material ensures reversible electron exchange with one of the oxidation–reduction systems; (3) the agreement between the oxidation potentials measured by different electrodes constitutes an adequate criterion of the attainment of equilibrium in the electrode–solution system.

The choice of the electrode material is based on information concerning the characteristics of the chemical interactions in solution and also on the results of studies designed to determine the limits of the indifference of the electrode materials and the kinetic parameters of electrode processes[8,16–18].

Together with traditional smooth platinum and gold electrodes, iridium and rhodium[7,19–22] as well as mercury[10,23] electrodes are used in oxidation–reduction measurements. The search for new electrode materials and new types of electrodes has led to the development of thin-layer platinum electrodes[8,24,25], electrodes made of semiconducting tin dioxide[26–28], glass electrodes for oxidation–reduction measurements[29,30], electrodes based on polymeric organic semiconductors[31,32], and modified graphite electrodes[33].

Thin-layer platinum electrodes are catalytically active in relation to many oxidation–reduction interactions[8], which permits measurements of the oxidation potential in those cases where homogeneous electron exchange is highly inhibited. However, the high catalytic activity of thin-layer platinum electrodes hinders their use when the stability of individual solution components breaks down and in kinetic studies.

Glass electrodes with an electron response have been developed on the basis of results of systematic studies of the dependence of the electrode properties of glasses on their chemical composition[29,30,34–37]. The possibility of using these electrodes in oxidation–reduction measurements is determined by the chemical indifference of glasses and the high electronic conductivity associated with the introduction of iron or titanium oxides into the composition of the glasses. It has been shown[10,11,38,39] that glass electrodes possess important characteristics such as insensitivity to oxygen and hydrogen, and that they are suitable for the measurement of the oxidation potential beyond the limits of the thermodynamic stability of water. The semiconducting properties of glasses determine their specificity in relation to systems with low oxidation potentials, which provides a basis for further studies on these lines. A semiconductor electrode, reversible in alkaline media, has been developed for the oxygen–hydrogen peroxide system, which is of both theoretical and practical interest[10,39].

The improvement of the experimental formulation of potentiometric measurements is of great importance. Special hermetically sealed apparatus, which eliminate the access of air, have been constructed for the determination of the oxidation potential under the conditions of varying concentrations of individual solution components[7,19,21,40,41].

V. PROTOLYTIC EQUILIBRIA

Clark[6,42] showed that the oxidation potentials of organic reversible oxidation–reduction systems are involved in a complex relation with oxidation–reduction and protolytic equilibria in solutions. In relation to individual examples, Clark formulated the fundamental postulates of the thermodynamic theory of the phenomenon and proposed a graphical method for the determination of the protolytic dissociation constants. During the subsequent development of this research, the study of the protolytic processes occurring in oxidation–reduction systems in a general form was undertaken[7,40,43,44]. Two types of systems were investigated. The first includes systems where the oxidised form is a q-basic acid and the reduced form is a p-basic acid. Regardless of the nature of the protogenic (proton-accepting) groups, their protolytic dissociation takes place as a result of isotypical reactions of the following type:

$$RH_j + H_2O \rightleftarrows RH_{j-1} + H_3O^+ \ . \qquad (7)$$

For systems of the second type, the concluding $(q+1)$th stage of the successive reactions of type (7) consists of the formation of the free base of the oxidised form:

$$R^+ \cdot H_2O + H_2O \rightleftarrows ROH + H_3O^+ \ . \qquad (8)$$

The regions where individual protolytic forms exist in the oxidised and reduced states are determined by the ratios of the protolytic dissociation constants and the pH values. The relation linking the electron transfer processes between protolytic forms and processes involving proton exchange with solvent molecules is reflected in the equations for the oxidation potential ϕ

(a) type I systems:

$$\varphi = \varphi^0 + \frac{\vartheta}{n}\lg\frac{c_o}{c_r} + \frac{\vartheta}{n}\lg\sum_{i=1}^{p} h^{p-i}B_i^{(r)} - \frac{\vartheta}{n}\lg\sum_{j=0}^{q} h^{q-j}B_j^{(o)}; \qquad (9)$$

(b) type II systems:

$$\varphi = \varphi^0 + \frac{\vartheta}{n}\lg\frac{c_o}{c_r} + \frac{\vartheta}{n}\lg\sum_{i=1}^{p} h^{p-i}B_i^{(r)} - \frac{\vartheta}{n}\lg\sum_{j=0}^{q} h^{q+1-j}B_j^{(o)} + \frac{\vartheta}{n}\lg h, \qquad (10)$$

where c_o and c_r are the overall concentrations of all the protolytic forms in the oxidised and reduced states respectively, $B_j^{(o)}$ and $B_i^{(r)}$ are the overall apparent jth and ith dissociation constants, and h is the activity of hydrogen ions. Eqns.(9) and (10) make it possible to predict the properties

of the oxidation–reduction system in the form of its dependence on the oxidation potential and the pH.

The experimental data are thermodynamically highly rigorous and can be very readily interpreted with a consequent high accuracy of the determination of the protolytic dissociation constants when the following oxidation voltage is introduced[7,40,44]:

$$\mathscr{E} = \varphi - \vartheta \lg h. \qquad (11)$$

The oxidation voltage is numerically equal to the e.m.f. of the galvanic cell comprising the hydrogen (glass) and oxidation–reduction half-cells. The properties of the oxidation voltage have been formulated in the following postulates[7,44].

(a) The $\mathscr{E} = \mathscr{E}$ (pH) curve consists of linear sections joined by smooth bends; the number of these sections is equal to the number of all the protolytic forms in the oxidised and reduced states plus one.

(b) The slopes, equal to the partial derivative $(\partial\mathscr{E}/\partial\,\mathrm{pH})_{pc_o pc_r}$, depend on the predominance of one of the protolytic forms in the oxidised state and one form in the reduced state and can be predicted with the aid of Eqns.(9)–(11).

(c) Each bend in the curve and the establishment of a linear section with another slope correspond to a specific stage of the protolytic dissociation; an increase in the slope of the linear section with increase of pH is a sign of the dissociation of the oxidised form and its decrease is a sign of the dissociation of the reduced form.

(d) Each dissociation stage alters the slope of the subsequent linear section of the $\mathscr{E} = \mathscr{E}$ (pH) curve by an amount ϑ/n.

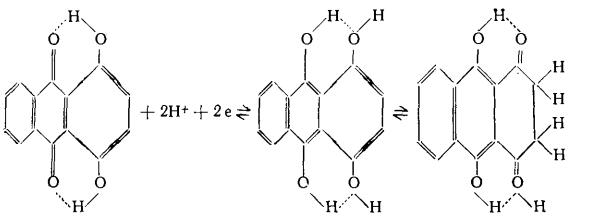
(e) The similarity of two dissociation constants of one of the forms leads to the disappearance of the corresponding linear section; the dissociation of the same protogenic group involved in both the oxidised and reduced forms induces the appearance of an inflection in the $\mathscr{E} = \mathscr{E}$ (pH) curve and a shift of the subsequent linear section parallel to the preceding one; the identity of the dissociation constants should cancel out their influence on the shape of the curve.

(f) The pK for protolytic dissociation is numerically equal to the pH at the point of intersection of the lines obtained by producing two neighbouring sections.

In a consecutive two-stage dissociation of the reduced form the $\mathscr{E} = \mathscr{E}$ (pH) curve becomes concave relative to the abscissa axis, while in the case of the corresponding dissociation of the oxidised form it becomes convex. If the dissociation constants corresponding to these two-stage processes are similar, then the curves pass through an extremum, The appearance of the latter makes it possible to determine stepwise dissociation constants with similar values; the graphical determination with the aid of the $\phi = \phi$ (pH) curve makes it possible to find only their product.

The study of type I systems in relation to the Alizarin C–leuco-Alizarin C system[7,45,46] and of type II systems in relation to the Toluidine Blue–leuco-Toluidine Blue and Methylene Blue systems[7,40,47–49] demonstrated the complete agreement between the theory and experiment. A quantitative characteristic of the oxidation–reduction and protolytic properties, which includes the dependence of the oxidation potential and the oxidation voltage on the pH, the stepwise protolytic dissociation constants, and the distribution of the relative contents of the protolytic forms as a function of pH, has been obtained for the systems investigated.

Since systems formed by quinone or quinone imine and their reduced forms served as prototypes of reversible organic systems, the number of proton-donating (proton-accepting) groups in the reduced state is two greater than in the oxidised state. The study of systems formed by anthraquinone derivatives and their leuco-forms, which contain nucleophilic substituents (OH or NH_2) in the *para*-positions of their aromatic side rings, showed that, on reduction, the number of protogenic groups in these systems does not change or increases by unity[50–56]. The manifestation of these anomalous properties is due to the retention of the quinonoid structure in the leuco-form, which has been shown experimentally[53] to be a consequence of a desmotropic transition; for example, the following transition occurs for quinizarin:



The second stage can be regarded as a result of the partial intramolecular oxidation of the extreme ring by the central ring, which is promoted by strong intramolecular hydrogen bonds.

By comparing the $\mathscr{E} = \mathscr{E}$(pH) relations and the electronic absorption spectra of the six anthraquinone dues investigated and their leuco-forms in CCl_4 and aqueous alcoholic solutions, the sequence of the dissociations of the protogenic groups was established[55]. The OH groups in the β-position are the first to dissociate. Their acid properties are enhanced on conversion into the leuco-form. As a result of the formation of strong intramolecular hydrogen bonds, the acid properties of the OH groups in the β-position are appreciably weakened.

Together with protolytic dissociation, other processes, in the first place association, can occur in organic systems. The study of the Neutral Red–leuco-Neutral Red system[57–59] showed that, in consequence of association, its oxidation potential becomes a function not only of the activity of hydrogen ions but also of the concentration of form RH^+ of Neutral Red, which is capable of association:

$$\varphi = \varphi^0 + \frac{\vartheta}{2}\lg\frac{c_o}{c_r} + \frac{\vartheta}{2}\lg(h^2 + hK_1^{(r)} + B_2^{(r)}) + \vartheta\lg h - \frac{\vartheta}{2}\lg(K_1^{(o)} + Ah), \qquad (12)$$

where

$$A = 1 + 2K_2^{(o)}[RH^+] + 4(K_2^{(o)}K_4^{(o)})^2[RH^+]^3,$$

and $K_2^{(o)}$ and $K_4^{(o)}$ are the formation constants of the dimer and tetramer.

The formation of the associated species was demonstrated and its identification with a specific protolytic form was achieved by analysing the partial relations $\phi = \phi(\lg c_o)$, $\phi = \phi(\lg c_r)$, and $\phi = \phi(\lg c)$, where $c = c_o + c_r$, obtained for the pH ranges corresponding to the conditions where particular protolytic forms predominate. These relations are used to find the compositions and the formation constants of the associated species. Association, taken into account in Eqn.(12) by the quantity A, influences only the protolytic dissociation constant of the associable species RH^+ and does not influence the protolytic equilibria of other forms. Association does not affect the numerical dissociation constants of the forms determined graphically from $\phi = \phi$ (pH) relations.

The oxidation of Neutral Red yielded a hitherto unknown compound, which is apparently a charge-transfer complex of the quinhydrone type[60]. It is stable in the crystalline state but in solution it is slowly oxidised by atmospheric oxygen. Its protolytic properties differ from those of the dye and its leuco-form.

VI. COMPLEX FORMATION

In oxidation-reduction systems formed by ions of the same metal in two oxidation states the appearance of complexes of these ions is reflected in the oxidation potential. Two fields differing in their interpretation of the experimental relations are being established[61,62]. In studies on one of them the compositions of the complexes and their stability constants are found with the aid of secondary concentration variables—the formation functions and degrees of formation and complexation (Rossotti and Rossotti[63], chapters 4 and 7). The second field arose and is being developed in the studies of Nikol'skii and his school. In view of the analogy between protolytic process and complex formation, Nikol'skii[64] suggested that complex formation be studied by methods developed for the investigation of protolytic equilibria in oxidation–reduction systems. The experimental study of the iron(III)–iron(II)–acetic acid–water system[65] confirmed the likely usefulness of this approach and initiated the theoretical and experimental studies on complex formation in reversible oxidation–reduction systems consisting of the aquo-complexes of the metal in two oxidation states.

In the course of the development of the thermodynamic theory[7,8,61,62,66], the entire set of reversible reactions leading to the formation of the complexes $M_qH_kA_x(OH)_y \cdot (H_2O)_z^{(qm+k-bx-y)+}$ (oxidised state) and $M_pH_lA_u(OH)_v \cdot (H_2O)_w^{[p(m-n)+l-bu-v]+}$ (reduced state) was taken into account. It is assumed that complexes are formed in aqueous solution of an acid H_bA, with a constant ionic strength, as a result of the substitution by the acido-ligand $H_{b-s}A^{s-}$ of the water molecules coordinated in the aquo-complexes of M^{m+} and $M^{(m-n)+}$, polymerisation, and protolytic reactions including the hydrolysis and protolytic dissociation of the acid and the protonated complexes. The state of the system is described by the equation for the oxidation potential of the type[7]:

$$\varphi = \varphi^0 + \frac{\vartheta}{n}\lg\frac{c_o}{c_r} + \frac{\vartheta}{n}\lg\sum_{p=1}^{P}\sum_{u=0}^{U}\sum_{s=b}^{Bu}\sum_{v=0}^{V} p\,(\beta_{puvl}^{(r)})^{1/p}\,\rho_{puvl}^{(p-1)/p}\,(B_b^{(a)})^{u/p}\times$$
$$\times\, c_a^{u/p} h^{(l-v)/p}\mathcal{H}^{u/p} - \frac{\vartheta}{n}\lg\sum_{q=1}^{Q}\sum_{x=0}^{X}\sum_{s=b}^{Bx}\sum_{y=0}^{Y} q\times \qquad (13)$$
$$\times\,(\beta_{qxyk}^{(o)})^{1/q}\,\omega_{qxyk}^{(q-1)/q}\,(B_b^{(a)})^{x/q}\,c_a^{x/q}h^{(k-y)/q}\mathcal{H}^{-x/q},$$

where β are the overall stability constants of the complexes, $B_s^{(a)}$ and $B_b^{(a)}$ are the overall sth and bth protolytic dissociation constants of the acid, c_a is the overall concentration of the acid, c_o and c_r are the overall concentrations of the complexes including the aquo-complexes, in the oxidised and reduced states respectively, ω and ρ are the concentrations of the complexes, the superscripts o and r show that the given quantities refer to the oxidised and reduced states, while the subscripts $qxyk$ and $puvl$ indicate the compositions of the complexes. The influence of the protolytic dissociation of the acid on the oxidation potential is taken into account by the multiplier

$$\mathcal{H} = \sum_{s=0}^{b} h^{b-s}B_s^{(a)}.$$

It follows from Eqn.(13) that the oxidation potential is a function of four independent variables: h, c_a, c_o, and c_r. In the study of complex formation in mixed solvents and concentrated aqueous solutions, where the activity of water can vary appreciably, this quantity must be introduced into the equation for the oxidation potential.

The partial relations of the oxidation potential, i.e. its dependence on each independent concentration variable while the others are kept constant, are described by curves consisting of linear sections connected by smooth bends. The establishment of a linear section is possible only when complexes of a specific composition, in the oxidised and the reduced states, predominate.

The composition of the complexes, i.e. the sets of values of q, k, x, y and p, l, u, v, are determined by the successive inspection of the curves for all the partial relations of the oxidation potential, starting with the initial linear section of zero slope for each curve, indicating the presence in the system of aquo-complexes alone, or with the section for which the composition of the complexes is known. The slopes of the linear sections and the changes in them serve as a source of the required information.

The nuclearity of the complexes is determined from the slopes of the linear sections of the partial relations $\phi = \phi(pc_o)$ and $\phi = \phi(pc_r)$, since

$$\left(\frac{\partial\varphi}{\partial\, p\, c_o}\right)_{p\, c_r,\, p\, c_a,\, pH} = -\frac{\vartheta}{nq}, \qquad (14)$$

$$\left(\frac{\partial\varphi}{\partial\, p\, c_r}\right)_{p\, c_o, p\, c_a,\, pH} = \frac{\vartheta}{np}. \qquad (15)$$

The number of groups A^{b-} in the complexes can be found from the slope of the curve for the partial relation $\phi = \phi(pc_a)$, because

$$\left(\frac{\partial\varphi}{\partial\, p\, c_a}\right)_{p\, c_o,\, p\, c_r,\, pH} = \frac{\vartheta}{n}\left(\frac{x}{q} - \frac{u}{p}\right). \qquad (16)$$

The nuclearity (the numbers q and p) and the number of the groups A^{b-} in the complexes (the numbers x and u) can be determined fairly reliably and simply.

The $\phi = \phi$ (pH) curve depends in the general case on the activity of hydrogen ions in a complex manner. Owing to the protolytic dissociation of the acid, linear sections may not appear, or their slopes can be distorted, since

$$\left(\frac{\partial\varphi}{\partial\, pH}\right)_{p\, c_o,\, p\, c_r,\, p\, c_a} = -\frac{\vartheta}{n}\left[\frac{l-v}{p} - \frac{k-y}{q} + \left(\frac{u}{p} - \frac{x}{q}\right)\sum_{s=0}^{b}(b-s)\,h^{b-s}B_s^{(a)}/\mathcal{H}\right]. \qquad (17)$$

The differences k–y and l–v in such systems can be determined with the aid of Eqns.(17) by substituting in the latter the values of the derivative found graphically at selected points. In the analysis of the $\phi = \phi$ (pH) curves one must take into account the intramolecular neutralisation reactions[7], because the differences $k-y$ and $l-v$ indicate either the basicity of the complex, when $k > y$, and $l > v$, or the number of its OH groups, when $y > k$ and $v > l$. Intramolecular neutralisation reactions apparently involve proton transfer from the protonated ligand to the OH group with conversion of the latter into a water molecule. The proton transfer is facilitated by the presence of intramolecular hydrogen bonds in the complex.

Complex formation in oxidation–reduction systems containing metal ions in two oxidation states and two different ligands—the anions of the acids H_bA and $H_\beta L$, includes competitive and mixed complex formation and hydrolysis. The oxidation potential becomes a function of five independent concentration variables, including the overall concentrations of the two acids c_a and c_α:[67]

$$\varphi = \varphi^0(c_o,\, c_r,\, c_a,\, c_\alpha,\, h). \qquad (18)$$

Analysis of Eqn.(18) together with the study of the characteristics of the mixed complex formation made it possible to determine the conditions under which a quantitative investigation of the formation of simple and mixed complexes becomes possible.

The formation of heteropolynuclear complexes containing the ions of two metals is no less complex. A thermodynamic description of heteropolynuclear complex formation has been

achieved in relation to the Fe(III)–F(II)–M(III) system in an aqueous solution of an acid HA, where M(III) is not involved in oxidation–reduction interactions with bivalent and tervalent iron[7,68].

The equation of the oxidation potential expresses the dependence of the latter on five independent variables, namely the overall concentrations of tervalent and bivalent iron, the ions of the metal M(III) and the acid HA, as well as the activity of hydrogen ions. The slopes of the linear sections of the partial relations $\phi = \phi(pc_O)$ and $\phi = \phi(pM)$ make it possible to determine the nuclearity of the heteropolynuclear complex with respect to Fe(III) and M(III) respectively. Information about the number of anions A and hydroxy-groups in the heteropolynuclear complex can be obtained with the aid of partial relations between the oxidation potential and pc_a and pH subject to the condition that the composition of the coexisting complex of the M(III) ion is known.

The reactions involving the formation of complexes in heterogeneous oxidation–reduction systems metal ion (solution)–metal[7,69] and complex formation with ligands constituting an oxidation–reduction system[7,70] have also been examined theoretically.

In oxidation–reduction measurements the necessary condition for the determination of the composition and stability constants of ionic and molecular forms of the oxidation–reduction system is the validity of Eqn.(6) for all the types of species whose concentrations vary in the solution composition ranges investigated. This is usually achieved either by employing fairly dilute solutions with respect to electrolytes at a constant ionic strength or by using a constant and high concentration of a supporting salt, which is an indifferent and strong electrolyte, for example, sodium or lithium perchlorates, etc.

In the latter case the compositions of the complexes are determined without taking into account their association with the cation or anion of the supporting salt. The study of the association of the components of an oxidation–reduction system with the ions of the supporting salt therefore constitutes an independent problem, the solution of which must be obtained at a variable ionic strength. A method has been developed for the investigation of complex formation (ionic association) between ferrocenium cations and Cl^- and ClO_4^- anions, under conditions where the concentration of the main electrolyte (HCl, $HClO_4$) varies within wide limits (0.01–3 M).[71]

A characteristic feature of the method is that the concentration variable employed is a function of the concentration of the acid and the mean activity coefficient of the main electrolyte ($\lg c_a$, $\lg c_a y_\pm$, or $\lg c_a y_\pm^2$) such that the effects of the "non-ideality" of the test system are compensated to the maximum extent in the partial derivative of the oxidation potential. The study of the complex-forming capacity of the ferrocenium nucleus in relation to the Cl^-, SCN^-, ClO_4^-, SO_4^{2-}, NO_3^-, and Br^- ions by various methods[7,72–74] confirmed the reliability of the proposed procedure.

By analogy with the oxidation voltage [Eqn.(11)], the following quantity was introduced[7]:

$$\mathscr{E}_A = \varphi + \vartheta \lg[A]. \qquad (19)$$

The quantity $\mathscr{E}_A$, called the oxidation voltage on the ligand scale, is numerically equal to the e.m.f. of a galvanic cell consisting of an oxidation–reduction half-cell and a half-cell reversible with respect to the anion A. The properties of the partial relation $\mathscr{E}_A = \mathscr{E}_A(pH)$ resemble those of the oxidation voltage. The use of the oxidation voltage on the ligand scale is limited by the restricted set of reversible electrodes. The complex formation reactions in the Fe(III)–Fe(II)–HCl–water system have been investigated with the aid of the function $\mathscr{E}_A$.[75–77]

The stability and hydrolysis constants in relatively simple systems are determined graphically or by simple computational methods[7]. A quantitative description of the chemical interactions, leading to the formation of complex compounds having an involved composition and frequently present simultaneously, is achieved with the aid of computers[7,72–82]. In this case the stability constants of the complexes are regarded as parameters of a regression relation, which is expressed by the equation of the oxidation potential [Eqn.(13)]. The above parameters are found by the method of least squares using a program for the direct minimisation of the sum of squares of deviations of the experimental oxidation potentials from the theoretical values. A combination of random search and coordinate-by-coordinate procedures is useful as a minimisation method.

The set of complexes which is sufficient for the description of all the partial relations between the oxidation potential and independent concentration variables, i.e. the entire set of experimental data, can be refined by comparing the content of a particular complex and the overall error referred to as the limit of sensitivity[7,78]:

$$\delta = |10^{\pm n\tau/\vartheta} - 1| \cdot 100\%, \qquad (20)$$

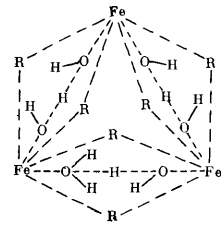
where τ is the accuracy of the potentiometric measurements. If the maximum content of the complex is less than δ, then its presence is undetectable and it can be disregarded. In general, one should bear in mind that the set of the stability constants of complexes obtained with the aid of the most sophisticated programs can be regarded as compatible with the available experimental data.

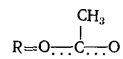
The experimental study of complex formation in systems formed by metals in two oxidation states and various ligands promoted the development of a theory of oxidation–reduction measurements and the elucidation of the fundamental characteristics of the reactions occurring in inorganic–reduction systems.

The complex formation reactions have been studied in particular detail in the Fe(III)–Fe(II) system in aqueous solutions of aliphatic acids (in the formic acid–valeric acid series), chloroacetic, aminoacetic, and hydroxyacetic acids, acrylic acid[7,19,21,65,83–106], dibasic aliphatic acids[107–110], aromatic acids[111–115], and strong inorganic acids (hydrochloric and sulphuric)[75–77,116]. The iron complexes were studied in aqueous solutions containing the anions of two acids (acetate ions and those of salicylic and sulphosalicylic acids or thiocyanate ions, ethylenediaminetetraacetate anions, and thiocyanate ions)[72,73,117–121]. The hydrolysis of tervalent iron has been studied in detail[122–128]. The formation of heteropolynuclear hydroxoacetato-complexes of tervalent iron and chromium has been investigated in aqueous acetic acid solutions[129–134].

Appropriate treatment of the experimental data made it possible to obtain the quantitative characteristics of the reversible complex formation reactions which include information about the compositions of the complexes, their stability constants, and the regions where they exist. The influence of temperature and ionic strength on the above characteristics was investigated for the Fe(III)–Fe(II) system in aqueous solutions of acids in the formic acid–valeric acid series[89,90,92] and in perchloric acid (hydrolytic reactions)[124,128]. The thermodynamic formation functions of the complexes of bivalent and tervalent iron were found from the results of these investigations by the temperature coefficient method. Direct calorimetric determinations of the enthalpy of formation were carried out for a number of complexes[85] by thermodynamic titration[135].

The quantitative study of the reversible formation of complexes of bivalent and tervalent iron in aqueous solutions has led to the following conclusions. The stability of the complexes increases with increase of temperature, ionic strength, and acid concentration. These factors are manifested particularly clearly in the case of the trinuclear complex having the composition $Fe_3A_6(OH)_2^+$, which predominates over a wide range of compositions; this has been explained by the conversion of the complex into a cyclic structure as a result of ring closure by linkages between coordinated aliphatic acid anions via iron atoms[7]:

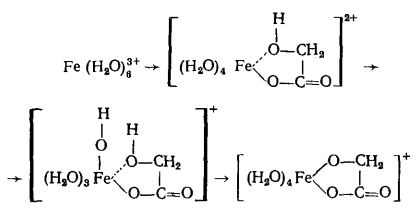




(21)

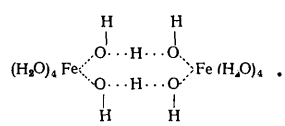
The cyclic structure is supported by the thermodynamic functions for the formation of the above complex and the ease with which it is converted into mono- and di-nuclear complex species and is formed from them. On crystallisation, structure (21) is apparently converted into an Orgel structure[136], according to which three metal atoms are combined via a single oxide ion and the formula $M_3OA_6(H_2O)_3^+$ must therefore be attributed to the complex.

Protolytic processes determine the characteristics of the complex formation in solutions of acids containing two and more protogenic groups. The deprotonation of the alcoholic group in the coordinated ligands (hydroxyacid anions) is due to the weakening of the O–H bond as a result of the polarising effect of the metal atom and, what is most important, as a result of the intramolecular neutralisation reaction. Here one takes into account the fact that the hydroxy-group is coordinated via the oxygen in the deprotonated state and its dissociation strengthens the corresponding chelate. In conformity with the hypothesis of the intramolecular neutralisation reaction, the formation of the deprotonated iron(III) glycolate complex FeA^+ can be represented by the following scheme[106]:



(22)

The formation of hydroxo-complexes of tervalent iron is promoted by the increase of the concentration of metal ions, temperature, and the concentration of the supporting electrolyte. It is suggested that iron(III) ions in the complex are linked via OH groups and water molecules[128]:



(23)

Hydrolysis and complex formation are in general competing processes. In solutions of weak monobasic organic acids, mixed di- and tri-nuclear complexes incorporating the OH group are formed.

New results have been obtained in a study designed to discover chemical interactions by oxidation–reduction measurements in Ce(IV)–Ce(III) systems[137,138] and in the heterogeneous cadmium ion–cadmium amalgam[69,78,81,139] and indium ion–indium amalgam[140] systems. The influence of the relatively unstable species on the nature of the partial relations of the oxidation potential has been demonstrated for these systems and those mentioned above. The study of the cadmium ion–cadmium system is of fundamental importance, since it confirmed experimentally the applicability of oxidation–reduction measurements in the study of chemical interactions in heterogeneous oxidation–reduction systems and hence greatly extended the scope of such measurements.

Complex formation with ligands constituting an oxidation–reduction system was first investigated for the Alizarin C–leuco-Alizarin C–M(III) systems (M = Al, Ga, or In).[141–143] Joint consideration of the partial relations between the oxidation potential and the concentration parameters together with the results of a spectrophotometric study made it possible to establish the sequence of reversible processes occurring in the system and to determine the compositions of the Alizarinate and leuco-Alizarinate complexes, their stability constants, and the protolytic dissociation constants of the ligands in the coordinated state. The acid properties of the latter are enhanced owing to the polarising influence of the metal atom.

VII. REDOXITES

By a redoxite we understand a homogeneous variable-composition phase whose components form a reversible oxidation–reduction system and can be involved in reversible oxidation–reduction interaction with aqueous solutions and oxidation–reduction systems[7]. It is necessary that, when the redoxite comes into contact with aqueous electrolyte solutions, its oxidised and reduced forms should not dissolve appreciably in the aqueous phase.

It is possible to distinguish three classes of redoxites: redox polymers[144,145]; ion exchangers saturated by variable-valence metals[146,147]; solutions of hydrophobic oxidation–reduction systems in solvents immiscible with water–liquid redoxites[7]. The properties of liquid redoxites have been studied mainly by Nikol'skii's school.

A characteristic feature of liquid redoxites is that the equilibrium between the redoxite and the aqueous solution is established rapidly, the measurement of the oxidation potential does not require the introduction of a mediator into the equilibrium aqueous solution[148], and the measurements of the potentials themselves are carried out using an indifferent electrode in the redoxite phase[149]. Under the conditions of the redoxite–aquoues solution phase equilibrium and when fairly dilute aqueous solutions are used, the chemical potentials of water and the non-aqueous solvent hardly change under isothermal-isobaric conditions. Therefore, in the determination of the state of the components of the oxidation–reduction system in the redoxite phase the involvement of the solvent species and water in the corresponding processes is not observed. The relation between the composition of the phases of the heterogeneous redoxite–aqueous solution system and the oxidation potential of the redoxite has been studied theoretically using as the independent variables the concentrations of the substances in the phase where they are largely concentrated[150–153]. This choice of

variables makes it possible to characterise the phase compositions solely in terms of the macrocomponents, which significantly facilitates the experimental study and the oxidation–reduction reaction consequently involves extraction of substances from one phase to the other.

It has been shown experimentally[154,155] and proved theoretically[7,156] that a fundamental characteristic of liquid redoxites is that it is always possible to specify a region in the aqueous solution where an indifferent electrode combined with the redoxite phase constitutes an ion-selective electrode for one of the ions of the aqueous solution. Borate[157], perchlorate[158], bromide, and iodide[159] ion-selective electrodes have been proposed on the basis of redoxites.

The oxidation–reduction and other properties of redoxites have been studied in greatest detail on the basis of the following reversible oxidation–reduction systems: (a) alkylferrocene–alkylferrocenium[7,149]; (b) quinone–hydroquinone and their derivatives[160]; (c) Alizarin–leuco-Alizarin[154,161]; (d) Nile Blue–leuco-Nile Blue[162]. In the determination of the state of the components of the oxidation–reduction system in the redoxite phase, it was found that 1:1 and 1:2 ionic association reactions between the ferrocenium cation and anions develop in system (a) and that protolytic dissociation coupled with the formation of ionic associated species with the cations of quaternary ammonium bases takes place in systems (b) and (c).

The study of solid redoxites is complicated by the low rate of the oxidation–reduction reaction between the redoxite and aqueous solution[144]. It has been found that protolytic and ion-exchange processes involving the redoxite are fairly rapid and their study is therefore not difficult, provided that electron exchange equilibrium has been established beforehand in the redoxite–solution system[163]. This permitted extensive experimental studies on redoxites of the phenothiazine type on the basis of polyene fibres[163–168]. The representation of the experimental data by the dependence of the oxidation potential of the redoxite on the pH makes it possible to find separately the number of protogenic groups due to the dye- and leuco-dye in the redoxite and to determine their dissociation constants. On the basis of the proton-donating groups manifested, it is possible to discover whether the bond formed by the dye and the leuco-dye is chemical or covalent[154]. The relation between the oxidation–reduction and protolytic properties of redoxites has been proved theoretically[150].

REFERENCES

1. G.Charlot, "Les Méthodes de la Chimie Analytique. Analyse Quantitative Minérale" (Translated into Russian), Izd.Khimiya, Moscow, 1969, Chapter 3.
2. E.Bishop (Editor), "Indicators" (Translated into Russian), Izd.Mir, Moscow, 1976, Vol.2, Chapter 8.
3. G.Hoytink, in "Elektrokhimiya Metallov v Nevodnykh Rastvorakh" (The Electrochemistry of Metals in Non-Aqueous Solutions) (Translated into Russian), Izd.Mir, Moscow, 1974, p.356.
4. C.K.Mann and K.K.Barns, "Electrochemical Reactions in Nonaqueous Systems" (Translated into Russian), Izd.Khimiya, Moscow, 1974.
5. L.Michaelis, "Oxydations-Reductions-Potentiale" (Translated into Russian), ONTI, Moscow, 1936.
6. W.M.Clark, "Oxidation-Reduction Potentials of Organic Systems", Williams and Wilkins, Baltimore, 1960.
7. B.P.Nikol'skii, V.V.Pal'chevskii, A.A.Pendin, and Kh.M.Yakubov, "Oksredmetriya" (Oxidation-Reduction Measurements), Izd.Khimiya, Leningrad, 1975.
8. M.S.Zakhar'evskii, "Oksredmetriya" (Oxidation-Reduction Measurements), Izd.Khimiya, Leningrad, 1967.
9. B.B.Nikol'skii and V.V.Pal'chevskii, "Tezisy Dokladov V Vsesoyuznoi Mendeleevskoi Diskussii" (Abstracts of Reports at the Vth All-Union Mendeleev Debate), Izd.Nauka, Leningrad, 1978, p.192.
10. M.M.Shul'ts, A.M.Pisarevskii, and I.P.Polozova, Elektrokhimiya, 13, 939 (1977).
11. E.V.Davtyan, V.G.Krunchak, A.M.Pisarevskii, I.L.Polozova, V.M.Tarasova, and A.N.Khutsishvili in "Metody i Pribory dlya Analiza Zhidkikh Sred" (Methods and Apparatus for the Analysis of Liquid Media), Izd.Samostoyatel'nogo Konstruktorskogo Byuro Analiticheskogo Priborostroeniya, Tbilisi, 1975, Vol.3, Part 1.
12. R.N.Adams, "Electrochemistry of Solid Electrodes", M.Dekker, New York, 1960.
13. M.Spiro and A.B.Ravno, J.Chem.Soc., 78 (1965).
14. F.Basolo and R.G.Pearson, "Mechanisms of Inorganic Reactions" (Translated into Russian), Izd.Mir, Moscow, 1971, Chapter 6.
15. R.Tamamushi, "Kinetic Parameters of Electrode Reactions", Saitama, Tokyo, 1972.
16. M.M.Shul'ts, A.M.Pisarevskii, Yu.A.Chudinova, and V.A.Kukushkina, Elektrokhimiya, 9, 211 (1973).
17. A.M.Pisarevskii and Yu.A.Chudinova, in "V Vsesoyuznoe Soveshchanie po Elektrokhimii" (The Vth All-Union Conference on Electrochemistry), Izd.Nauka, Moscow, 1974, Vol.2, p.363.
18. V.I.Kravtsov and G.P.Tsayun, Elektrokhimiya, 6, 1434 (1970); 6, 1485 (1970).
19. B.P.Nikol'skii, V.P.Pal'tsevskii, and Kh.M.Yakubov, in "Khimiya i Termodinamika Rastvorov" (The Chemistry and Thermodynamics of Solutions), Izd. Leningrad.Gos Univ., Leningrad, 1974, p.203.
20. M.V.Amelina, V.G.Krunchak, V.V.Pal'chevskii, and R.I.Sosnovskii, "Trudy Vsesoyuznogo Nauchno-Issledovatel'skogo Instituta Tsellyulozno-Bumazhnoi Promyshlennosti" (Transactions of the All-Union Institute of the Cellulose and Paper Industry), 1969, No.54, p.127.
21. Kh.M.Yakubov, "Primenenie Oksredmetrii k Izucheniyu Kompleksoobrazovaniya" (Application of Oxidation-Reduction Titrimetry in the Study of Complex Formation), Izd.Donish, Dushanbe, 1966.
22. L.F.Hewitt, "Oxidation-reduction Potentials in Bacteriology and Biochemistry", Livingstone, Edinburgh, 1950, Chapter 2.
23. W.M.Clark and B.Cohen, Publ.Health Repts., 38, 933 (1923).
24. M.S.Zakhar'evskii and K.M.Vasilenko, Uch.Zap. Leningrad.Gos.Univ., 272, No.18, 48 (1959).
25. M.S.Zakhar'evksii and V.A.Rabinovich, Zavod.Lab., 27, 1158 (1961).
26. M.S.Zakhar'evskii, T.I.L'vova, I.N.Kuznetsova, and B.I.Kryzhanovskii, Zavod.Lab., 30, 1196 (1964).
27. B.P.Nikol'skii, M.S.Zakhar'evskii, and T.I.L'vova, in "Sovremennye Metody Analiza" (Modern Analytical Methods), Izd.Nauka, Moscow, 1965, p.209.
28. T.Kawana, R.K.Darlington, and D.W.Leedy, Anal. Chem., 36, 2023 (1964).
29. A.A.Belyustin, A.M.Pisarevskii, M.M.Shul'ts, and B.P.Nikol'skii, Dokl.Akad.Nauk SSSR, 154, 404 (1964).
30. A.M.Pisarevskii, M.M.Shul'ts, B.P.Nikol'skii, and A.A.Belyustin, Dokl.Akad.Nauk SSSR, 187, 364 (1969).

31. L.I.Boguslavskii, Zhur.Fiz.Khim., 39, 263 (1965) [Russ.J.Phys.Chem., No.1 (1965)].
32. C.Liteanu, E.Hopirtean, and I.Silberg, Talanta, 24, 589 (1977).
33. E.Punger, Anal.Letters, 1, 213 (1968); Anal.Chim. Acta, 43, 289 (1968).
34. G.S.Bagdasarova, A.A.Belyustin, and A.M.Pisarevskii, Elektrokhimiya, 4, 1329 (1968).
35. G.S.Bagdasarova, A.A.Belyustin, A.M.Pisarevskii, and M.M.Shul'ts, Elektrokhimiya, 4, 1239 (1968).
36. A.M.Pisarevskii, A.A.Belyustin, S.E.Volkov, and O.S.Ershov, in "Stekloobraznoe Sostoyanie" (The Vitreous State), Erevan, 1974, Vol.3, p.186.
37. S.E.Volkov, A.M.Pisarevskii, T.G.Asyun'kina, and M.M.Shul'ts, Fizika i Khimiya Stekla, 1, 168 (1975).
38. E.V.Davtyan, V.G.Krunchak, T.I.L'vova, V.V.Pal'chevskii, A.M.Pisarevskii, A.G.Rodichev, and A.N.Khutsishvili, in "Metody i Pribori dlya Analiza Zhidkikh Sred" (Methods and Apparatus for the Analysis of Liquid Media), Izd.Samostoyatel'nogo Konstruktorskogo Byuro Analiticheskogo Priborostroeniya, Tbilisi, 1975, Vol.3, Part 2, p.165.
39. I.P.Polozova, A.M.Pisarevskii, and M.M.Shul'ts, Elektrokhimiya, 13, 1560 (1977).
40. B.P.Nikol'skii and V.V.Pal'chevskii, Zhur.Fiz.Khim., 32, 1280 (1958).
41. V.I.Kravtsov and V.P.Tsayun, Elektrokhimiya, 6, 691 (1970).
42. W.M.Clark, Chem.Rev., 2, 127 (1925).
43. B.P.Nikol'skii and V.V.Pal'chevskii, in "Kompleksoobrazovanie v Okislitel'no–Vosstanovitel'nykh Sistemakh" (Complex Formation in Oxidation–Reduction Systems), Izd.Tadzhik.Gos.Univ., Dushanbe, 1973, No.2, p.98.
44. B.P.Nikol'skii and V.V.Pal'chevskii, in "Kompleksoobrazovanie v Okislitel'no–Vosstanovitel'nykh Sistemakh" (Complex Formation in Oxidation–Reduction Systems), Izd.Tadzhik.Gos.Univ., Dushanbe, 1973, pp.98–107.
45. B.P.Nikol'skii, V.V.Pal'chevskii, and N.M.Asadullina, Dokl.Akad.Nauk SSSR, 193, 831 (1970).
46. B.P.Nikol'skii, N.M.Asadullina, V.V.Pal'chevskii, and G.V.Semenov, Dokl.Akad.Nauk SSSR, 193, 1332 (1970).
47. B.P.Nikol'skii and V.V.Pal'chevskii, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 532 (1957).
48. B.P.Nikol'skii, M.S.Zakhar'evskii, and V.V.Pal'chevskii, Uch.Zap.Leningrad.Gos.Univ., 211, No.15, 26 (1957).
49. B.P.Nikol'skii and V.V.Pal'chevskii, Zhur.Fiz.Khim., 32, 1506 (1958).
50. V.V.Niyazmukhamedova, V.V.Pal'chevskii, and I.Ya.Kolontarov, in "Kompleksoobrazovanie v Okislitel'no–Vosstanovitel'nykh Sistemakh" (Complex Formation in Oxidation–Reduction Systems), Izd. Tadzhik.Gos.Univ., Dushanbe, 1972, No.1, p.129.
51. V.V.Shvidkaya, E.E.Yudovich, V.V.Pal'chevskii, and I.Ya.Kalontarov, in "Kompleksoobrazovanie v Okislitel'no–Vosstanovitel'nykh Sistemakh" (Complex Formation in Oxidation–Reduction Systems), Izd.Tadzhik.Gos.Univ., Dushanbe, 1973, No.2, p.108.
52. V.V.Shvidkaya, V.V.Pal'chevskii, E.E.Yudovich, and I.Ya.Kalontarov, in "Kompleksoobrazovanie v Okislitel'no–Vosstanovitel'nykh Sistemakh" (Complex Formation in Oxidation–Reduction Systems), Izd.Tadzhik.Gos.Univ., Dushanbe, 1973, No.2, p.112.
53. V.V.Shvidkaya, V.V.Pal'chevskii, E.E.Yudovich, and I.Ya.Kalontarov, in "Kompleksoobrazovanie v Okislitel'no–Vosstanovitel'nykh Sistemakh" (Complex Formation in Oxidation–Reduction Systems), Izd.Tadzhik.Gos.Univ., Dushanbe, 1973, No.2, p.119.
54. V.V.Pal'chevskii, V.V.Shvidkaya, and E.E.Yudovich, in "Vzaimodeistviya v Rastvorakh Okislitel'no–Vosstanovitel'nykh Sistem" (Interactions in Solutions of Oxidation–Reduction Systems), Izd.Leningrad. Gos.Univ., Leningrad, 1977, p.104.
55. V.V.Pal'chevskii, V.V.Shvidkaya, and E.E.Yudovich, in "Vzaimodeistviya v Rastvorakh Okislitel'no–Vosstanovitel'nykh Sistem" (Interactions in Solutions of Oxidation–Reduction Systems), Izd.Leningrad. Goz.Univ., Leningrad, 1977, p.108.
56. V.V.Pal'chevskii, E.K.Skaletskii, A.A.Tulub, and E.E.Yudovich, Zhur.Fiz.Khim., 52, 1233 (1979) [Russ.J.Phys.Chem., No.5 (1979)].
57. B.P.Nikol'skii, V.V.Pal'chevskii, L.A.Polyanskaya, and V.V.Boriskin, Dokl.Akad.Nauk SSSR, 193, 352 (1970).
58. B.P.Nikol'skii, V.V.Pal'chevskii, L.A.Polyanskaya, and A.G.Rodichev, Dokl.Akad.Nauk SSSR, 194, 1334 (1970).
59. B.P.Nikol'skii, V.V.Pal'chevskii, L.A.Polyanskaya, N.P.Kiseleva, and G.F.Pustarnakova, Dokl.Akad. Nauk SSSR, 196, 1365 (1971).
60. B.P.Nikol'skii, V.V.Pal'chevskii, and L.A.Polyanskaya, Vestnik Leningrad.Univ., No.4, Issue 1, 16 (1970).
61. M.S.Zakhar'evskii and V.V.Pal'chevskii, Vestnik Leningrad.Univ., No.22, Issue 4, 121 (1964).
62. M.S.Zakhar'evskii and V.V.Pal'chevskii, in "Khimiya i Termodinamika Rastvorov" (The Chemistry and Thermodynamics of Solutions), Izd.Leningrad.Gos. Univ., Leningrad, 1964, p.184.
63. F.J.C.Rossotti and H.S.Rossotti, "Determination of Stability Constants and Other Equilibrium Constants in Solutions" (Translated into Russian), Izd.Mir, Moscow, 1965.
64. B.P.Nikol'skii, in "Termodinamika i Stroenie Rastvorov" (Thermodynamics and Structure of Solutions), Izd.Akad.Nauk SSSR, Moscow, 1959, p.126.
65. B.P.Nikol'skii, V.V.Pal'chevskii, and R.G.Gorbunova, Zhur.Neorg.Khim., 6, 606 (1961)[Russ.J. Inorg.Chem., No.3 (1961)]; "Tezisy Dokladov VIII Vsesoyuznogo Soveshchaniya po Khimii Kompleksnykh Soedinenii" (Abstracts of Reports at the VIIIth All-Union Conference on the Chemistry of Complexes), Izd.Akad.Nauk Ukrain.SSR, Kiev, 1959, p.97.
66. V.V.Pal'chevskii and Kh.M.Yakubov, in "Kompleksoobrazovanie v Okislitel'no-Vosstanovitel'nykh Sistemakh" (Complex Formation in Oxidation-Reduction Systems), Izd.Tadzhik.Gos.Univ., Dushanbe, 1972, p.5.
67. V.V.Pal'chevskii and K.D.Shirko, in "Vzaimodeistviya v Rastvorakh Okislitel'no–Vosstanovitel'nykh Sistem" (Interactions in Solutions of Oxidation–Reduction Systems), Izd.Leningrad.Gos.Univ., Leningrad, 1977, p.22.
68. V.V.Pal'chevskii, A.A.Pendin, Kh.M.Yakubov, E.Ya.Kalontarova, and M.M.Mansurov, in "Kompleksoobrazovanie v Okislitel'no–Vosstanovitel'nykh Sistemakh" (Complex Formation in Oxidation–Reduction Systems), Izd.Tadzhik.Gos.Univ., Dushanbe, 1973, p.31.

69. A.M.Antonova and V.V.Pal'chevskii, in "Kompleksoobrazovanie v Okislitel'no–Vosstanovitel'nykh Sistemakh" (Complex Formation in Oxidation–Reduction Systems), Izd.Tadzhik.Gos.Univ., Dushanbe, 1973, p.24.
70. B.P.Nikol'skii, V.V.Pal'chevskii, and N.M.Okun', in "Kompleksoobrazovanie v Okislitel'no–Vosstanovitel'nykh Sistemakh" (Complex Formation in Oxidation–Reduction Systems), Izd.Tadzhik.Gos.Univ., Dushanbe, 1973, p.121.
71. T.I.L'vova, A.A.Pendin, and B.P.Nikol'skii, Dokl. Akad.Nauk SSSR, 176, 586 (1967).
72. T.I.L'vova, A.A.Pendin, K.D.Shirko, and B.P.Nikol'skii, Vestnik.Leningrad.Univ., No.16, Issue 3, 116 (1967).
73. B.P.Nikol'skii, A.A.Pendin, and M.S.Zakhar'evskii, Zhur.Neorg.Khim., 12, 1803 (1967)[Russ.J.Inorg. Chem., No.7 (1967)].
74. I.Holeček, K.Handbir, and J.Klikorka, "Proceedings of the XXIst Conference on Coordination Chemistry, Bratislava, 1978", p.65.
75. V.V.Pal'chevskii and E.F.Strizhev, Vestnik.Leningrad.Univ., No.22, Issue 4, 159 (1968).
76. V.V.Pal'chevskii and E.F.Strizhev, Vestnik.Leningrad.Univ., No.4, Issue 1, 163 (1969).
77. B.P.Nikol'skii, V.V.Pal'chevskii, and E.F.Stryzhev, Vestnik.Leningrad.Univ., No.16, Issue 3, 116 (1969).
78. B.P.Nikol'skii, A.M.Antonova, V.V.Pal'chevskii, and V.N.Solntsev, Dokl.Akad.Nauk SSSR, 221, 669 (1975).
79. V.V.Pal'chevskii, V.N.Solntsev, and V.I.Shcherbakova, in "Vzaimodeistviya v Rastvorakh Okislitel'no–Vosstanovitel'nykh Sistem" (Complex Formation in Oxidation–Reduction Systems), Izd.Leningrad.Gos. Univ., Leningrad, 1977, p.29.
80. B.P.Nikol'skii, V.V.Pal'chevskii, V.N.Solntsev, and V.I.Shcherbakova, in "Vzaimodeistviya v Rastvorakh Okislitel'no–Vosstanovitel'nykh Sistem" (Complex Formation in Oxidation–Reduction Systems), Izd. Leningrad.Gos.Univ., Leningrad, 1977, p.41.
81. A.M.Antonova, G.V.Konstantinova, V.V.Pal'chevskii, and V.N.Solntsev, in "Vzaimodeistviya v Rastvorakh Okislitel'no–Vosstanovitel'nykh Sistem" (Complex Formation in Oxidation–Reduction Systems), Izd, Leningrad.Gos.Univ., Leningrad, 1977, p.50.
82. A.M.Antonova and V.V.Pal'chevskii, in "Vzaimodeistviya v Rastvorakh Okislitel'no–Vosstanovitel'nykh Sistem" (Complex Formation in Oxidation–Reduction Systems), Izd.Leningrad.Gos.Univ., Leningrad, 1977, p.134.
83. Kh.M.Yakubov, V.V.Pal'chevskii, and L.P.Bogdanova, Dokl.Akad.Nauk Tadzh.SSR, 7, No.3, 24 (1964).
84. B.P.Nikol'skii, V.V.Pal'chevskii, and Kh.M.Yakubov, in "Khimiya i Termodinamika Rastvorov" (The Chemistry and Thermodynamics of Solutions), Izd.Leningrad.Univ., Leningrad, 1964, p.220.
85. B.P.Nikol'skii, V.V.Pal'chevskii, and Kh.M.Yakubov, in "Khimiya i Termodinamika Rastvorov" (The Chemistry and Thermodynamics of Solutions), Izd.Leningrad.Univ., Leningrad, 1964, p.231.
86. Kh.M.Yakubov, V.V.Pal'chevskii, and B.I.Seredin, Vestnik.Leningrad.Univ., No.4, Issue 1, 80 (1965).
87. Kh.M.Yakubov, V.V.Pal'chevskii, and G.G.Selikhov, Vestnik Leningrad.Univ., No.4, Issue 1, 87 (1965).
88. Kh.M.Yakubov, V.V.Pal'chevskii, and E.Ya.Offengenden, in "Kompleksoobrazovanie v Okislitel'no–Vosstanovitel'nykh Sistemakh" (Complex Formation in Oxidation–Reduction Systems), Izd.Tadzhik.Gos. Univ., Dushanbe, 1972, p.25.
89. Kh.M.Yakubov, E.Ya.Offengenden, and V.V.Pal'chevskii, in "Kompleksoobrazovanie v Okislitel'no–Vosstanovitel'nykh Sistemakh" (Complex Formation in Oxidation–Reduction Systems), Izd.Tadzhik.Gos. Univ., Dushanbe, 1972, p.34.
90. Kh.M.Yakubov, E.Ya.Offengenden, and V.V.Pal'chevskii, in "Kompleksoobrazovanie v Okislitel'no–Vosstanovitel'nykh Sistemakh" (Complex Formation in Oxidation–Reduction Systems), Izd.Tadzhik.Gos. Univ., Dushanbe, 1972, p.40.
91. Kh.M.Yakubov and E.Ya.Offengenden, in "Kompleksoobrazovanie v Okislitel'no–Vosstanovitel'nykh Sistemakh" (Complex Formation in Oxidation–Reduction Systems), Izd.Tadzhik.Gos.Univ., Dushanbe, 1972, pp.66–70.
92. Kh.M.Yakubov, V.V.Pal'chevskii, Z.N.Yusupov, and M.M.Rakhimova, in "Kompleksoobrazovanie v Okislitel'no–Vosstanovitel'nykh Sistemakh" (Complex Formation in Oxidation–Reduction Systems), Izd. Tadzhik.Gos.Univ., Dushanbe, 1972, p.72.
93. Kh.M.Yakubov and Z.N.Yusupov, in "Kompleksoobrazovanie v Okislitel'no–Vosstanovitel'nykh Sistemakh" (Complex Formation in Oxidation–Reduction Systems), Izd.Tadzhik.Gos.Univ., Dushanbe, 1976, No.3, p.58.
94. B.P.Nikol'skii, A.V.Kalyamin, V.A.Kuvshinov, V.V.Pal'chevskii, S.B.Tomilov, and Kh.M.Yakubov, Dokl.Akad.Nauk SSSR, 219, 659 (1974).
95. Kh.M.Yakubov and M.A.Ismailova, in "Kompleksoobrazovanie v Okislitel'no–Vosstanovitel'nykh Sistemakh" (Complex Formation in Oxidation–Reduction Systems), Izd.Tadzhik.Gos.Univ., Dushanbe, 1976, No.3, p.5.
96. Kh.M.Yakubov and E.Ya.Offengenden, in "Kompleksoobrazovanie v Okislitel'no–Vosstanovitel'nykh Sistemakh" (Complex Formation in Oxidation–Reduction Systems), Izd.Tadzhik.Gos.Univ., Dushanbe, 1976, p.170.
97. Kh.M.Yakubov, E.Ya.Offengenden, and Z.N.Yusupov, Koord.Khim., 3, 1400 (1977).
98. V.V.Pal'chevskii, E.Kh.Tkachuk, and Kh.M.Yakubov, Dokl.Akad.Nauk Tadzh.SSR,13, No.11,41(1970).
99. B.P.Nikol'skii, V.V.Pal'chevskii, A.A.Pendin, E.Kh.Tkachuk, S.N.Isaeva, and Kh.M.Yakubov, Dokl.Akad.Nauk SSSR, 196, 609 (1971).
100. V.V.Pal'chevskii, E.Kh.Tkachuk, and Kh.M.Yakubov, in "Kompleksoobrazovanie v Okislitel'no–Vosstanovitel'nykh Sistemakh" (Complex Formation in Oxidation–Reduction Systems), Izd.Tadzhik.Gos.Univ., Dushanbe, 1973, No.2, p.49.
101. V.V.Pal'chevskii, E.Kh.Tkachuk, and Kh.M.Yakubov, in "Kompleksoobrazovanie v Okislitel'no–Vosstanovitel'nykh Sistemakh" (Complex Formation in Oxidation–Reduction Systems), Izd.Tadzhik.Gos.Univ., Dushanbe, 1973, No.2, p.81.
102. V.V.Pal'chevskii and E.Kh.Tkachuk, in "Kompleksoobrazovanie v Okislitel'no–Vosstanovitel'nykh Sistemakh" (Complex Formation in Oxidation–Reduction Systems), Izd.Tadzhik.Gos.Univ., Dushanbe, 1973, No.2, p.59.
103. V.V.Pal'chevskii, V.I.Shcherbakova, and I.Yu.Maklakova, Vestnik.Leningrad.Univ., No.22, Issue 4, 145 (1974).

104. V.I.Nikol'skii, V.V.Pal'chevskii, V.N.Solntsev, and V.I.Shcherbakova, "Tezisy Dokladov XII Vsesoyuznogo Soveshchaniya po Khimii Kompleksnykh Soedinenii" (Abstracts of Reports at the XIIth All-Union Conference on the Chemistry of Complex Compounds), Izd.Nauka, Novosibirsk, 1975, p.38.
105. B.P.Nikol'skii, V.V.Pal'chevskii, and V.I.Shcherbakova, Zhur.Fiz.Khim., **49**, 1564 (1975)[Russ.J.Phys. Chem., No.6 (1975)].
106. B.P.Nikol'skii, V.V.Pal'chevskii, and V.I.Shcherbakova, in "Vzaimodeistviya v Rastvorakh Okislitel'no–Vosstanovitel'nykh Sistem" (Interactions in Solutions of Oxidation–Reduction Systems), Izd.Leningrad.Gos. Univ., Leningrad, 1977, p.57.
107. V.P.Nikol'skii, Kh.M.Yakubov, L.V.Kvyatkovskaya, and V.V.Pal'chevskii, in "Kompleksoobrazovanie v Okislitel'no–Vosstanovitel'nykh Sistemakh" (Complex Formation in Oxidation–Reduction Systems), Izd. Tadzhik.Gos.Univ., Dushanbe, 1972, p.88.
108. Kh.M.Yakubov, L.V.Kvyatkovskaya, V.A.Kuvshinov, and V.V.Pal'chevskii, in "Kompleksoobrazovanie v Okislitel'no–Vosstanovitel'nykh Sistemakh"(Complex Formation in Oxidation–Reduction Systems), Izd. Tadzhik.Gos.Univ., Dushanbe, 1972, p.94.
109. Kh.M.Yakubov, V.V.Pal'chevskii, L.V.Kvyatkovskaya, and G.Kh.Kolonova, in "Kompleksoobrazovanie v Okislitel'no–Vosstanovitel'nykh Sistemakh" (Complex Formation in Oxidation–Reduction Systems), Izd.Tadzhik.Gos.Univ., Dushanbe, 1972, p.100.
110. L.V.Kvyatkovskaya, V.V.Pal'chevskii, M.M.Yunusov, and Kh.M.Yakubov, in "Vzaimodeistviya v Rastvorakh Okislitel'no–Vosstanovitel'nykh Sistem" (Interactions in Solutions of Oxidation–Reduction Systems), Izd.Leningrad.Gos.Univ., Leningrad, 1977, p.80.
111. V.V.Pal'chevskii, A.D.Chegodaeva, and I.B.Margolina, Vestnik.Leningrad.Univ., No.10, Issue 2, 166 (1970).
112. B.P.Nikol'skii, V.V.Pal'chevskii, A.D.Chegodaeva, Kh.M.Yakubov, and T.V.Sambur, Dokl.Akad.Nauk SSSR, **192**, 102 (1970).
113. B.P.Nikol'skii, V.V.Pal'chevskii, A.D.Chegodaeva, and N.K.Barkova, Dokl.Akad.Nauk SSSR, **194**, 1100 (1970).
114. V.I.Kravtsov, V.A.Shablina, and A.A.Kozulyaev, Elektrokhimiya, **9**, 904 (1973).
115. L.V.Ivoilova and V.I.Kravtsov, Elektrokhimiya, **13**, 577 (1977).
116. B.P.Nikol'skii, V.V.Pal'chevskii, and Fan Ty Bang, Dokl.Akad.Nauk SSSR, **209**, 624 (1973).
117. K.D.Shirko, V.V.Pal'chevskii, and V.I.Shcherbakova, in "Kompleksoobrazovanie v Okislitel'no–Vosstanovitel'nykh Sistemakh" (Complex Formation in Oxidation–Reduction Systems), Izd.Tadzhik.Gos. Univ., Dushanbe, 1973, No.2, p.64.
118. K.D.Shirko, V.V.Pal'chevskii, Kh.M.Yakubov, and S.O.Oripov, in "Kompleksoobrazovanie v Okislitel'no–Vosstanovitel'nykh Sistemakh" (Complex Formation in Oxidation–Reduction Systems), Izd.Tadzhik.Gos. Univ., Dushanbe, 1973, No.2, p.72.
119. V.V.Pal'chevskii and K.D.Shirko, in "Vzaimodeistviya v Rastvorakh Okislitel'no–Vosstanovitel'nykh Sistem" (Interactions in Solutions of Oxidation–Reduction Systems), Izd.Leningrad.Gos.Univ., Leningrad, 1977, p.64.
120. Z.R.Baratova, V.V.Pal'chevskii, K.D.Shirko, and Kh.M.Yakubov, in "Vzaimodeistviya v Rastvorakh Okislitel'no–Vosstanovitel'nykh Sistem" (Interactions in Solutions of Oxidation–Reduction Systems), Izd. Leningrad.Gos.Univ., 1977, p.70.
121. Z.R.Baratova, V.V.Pal'chevskii, K.D.Shirko, and Kh.M.Yakubov, in "Vzaimodeistviya v Rastvorakh Okislitel'no–Vosstanovitel'nykh Sistem" (Interactions in Solutions of Oxidation–Reduction Systems), Izd. Leningrad.Gos.Univ., Leningrad, 1977, p.75.
122. V.V.Pal'chevskii and Kh.M.Yakubov, Dokl.Akad. Nauk Tadzh.SSR, 6, No.1, 17 (1963).
123. Kh.M.Yakubov and V.V.Pal'chevskii, Dokl.Akad. Nauk Tadzh.SSR, 7, No.4, 16 (1964).
124. Kh.M.Yakubov, E.Ya.Offengenden, and V.V.Pal'chevskii, in "Kompleksoobrazovanie v Okislitel'no–Vosstanovitel'nykh Sistemakh" (Complex Formation in Oxidation–Reduction Systems), Izd.Tadzhik.Gos. Univ., Dushanbe, 1972, p.52.
125. V.V.Pal'chevskii and Fan Ty Bang, Vestnik.Leningrad.Univ., No.4, Issue 1, 116 (1974).
126. B.P.Nikol'skii, A.V.Kalyamin, V.A.Kuvshinov, V.V.Pal'chevskii, S.B.Tomilov, and Kh.M.Yakubov, Dokl.Akad.Nauk SSSR, 217, 107 (1974).
127. E.G.Gatilova, M.S.Zakhar'evskii, I.N.Kuznetsova, B.P.Nikol'skii, V.V.Pal'chevskii, A.A.Pendin, and Kh.M.Yakubov, in "Khimiya v Tadzhikistane" (Chemistry in Tajikistan), Izd.Donish, Dushanbe, 1974, p.246.
128. Kh.M.Yakubov and M.A.Ismailova, in "Kompleksoobrazovanie v Okislitel'no–Vosstanovitel'nykh Sistemakh" (Complex Formation in Oxidation–Reduction Systems), Izd.Tadzhik.Gos.Univ., Dushanbe, 1976, No.3, p.5.
129. B.P.Nikol'skii, E.Ya.Kalontarova, M.M.Mansurov, V.V.Pal'chevskii, A.A.Pendin, and Kh.M.Yakubov, Zhur.Fiz.Khim., **46**, 2333 (1972)[Russ.J.Phys.Chem., No.9 (1972)].
130. B.P.Nikol'skii, V.V.Pal'chevskii, A.A.Pendin, Kh.M.Yakubov, E.Ya.Offengenden, and E.Ya.Kalontarova, Dokl.Akad.Nauk SSSR, **200**, 128 (1971).
131. V.V.Pal'chevskii, A.A.Pendin, Kh.M.Yakubov, E.Ya.Kalontarova, and E.Ya.Offengenden, Dokl. Akad.Nauk Tadzh.SSR, 14, No.8, 33 (1971); B.P.Nikolsky, V.V.Palchevsky, A.A.Pendin, H.M.Yakubov, and E.Ya.Kalontarova, "Proceedings of the XIIIth Conference on Coordination Chemistry, Cracow, 1970", p.137.
132. V.V.Pal'chevskii, A.A.Pendin, Kh.M.Yakubov, M.M.Mansurov, and I.G.Shanyavskii, in "Kompleksoobrazovanie v Okislitel'no–Vosstanovitel'nykh Sistemakh" (Complex Formation in Oxidation–Reduction Systems), Izd.Tadzh.Gos.Univ., Dushanbe, 1972, p.114.
133. E.Ya.Kalontarova, M.M.Mansurov, A.A.Pendin, and Kh.M.Yakubov, in "Vzaimodeistviya v Rastvorakh Okislitel'no–Vosstanovitel'nykh Sistem" (Interactions in Solutions of Oxidation–Reduction Systems), Izd.Leningrad.Gos.Univ., Leningrad, 1977, p.92.
134. M.M.Mansurov, in "Vzaimodeistviya v Rastvorakh Okislitel'no–Vosstanovitel'nykh Sistem" (Interactions in Solutions of Oxidation–Reduction Systems), Izd. Leningrad.Gos.Univ., Leningrad, 1977, p.88.
135. Kh.M.Yakubov, E.Ya.Offengenden, and A.E.Babakhanov, Dokl.Akad.Nauk Tadzh.SSR, **18**, No.2, 39 (1975).
136. L.E.Orgel, Nature, **187**, No.4736, 504 (1960).
137. I.M.Batyaev, V.V.Pal'chevskii, M.S.Zakhar'evskii, and E.F.Strizhev, in "Fiziko-Khimicheskie Svoistva Rastvorov" (Physicochemical Properties of Solutions), Izd.Leningrad.Gos.Univ., Leningrad, 1964, p.148.

138. V.I.Kravtsov, L.Ya.Smirnova, and O.A.Babishcheva, Elektrokhimiya, 13, 1487 (1977).
139. A.M.Antonova, B.P.Nikol'skii, and V.V.Pal'chevskii, in "Kompleksoobrazovanie v Okislitel'no–Vosstanovitel'nykh Sistemakh" (Complex Formation in Oxidation–Reduction Systems), Izd.Tadzhik.Gos.Univ., Dushanbe, 1973, No.2, p.39.
140. V.N.Statsyuk, V.I.Kravtsov, and E.A.Mambetkaziev, Elektrokhimiya, 13, 1195 (1977).
141. B.P.Nikol'skii, N.M.Okun', V.V.Pal'chevskii, and L.I.Starikova, Vestnik.Leningrad.Univ., No.4, Issue 1, 10 (1971).
142. B.P.Nikol'skii, V.V.Pal'chevskii, and N.M.Okun', Dokl.Akad.Nauk SSSR, 198, 851 (1971).
143. B.P.Nikol'skii, V.V.Pal'chevskii, N.M.Okun', and A.M.Antonova, Dokl.Akad.Nauk SSSR, 199, 111 (1971).
144. H.G.Cassidy and K.A.Kun, "Electron–Transfer Polymers" (Translated into Russian), Izd.Khimiya, Leningrad, 1975.
145. G.Manecke and R.Reuter, J.Polymer Science, Polymer Symp., 62, 227 (1978).
146. B.Sansoni, Chem.Techn., 10, 580 (1958).
147. A.V.Kozhevnikov, "Elektronoobmenniki" (Electron Exchangers), Izd.Khimiya, Leningrad, 1972.
148. A.A.Pendin and R.A.Abakumova, Elektrokhimiya, 10, 555 (1974).
149. M.A.Trofimov, P.K.Leont'evskaya, A.A.Pendin, and B.P.Nikol'skii, Dokl.Akad.Nauk SSSR, 212, 378 (1973).
150. B.P.Nikol'skii, A.A.Pendin, V.V.Pal'chevskii, and R.A.Abakumova, Elektrokhimiya, 7, 427 (1971).
151. A.A.Pendin, M.A.Trofimov, and B.P.Nikol'skii, Dokl.Akad.Nauk SSSR, 219, 1177 (1974).
152. B.P.Nikol'skii, Sh.K.Norov, V.V.Pal'chevskii, and A.A.Pendin, Dokl.Akad.Nauk SSSR, 221, 868 (1975).
153. A.A.Pendin, M.A.Trofimov, and B.P.Nikol'skii, Elektrokhimiya, 9, 1526 (1975).
154. Sh.K.Norov, V.V.Pal'chevskii, and A.A.Pendin, in "Vzaimodeistviya v Rastvorakh Okislitel'no–Vosstanovitel'nykh Sistem" (Interactions in Solutions of Oxidation–Reduction Systems), Izd.Leningrad.Gos. Univ., Leningrad, 1977, p.170.
155. A.A.Pendin, M.A.Trofimov, and V.V.Khorunzhii, in "Vzaimodeistviya v Rastvorakh Okislitel'no–Vosstanovitel'nykh Sistem" (Interactions in Solutions of Oxidation–Reduction Systems), Izd.Leningrad. Gos.Univ., Leningrad, 1977, p.179.
156. Sh.K.Norov, V.V.Pal'chevskii, and A.A.Pendin, in "Vzaimodeistviya v Rastvorakh Okislitel'no–Vosstanovitel'nykh Sistem" (Interactions in Solutions of Oxidation–Reduction Systems), Izd.Leningrad. Gos.Univ., Leningrad, 1977, p.161.
157. M.A.Trofimov, I.M.Shul'ts, P.K.Leont'evskaya, and A.A.Pendin, in "Vzaimodeistviya v Rastvorakh Okislitel'no–Vosstanovitel'nykh Sistem" (Interactions in Solutions of Oxidation–Reduction Systems), Izd. Leningrad.Gos.Univ., Leningrad, 1977, p.174.
158. Sh.K.Norov, V.V.Pal'chevskii, and A.A.Pendin, in "Vzaimodeistviya v Rastvorakh Okislitel'no–Vosstanovitel'nykh Sistem" (Interactions in Solutions of Oxidation–Reduction Systems), Izd.Leningrad.Gos. Univ., Leningrad, 1977, p.170.
159. A.A.Pendin, M.A.Trofimov, P.K.Leont'evskaya, and B.P.Nikol'skii, Dokl.Akad.Nauk SSSR, 213, 145 (1973).
160. V.V.Khorunzhii, M.A.Trofimov, V.V.Pal'chevskii, and A.A.Pendin, in "Ionnyi Obmen i Ionometriya" (Ion Exchange and Ionometry), Izd.Leningrad.Gos. Univ., Leningrad, 1979, No.2, p.234.
161. Sh.K.Norov, V.V.Pal'chevskii, and A.A.Pendin, in "Vzaimodeistviya v Rastvorakh Okislitel'no–Vosstanovitel'nykh Sistem" (Interactions in Solutions of Oxidation–Reduction Systems), Izd.Leningrad. Gos.Univ., Leningrad, 1977, p.145.
162. R.A.Abakumova, M.V.Kudryashova, V.V.Pal'chevskii, and G.V.Konstantinova, in "Vzaimodeistviya v Rastvorakh Okislitel'no–Vosstanovitel'nykh Sistem" (Interactions in Solutions of Oxidation–Reduction Systems), Izd.Leningrad.Gos.Univ., Leningrad, 1977, p.155.
163. I.I.Borshcheva, L.A.Vol'f, Yu.K.Kirilenko, S.V.Burinskii, R.A.Abakumova, and V.V.Pal'chevskii, Zhur.Prikl.Khim., 43, 2575 (1970).
164. B.P.Nikol'skii, V.V.Pal'chevskii, R.A.Abakumova, Z.N.Yusupov, I.I.Shamolina, L.A.Vol'f, and Kh.M.Yakubov, Dokl.Akad.Nauk SSSR, 197, 1341 (1971).
165. I.I.Shamolina, L.A.Vol'f, A.I.Meos, R.A.Abakumova, and V.V.Pal'chevskii, Zhur.Prikl.Khim., 46, 1392 (1973).
166. R.A.Abakumova, G.B.Zakhvataev, V.V.Pal'chevskii, I.Yu.Sapurina, L.V.Emets, and I.I.Shamolina, Vestnik.Leningrad.Univ., No.16, Issue 3, 160 (1976).
167. V.V.Pal'chevskii, R.A.Abakumova, I.I.Shamolina, L.A.Vol'f, L.A.Belyakova, and Sh.K.Norov, Zhur. Prikl.Khim., 49, 166 (1976).
168. V.V.Pal'chevskii, G.B.Zakhvataev, R.A.Abakumova, and I.Yu.Sapurina, in "Ionnyi Obmen i Ionometriya" (Ion Exchange and Ionometry), Izd.Leningrad.Gos. Univ., 1876, No.1, p.92.

Leningrad State University

Tadjik State University

Translated from *Uspekhi Khimii*, **49**, 1880-1903 (1980) U.D.C. 541.135.53

Dynamics of the Potential and the Mechanism of Action of Ion-selective Glass Electrodes

A.A.Belyustin

Studies on the dynamics of the potential of glass electrodes with hydrogen and metal ion functions are considered. The transient processes occurring in the concentration jump in the region of response to one cation and with partial or complete transition to response to another cation are classified. The transition phenomena are described on the basis of the thermodynamics of ion exchange and diffusion kinetics in the liquid and solid phases. The influence of ion-exchange processes in the surface layers of glasses and at the interface with the solution on the dynamics of the glass electrode potential is considered. The bibliography includes 90 references.

CONTENTS

I. Introduction 920
II. Dynamics of the potential in the region of response to one cation 921
III. Transition from response to one cation to response to another 925
IV. Conclusion 930

I. INTRODUCTION

Ionometry—potentiometry using ion-selective membrane electrodes (ISE) of different types and designed for different purposes—has been developing vigorously during the last decade. Numerous monographs, collections of papers, and reviews dealing with the development, principles of operation, and applications of ISE have been published; a specialist journal began publication in 1979.[1] However, in this stream of information there has been a surprisingly small proportion of studies devoted to the dynamic properties of ion-selective electrodes. This was already noted in the first theoretical review of the dynamics of the ISE potential[2]. Since then the position has altered somewhat; at any rate, among the characteristics of ISE mention is now always made of the time when they attain a stationary potential.

The study of the dynamics of the potential of ISE is important primarily for their practical applications as devices whereby processes can be monitored potentiometrically and regulated. In industrial apparatus and in research carried out using ISE it is necessary that the response time of the ISE to a change in the concentration of the relevant substance is shorter than the time taken to complete the given process with participation of this substance. The response time of ISE is influenced by a multiplicity of factors: the nature of the membrane of the ISE, their design, the hydrodynamic and temperature conditions of the experiment, the concentration and qualitative composition of the solution, etc. The knowledge of the quantitative relation between these factors and the ISE response time determines the correct employment of such electrodes.

The present review deals mainly with theoretical aspects of the problem. A thermodynamic theory of the membrane potential of ISE with membranes of glass or other ion-exchange materials has now been established. According to this theory, the stationary membrane potential consists of interfacial (Donnan) potential jumps on either side of the membrane and the diffusion potential within the membrane phase, determined by the opposed streams of ions involved in the exchange and by the difference between their mobilities ($\bar{u}$). The equilibrium mobilities, more precisely their functions such as the transport numbers $\bar{t}_i$ and their ratios, enter into important characteristics of the electrode function such as the slope[3] of the relation between E and the logarithm of the ionic activity:

$$dE/d\ln a_i = \bar{t}_i RT/F, \quad (1)$$

the potential coefficient of the selectivity of the function in the system of ions I^+ and J^+:

$$K_{ij}^{pot} = K_{ij}\bar{u}_j/\bar{u}_i, \quad (2)$$

and Nikol'skii's fundamental equation of the thermodynamic ion-exchange theory of ISE[4]:

$$\varphi = \varphi^0 + \frac{RT}{F}\ln(a_i + K_{ij}^{pot}a_j). \quad (3)$$

Here ϕ is the electrode potential, ϕ^0 the standard potential, E the e.m.f. of the galvanic cell, a_i and a_j are the activities of the ions I^+ and J^+ in solution, $\bar{u}_i$ and $\bar{u}_j$ their mobilities in the glass, K_{ij} is the ion exchange constant (the energy factor), $\bar{u}_j/\bar{u}_i$ the migration factor, R the gas constant, T the absolute temperature, and F the Faraday.

Information about the migration factor cannot be obtained from the potentiometric experiments alone. For this purpose, additional experiments are required, particularly the study of the fluxes of ions entering and leaving, the kinetics of the attainment of a steady potential, etc. It is not clear *a priori* whether the ionic mobilities in the surface layers of the glass, altered by the interaction with solutions, are the same as for the unchanged glass. In kinetic experiments components of the potential which disappear in the stationary state may be manifested.

For various reasons, the present review will be confined to glass electrodes (GE) of different kinds and designed for different purposes. Firstly, GE, particularly those for potentiometric pH titrations, are the most widely used ISE in both laboratory practice and for industrial monitoring and regulation. Secondly, the equilibrium (stationary) properties of GE have been most thoroughly investigated. Thirdly, the theory of the stationary electrode behaviour of Ge has been most thoroughly developed and in this respect GE can serve as a kind of model for other ISE, at least those with an ion-exchange membrane. It has been suggested that the kinetic concepts developed for GE can also be partly extended to other ISE and conversely.

The results of the study of the dynamic properties of GE will be considered mainly from the standpoint of the mechanism of their action under particular experimental conditions. Attention has been concentrated on the electrochemical method of concentration jumps[5] as one which is most consistent with, on the one hand, the high-resistance system investigated and, on the other hand, with the usual conditions under which GE

are employed. If necessary, results (hitherto few but nevertheless significant) obtained by other electrochemical methods, involving the passage of a current through a GE from an external source, are invoked for the purpose of explanation.

The term transient processes will be given to the variation with time of the potential on passing from one stationary potential level to another. In the literature the term transient phenomena is sometimes understood as the non-monotonic variation of the potential during this period, but we shall employ it in its wider significance. As regards the classification of transient processes, the following can be distinguished for GE: (1) when the concentration of the solution is altered in the region of a stationary electrode function with respect to the given cation; (2) in the region of transition from the response with respect to one cation to the response with respect to another; (3) in the region of "acid deviations" associated with the influence of the anion on the cationic function; (4) when the solvent is altered and in non-aqueous solvents.

With few exceptions, the last two cases will not be considered in the present review. The consideration of the third case would require too much space; the available data are very contradictory, although there is no doubt that the potential varies rapidly with time in the region of the acid error (see, for example, Bates[6]). In the fourth case there is also a possibility of the observation of transient phenomena (see, for example, Ivanovskaya[7]), but, so far as the present author is aware, specific kinetic studies on the influence of the change of the solvent have not been carried out.

The principal aim of the present review is to survey the available data on the dynamics of the attainment of a steady potential of GE under various conditions and the results of attempts at a quantitative description of the transient phenomena and their theoretical treatment.

II. DYNAMICS OF THE POTENTIAL IN THE REGION OF RESPONSE TO ONE CATION

1. Experimental Results

Table 1 presents the results referring to the H^+ function of GE for potentiometric pH titrations and Table 2 deals with the dynamics of GE in the region of response to different metal ions. By virtue of specific features, the causes of which will become clear subsequently, the initial columns in Tables 1 and 2 differ somewhat. In Table 1 only H^+ is the potential-determining ion and it is not indicated. The preparation of GE, i.e. preliminary soaking in any one solution whose composition is in the region of the H^+ function, is important only for experimental, but not industrial, pH titration glasses and, if necessary, this will be mentioned in the text. The metal ion function of GE made of any glass and their dynamic properties are influenced significantly by the preliminary treatment and a separate column is provided for its characteristics in Table 2.

All the results for the H^+ function have been obtained under the conditions of special dynamic experiments with the fastest possible concentration jump. The authors of earlier

Table 1. Dynamics of the potentials of glass electrodes in the region of their H^+ function.

No.	Glass*	Solutions	Duration of concn jump, s	Response time or τ, s (20–25 °C)	Remarks	Refs.
1	NaCa-21$_4$06$_2$	buffer solution at pH > 1	$3\cdot10^{-3}$	$(3\div120)\cdot10^{-3}$; $\tau=3\cdot10^{-3}$	thickness of membrane 5–10 μm	8
2	lithium glass Electrofact 6C28		<1	$\tau_1=1.3$; $\tau_2=15$	flow rate 6 cm s^{-1}	9
3	NaCa-21$_4$06$_2$; general purpose lithium glass	acids in aqueous or aqueous organic solutions	—	—	classification of types of kinetic curves; extrapolation to $t=0$	10, 11
4	general purpose lithium glass	standard buffer solutions at pH 1–14, aqueous and non-aqueous	≪1	$t_{0.5}=0.25$ (aq.) $t_{0.5}=50$—200 (non-aq.)	response time in aqueous solutions shorter than the time of replacement of solutions	12
5	LiCsLa (HHT) type ESL-41-04	buffer solutions pH 1 ⇌ (3–10)	not indicated	$\tau=23$; τ from 13 to 38; $\tau=62$ (pH 9→1); $\tau=144$ (pH 1→9)	in a flow cell in a non-flow cell with stirring in a non-flow cell without stirring—extrema; see text	14
6	lithium glass; Corning pH 476022; 476051. Thomas pH 4855-B15	buffer solutions	~1	$\tau=2.8$ **; $\tau=2.3$ **; $\tau=6.9$ **	in a stream; no information about solutions, flow rate, etc.	15
7	not indicated	strong acids, pH 3; alkalies, pH 11; CH_3COOH; HCl (10^{-3} N) + NaCl (0.1 N) ⇌ HCl (10^{-3} N); HCl (10^{-3} N) + $MgCl_2$ (0.1 N) ⇌ HCl (10^{-3} N)		$t_{0.8}=4$	flow rate 27–42 cm s^{-1}	16
			~1		extrema, see text	
8	HHT, Na-20	pH 2.1 ⇌ 3.05	~1	$\tau_3=0.3$ (87%); $\tau_2=6$ (13%); $\tau_3<0.3$ (>70%); $\tau_2\cong7$ (≅20%); $\tau_1\cong100$ (~10%)	exact compositions of solutions at pH 2.1 and 3.05 respectively: 0.009 N HCl + 0.001 N NaCl and 0.001 N HCl + 0.009 N NaCl	17–20
	NaAl-2010; NaAl-2704	HCl 0.1 ⇌ 0.01 N		$\tau_3=1.3$ (~50%); $\tau_2=7.1$ (~30%); $\tau_1=33$ (~20%); $\tau_3\sim1.4$ (~75%); $\tau_2\sim8$ (~15%); $\tau_1\sim45$ (~15%)	treatment of data in terms of Eqn. (13), see below. The average values of τ_i are presented for direct and reverse experiments together with approximate values of $\Delta E_i^0/\Delta E$(%)	

* The designations of the compositions of the glasses, when they are known, are based on a system which can be understood from the following examples: NaCa-21$_4$06$_2$ is a glass containing (mole %) 21.4 Na_2O, 6.2 CaO, and the rest, i.e. 72.4, SiO_2; NaAl-2704—27 Na_2O 4 Al_2O_3 and 69 SiO_2. If the quantitative composition is unknown, the known qualitative characteristics of the composition are indicated, the symbols of the elements indicating the oxides; SiO_2 is not indicated: LiAl(Li_2O–Al_2O_3–SiO_2); LiCsLa (Li_2O–Cs_2O–La_2O_3–SiO_2), etc. Sometimes commercial designations of the electrodes and glasses are given: HHT, Beckman 39 046, etc. The same designations are used in Table 2 and in the text.

** The values of τ at 300 K; the corresponding activation energies are 7, 4.3 and 2.2 kcal mol^{-1}.

studies, where metal ion functions were investigated, were interested in the GE dynamics only incidentally and attention was concentrated on the stationary potentials. Nevertheless useful kinetic observations, summarised in Table 2, were made in such studies.

The principal factor for subsequent analysis is the relation between the time of the concentration jump and the time of the electrode response. The latter is expressed either by the degree of completion of the transient process between one stationary potential level and another ($t_{0.5}$, $t_{0.8}$, $t_{0.95}$) or simply by the time t when the process is believed to have been completed.

The majority of the potential–time curves in the region of variable concentrations under consideration are characterised by a monotonic exponential relation for which the following empirical expression will be adopted[2]:

$$E_t = E_1 + (E_2 - E_1)[1 - \exp(-Kt)], \quad (4)$$

where E_t is the e.m.f. at time t, E_1 and E_2 are the stationary e.m.f.'s in solutions *1* and *2*, and K is a constant. Henceforth, we shall use also the abbreviated formulation

$$\Delta E_t = \Delta E^0[1 - \exp(-t/\tau)], \quad (5)$$

where $\Delta E_t = E_t - E_1$, $\Delta E^0 = E_2 - E_1$, and $\tau = 1/K$.

The quantity τ is a convenient characteristic of an exponential transient process: $\tau \cong t_{0.63}$; $2\tau \cong t_{0.83}$; $3\tau \cong t_{0.95}$; $5\tau \cong t_{0.99}$. In certain cases the exponential approximation is satisfactory, while in others it is too inexact. Sometimes the process is described by the sum of several exponential relations[2,17–20] or other functions of time[2]. If the response times in Tables 1 and 2 are characterised by the quantity τ without further comment, the implication is that the exponential approximation is regarded as satisfactory.

Consideration of the "time of jump" and "response time" columns in Tables 1 and 2 leads to the conclusion that, in response to the concentration jump occurring over a period of

Table 2. Dynamics of the potentials of glass electrodes in the region of metal cation functions.

No.	Ion	Glass	Preparation of electrodes	Concn. range (–) or jump (⇌), equiv. litre^{-1}	Method and time of replacement of solution	Response time, s	Remarks	Refs.
1	Na^+	NaAl-1118, NaAl-2704	0.1 *N* NaCl, several days	$1.0—10^{-4}$	transposition accompanied by washing with water	$\leqslant 60$	properties stabilised after soaking for several hours	21
2	K^+	NaAl-2704, NaAlZn-270303, KAl-2005	0.1 *N* KCl, several months	$10^{-1}—10^{-4}$	ditto	10—20	properties stabilised after soaking for a week	21–23
3	Li^+	LiAl-2310 (BH-68), NaAl-1118	0.1 *N* LiCl, several days	$10^{-1}—10^{-2}$ $10^{-1}—10^{-2}$ 1—20	» » »	$>15 \cdot 60$ $\sim 15 \cdot 60$ $<15 \cdot 60$	$S_{exp} = S_{theor} = 2.3\,RT/F$ $S_{exp} < S_{theor}$ $S_{exp} \approx S_{theor}$, flow type electrode	21–23
4	Ag^+	NaAl-1118, NaAl-2704	0.1 *N* $AgNO_3$, not less than 24 h	$10^{-1}—10^{-6}$	»	~ 60	—	21, not transl. ditto 24
5	Tl^+	KAl-2005	0.1 *N* $TlNO_3$, not less than 12 h	$10^{-1}—10^{-4}$	»	$2 \cdot 60$	—	21
6	NH_4^+	NaAlZn-270303	0.1 *N* NH_4Cl, several months	$10^{-1}—10^{-4}$	»	10—20	see remark concerning item 2	21
7	Na^+	LiAl-2310 (BH-68), LiAl (BH-104)	0.1 *N* NaCl, storage	$10^{-1} \rightleftharpoons 10^{-2}$, $10^{-3} \rightleftharpoons 10^{-4}$	transpostion	$(2—7) \cdot 60$	wiping better than washing; response time is longer in dilute solutions	25
8	Na^+, K^+, Li^+, Rb^+, Cs^+	NaAl, NaB, NaTl, NaAlP, LiAl	soaking in solution of triethanolamine hydrochloride; pH 7.8	$0 \rightarrow 10^{-4} \rightarrow 10^{-3} \rightarrow 10^{-2} \rightarrow 10^{-1} \rightarrow 1.0$	transposition	$(5—60) \cdot 60$	"unprepared" electrodes, see text	26
9	Na^+, K^+	NaAl-2704 (Beckman 39137)	not indicated	$0 \rightleftharpoons 0.05 \rightleftharpoons 0.5 \rightleftharpoons 1.0$	immersion or dilution; 1.5 s	1.5—3.1		27
10	Na^+	NaAl-2704 (Beckman 39047) LiAl (Beckman 39046)	0.1 *N* NaCl, at least 24 h	$0.05 \rightarrow 0.01$	turbulent stream, 4.5×10^{-3} s	$\tau = 12.2 \cdot 10^{-3}$; $\tau = 27 \cdot 10^{-3}$	our calculation: pure RC-effect	28
11	Na^+, Li^+, Ag^+, NH_4^+, K^+	NaAl-2704 (Beckman 39047)	0.1 *N* M+, at least 24 h	$0.05 \rightarrow 0.01$	ditto	$t_{0.8} = 10 \cdot 10^{-3}$; $t_{0.9} = 0.2$	—	28
12	Na^+, Li^+, Ag^+	LiAl (Beckman, 39046)	ditto	ditto	»	—	pure RC-effect	28
13	K^+, NH_4^+	ditto	ditto	$0.05 \rightarrow 0.01$; $0.05 \rightarrow 0.1$	turbulent stream, 4.5×10^{-3} s	$\lg[(E_{eq} - E_t)/E_{eq}]$ varies linearly with $t^{1/2}$ during a period up to 2 min	—	28
14	Na^+	NaAl-2704, NaAl-2010 LiAl-1608	0.1 *N* NaCl, six days	$0.1 \rightleftarrows 0.01$	1 s	$\overrightarrow{\tau_3} = 0.6$ (100%); $\overleftarrow{\tau_3} = 0.4$ (100%); $t_{0.95} = 6$	calculation by Eqn.(13)	19, 20
15	K^+	NaAl-2704 NaAl-2010	0.1 *N* KCl, six days	ditto	1 s	$\overrightarrow{\tau_3} = 0.6$; $\overrightarrow{\tau_3} = 5.7$; $\overleftarrow{\tau_3} = 0.6$; $\overleftarrow{\tau_3} = 2.7$; $\overrightarrow{\tau_3} = 0.5$ (100%); $\overleftarrow{\tau_3} = 0.7$; $\overleftarrow{\tau_3} = 11$	calculation by Eqn.(13)	19, 20

approximately 1 s, the transient process in the region of the H^+ and M^+ functions is completed during a period less than 10 s; when the solution is changed (over a period of the order of milliseconds with the aid of special devices) the response time is also of the order of milliseconds. The latter result is of fundamental importance both for the characterisation of the electrode and for the understanding of the essential features of the processes controlling the dynamics of the attainment of a steady potential. We shall consider this in greater detail.

It is highly likely that the arrest of the establishment of a steady potential after the concentration jump achieved[8,28] over a period of several milliseconds is caused by the charging of a capacitance C through an ohmic resistance R: $\tau = RC$. It has been shown in at least one study[28] that, after an "instantaneous" change in the Na^+ concentration from 0.05 to 0.01 M, the $\Delta E_t - t$ curves for Beckman 39 047 and 39 046 glass electrodes (NaAl-2704 and LiAl respectively) resemble the curves after the "instantaneous" application of an $(RT/F) \ln (0.05/0.01) = 38$ mV potential pulse. The $\Delta E_t - t$ curves are different for each electrode (in conformity with the difference between the ohmic resistances).

For the same types of glasses (but for larger GE), $\tau = 1.8$ and 4.3 ms at 25 °C have been measured[29] (see also Lakshminarayanaiah[13]); hence the capacitances for the corresponding R were found to be 40 and 32 nF cm^{-2} respectively. For a tenfold difference between the values of R the values of τ were found to differ[28,29] approximately by a factor of two (12.2 and 27 ms—see Table 2). It may be that the values of τ include a contribution from an electrochemical transient process.

It has been found[30] that after a stepwise (after a period of approximately 10 μs) change in the potential of a GE of NaAl-2704 glass in NaCl solutions the relaxation process is completed in approximately 10 ms, which led to the conclusion that the standard exchange current density for the transient process $Na^+(glass) \rightleftharpoons Na^+(soln)$ is greater than 2×10^{-6} A cm^{-2}. All these facts permit the conclusion that the relaxation time for the transient processes $H^+(glass) \rightleftharpoons H^+(soln)$ and $Na^+(glass) \rightleftharpoons Na^+(soln)$ for GE subjected to an appropriate preliminary treatment is of the order of milliseconds or less.

It is seen from the data in Tables 1 and 2 that, for a slower change of solution, over a period of approximately 1 s, the GE response time is also approximately 1 s or (frequently) longer. One should note that in those cases where it was possible to observe processes completed in milliseconds after the change of solution, investigators did not follow the subsequent variation of the potential. Conversely, in observations on processes lasting seconds and minutes, we find that the millisecond process has already been completed and one can only conclude that the two groups of processes may have different mechanisms. Two groups of theories, devoted to the kinetics of glass and in general ion-selective electrodes, correspond to the two groups of processes and their characteristics.

2. Theoretical Treatment

The theories of the first group are based on the hypothesis of an energy barrier which must be overcome by ions in order to pass from solution to the glass and conversely[12,31] (for a description of the results of Johansson and Norberg[12], see Lakshminarayanaiah[13]). The theories of the transient overvoltage are analogous to this approach in electrochemical kinetics[32]. In theories of the second group the diffusion processes in the solution and in the glass (diffusion kinetics) are considered to be the cause of the slow attainment of the GE potential. Both groups of theories have been considered by Shatkay[2] and we shall confine ourselves to a brief description of the conclusions of earlier studies and a more detailed consideration of later investigations, which have not been included in the earlier review[2].

It may be expected, in confirmity with experimental data (Tables 1 and 2), that the efforts of theoreticians should be directed to the explanation of the exponential $\Delta E_t - t$ relation. Indeed, when a number of more or less well-founded assumptions are made, both groups of theories lead to equations of type (4) or (5). Judging from Shatkay's review[2], a particularly large number of assumptions, simplifications, and simple errors have been made by Rechnitz and Hameka[31]; fewer were made in Johansson and Norberg's study[12]. The physical significance of the parameter K in Eqn.(4) is difficult to interpret in this approach and its numerical value is difficult to predict.

As a result, in order to confirm the relation of type (4) which they obtained, Rechnitz and Hameka[31], for example, used the results of a study[26] of the dynamics of the attainment of the K^+ function of GE made from glasses based on the $Na_2O-Al_2O_3-SiO_2$ systems not subjected to an adequate preliminary treatment, as a result of which the attainment of a steady potential took tens of minutes. The same data have been used[2] for the correlation analysis of the applicability of Eqn.(4) and others. Johansson and Norberg[12] used their own data, obtained in aqueous and non-aqueous solutions (Table 1), to test this equation. They used $t_{0.5}$ as a characteristic of the time; this quantity proved to be three times greater for non-aqueous solutions than for aqueous solutions. The time $t_{0.5}$ which they found[12] for the GE response in aqueous solutions is closer to that found by Disteche and Dubuisson[8] and Rechnitz and Kugler[28] and also by Buck and Krull[29] and Kiprianov et al.[30] for the relaxation of electrical impulses. According to Buck's classification[33-35], this is the relaxation time of the space charge in the conducting system.

The second group of theories is based on the ideas of diffusion kinetics. It is assumed that the diffusion of ions to the exchange site in the glass takes place slowly with a coefficient D, via a diffusion layer of the solution with a thickness δ, which retards the attainment of a steady potential, while the attainment of ion-exchange equilibrium at the glass-solution interface (including the exchange of identical ions) is much faster. The Nernst equation holds at any instant t in the following form:

$$\varphi_t = \varphi^0 + \frac{RT}{F} \ln \frac{c_{k,t}}{\bar{c}_k}, \qquad (6)$$

where ϕ_t is the potential at the interface, ϕ^0 its standard value, $c_{k,t}$ the concentration of the potential-determining k^{th} ion in solution in the immediate vicinity of the exchange site, and $\bar{c}_k$ its concentration in the solid phase, which is constant under the conditions of the k^{th} function of the GE. Thus the determination of the $\phi_{k,t} - t$ or the $\Delta E_t - t$ relation reduces to determining the $c_{k,t} - t$ relation.

The latter is obtained as a solution of the differential equation of Fick's Second Law in the following form, for example [15]:

$$c_t = c_1 + (c_2 - c_1) \left\{ 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp \left[-\frac{\pi^2}{4} \frac{D}{\delta^2} (2n+1)^2 t \right] \right., \qquad (7)$$

where c_1 and c_2 are the concentrations in solutions *1* and *2* and the subscript k has been omitted.

The expansion is usually restricted to the first term of the series ($n = 0$), whereupon we obtain for the potential:

$$\varphi_t \approx \varphi_1 + \frac{RT}{F} \ln \left\{ 1 + \frac{c_2 - c_1}{c_1} \left[1 - \frac{4}{\pi} \exp (-t/\tau) \right] \right\}, \qquad (8)$$

where

$$\tau = \frac{4}{\pi^2}\frac{\delta^2}{D} \simeq \frac{\delta^2}{2.5D} \quad (8a)$$

Morf et al.[36] obtained the equation for ϕ_t in a somewhat different form:

$$\varphi_t = \varphi_2 + \frac{RT}{F}\ln\left[1 - \frac{c_2 - c_1}{c_2}\exp(-t/\tau)\right], \quad (9)$$

where

$$\tau = \delta^2/2D. \quad (9a)$$

Buck[35] formulated both equations [(8) and (9)] in the form usually employed in electrochemical literature:

$$\varphi_t = \varphi_1 + \frac{1}{f}\ln\left\{\exp(f\Delta\varphi) - \frac{4}{\pi}[\exp(f\Delta\varphi) - 1]\exp(-t/\tau)\right\} = \varphi_2 + \frac{1}{f}\ln\left\{1 - \frac{4}{\pi}[1 - \exp(-f\Delta\varphi)]\exp(-t/\tau)\right\}, \quad (10)$$

where $f = F/RT$, τ is defined by Eqn.(8a), and $\Delta\phi = \phi_2 - \phi_1$. In further simplifications of Eqns.(8) and (9) it is assumed that the concentration jump $\Delta c = c_2 - c_1$ and the corresponding potential jump $\Delta\phi$ are small, whereupon exponential equations are obtained, for example:

$$\varphi_t = \varphi_1 + \frac{RT}{F}\frac{\Delta c}{c_1}\left[1 - \frac{4}{\pi}\exp\left(-\frac{t}{\tau}\right)\right], \quad (11)$$

which can be reduced to equations of type (4) and (5) describing the $\Delta E_t - t$ relation for very short t.

The present author's calculation[20] by Eqns.(8) and (11) for specified $\tau = 1$ s and $\Delta c/c_1$ varying in the range $1 \leq |\Delta c/c_1| \leq 9$ demonstrated the following features. Firstly, the curves corresponding to an increase ($c_2 > c_1$) or decrease ($c_2 < c_1$) of concentration are markedly asymmetric, particularly for large Δc. With increase of the concentration of the ion, the curves are steeper than with its decrease. Secondly, the converse representation of Eqns.(8) and (11) on a semilogarithmic scale ($\lg \Delta E - t$) leads to linear plots passing through calculated points in the region where $t > 0.5$ s. For $t < 0.5$ s, the points deviate from the straight line; this is always the case for Eqn.(8) and for Eqn.(11) only when $|\Delta c/c_1| > 2$. Consequently extrapolation of the straight line from $t > 0.5$ s to $t = 0$ leads to a value of ϕ_1 which deviates more or less significantly from a specified value. However, it is important to note that the values of τ calculated on this basis are 1 ± 0.1 s, i.e. the "specified" value of τ is approximately maintained. From this it follows that in Eqn.(5), which we adopted previously as entirely empirical, the quantity τ can now be regarded as theoretically justified and can be calculated from Eqns.(8a) and (9a) for diffusion kinetics in the layers near the electrode.

The concept of diffusion through the electrode layer of solution (unstirred, Nernst, adhering, stagnant) as the stage which determines the retardation of the attainment of the steady potential of the GE has been used in many studies, including those quoted in Table 1.[9,15,16] The order of magnitude of the quantity τ corresponding to this process can be readily estimated using the known (for electrolyte solutions) thickness of the diffusion layer δ and the diffusion coefficient D of the binary electrolyte or the diffusion coefficient of the ion in the supporting electrolyte with the aid of the criteria defined by Eqns.(8a) or (9a). For $\delta \leq 10^{-2}$ cm and $D \cong 10^{-5}$ cm^2 s^{-1}, it is found that $\tau = 0.5$–5 s. The values of τ or τ_3 in Tables 1 and 2, for experiments where the change of solution was achieved over a period of approximately 1 s, are of the same order of magnitude, as already mentioned.

The study of Hershkovitch et al.[16], not included in Shatkay's review[2], constitutes a significant development of the above concepts. The authors regard the process as the reciprocal diffusion of ions and not as the diffusion of the electrolyte as a whole, as in the majority of previous instances. Account was also taken of the possibility of the generation or disappearance of active ions as a consequence of the reaction in the layer near the electrode. The fundamental differential equation has the following form:

$$\frac{\partial c_j}{\partial t} = D_j\frac{\partial^2 c_j}{\partial x^2} + R_j - \sum_k \frac{z_k}{z_j}(D_k - D_n)\frac{\partial}{\partial x}\left(t_j\frac{\partial c_k}{dx}\right), \quad (12)$$

where subscripts j, k, and n correspond to ions (cations and anions), z are the charges, x is the distance in the range $0 \leq x \leq \delta$, D are the diffusion coefficients, t_j is the transport number of the ion, and R_j is the rate of generation of the ion Jz_j.

For a solution of a strong binary electrolyte (acid or base), the first term is significant and the case discussed above obtains [equations of type (7) and (8)]. For solution flow rates of 27–42 cm s^{-1} in acid solutions at pH 3, the values of δ are in the range 0.014–0.016 cm and $t_{0.8}$ is up to 4 s. A satisfactory agreement has been achieved between the calculated and experimental curves. For a solution of a weak electrolyte (CH_3COOH), account is taken of R_j—in the present instance, the rate of dissociation. The experimental process is completed faster than predicted by the calculation, possibly owing to the obstacle-free penetration of electrolyte molecules through the charged component of the double layer. This can explain, in particular, the faster attainment of a steady potential in buffer solutions compared with unbuffered solutions. Finally, yet another special case was examined by Hershkovitch et al.[16]—mixed solutions of the type HCl + NaCl and HCl + $MgCl_2$. Experimental $\Delta E_t - t$ curves with extrema, due to the different mobilities of the two cations and the common anion in solution, were predicted and obtained for this case. Such extrema in the region of the H^+ function of the GE have been observed[14] in buffer solutions under unfavourable hydrodynamic conditions and in the region of metal ion functions by Friedman[22,37], Rechnitz[28,38], and Eisenman[21]. The above extrema, except that described by Mokhov and Leikvishvili[14], were usually attributed to the time-dependent sensitivity of the GE surface to one of the cations and will be considered in the next section. However, mention should be made of their possible "purely solution" origin.

Both in the study of Hershkovitch et al.[16] and in the studies quoted previously[9,15], as well as many others, the diffusion through the liquid "stagnant" layer is believed to be the main if not the only cause of the retardation of the attainment of a steady potential; for example, Hershkovitch et al.[16] did not even indicate the kind of glass used in the experiments. However, it has been noted[9] that, when an attempt is made to describe the attainment of a steady potential in later stages (for $t > 6$ s), it is found that this cannot be achieved with the aid of the exponential function (characterised by $\tau \cong 1$ s) used in the early stages and another exponential function (with $\tau \cong 15$ s) must be introduced. Markovic and Osburn[15] did not arrive at such conclusions, but in the case of one of the glasses they obtained an activation energy $E_a \cong 7$ kcal mole^{-1} for τ, which is greater than for "purely solution" diffusion. These facts necessitate the hypothesis of yet another process in the glass or at its interface with the solution. As already mentioned, the electrochemical exchange reaction is very rapid (over a period of milliseconds). It is natural to suppose that, for $\tau \cong 10$ s, we are dealing with diffusion in the solid phase.

Tables 1 and 2 present the results of a number of studies[17-20] in terms of the values of τ_i corresponding to the equation

$$\Delta E_t = \sum_{i=1}^{3} \Delta E_i^0 [1 - \exp(-t/\tau_i)], \quad (13)$$

where

$$\Delta E_i^0 = |E_{i\,t\to\infty} - E_{i,t=0}| \quad (13a)$$

is the jump in e.m.f. corresponding to the completion of the ith process;

$$\Delta E^0 = \sum_{i=1}^{3} \Delta E_i^0 \quad (13b)$$

is the overall jump in e.m.f. after the completion of all the processes. Thus $\Delta E_i^0/\Delta E^0$ is the contribution of the given process to the overall jump.

In the above studies not more than three exponential components were required to describe the dynamic GE curves with an average error of ±20% for identical GE subject to an error in the measurement of e.m.f. of 1 mV. The numbering of the exponential functions, starting from the "slowest", corresponds to the order in which the experimental curves are represented on the semilogarithmic scale. The "fastest" exponential function, characterised by $\tau_3 \leqslant 1$ s and $\Delta E_3^0/\Delta E > 50\%$ (frequently >75%) has been attributed[20] to processes involving the slow replacement of the stagnant layer of liquid near the electrode. The next exponential function ($2\text{ s} < \tau_2 < 20$ s; $10\% \leqslant \Delta E_2^0/\Delta E^0 \leqslant 30\%$) was attributed to the diffusion of acid within the pores of a thin (approximately 10^{-5} cm) surface layer of glass (see also Buck[39]). For glass Na-20, the activation energy for this process is approximately 7 kcal mole^{-1}. The quantities τ_3 and τ_2 "sense" the difference in the roughness and porosity of the GE surfaces, for example a flame-polished surface and a surface subjected to etching with an HF solution, the difference in the acid anion (HCl and H_2SO_4), and the direction of the change in the concentration of the solution.

The last exponential function ($\tau_1 \cong 100$ s with $\Delta E_1^0/\Delta E^0 \leqslant 10\%$) can be attributed, if it is manifested at all, to the mutual diffusion of the cations in the glass pores, i.e. in the solid phase; $D \leqslant 10^{-12}$ cm^{-2} s^{-1}. In many cases there are two exponential functions. For the Na^+ ion and GE made from sodium–aluminosilicate glasses, there is a single exponential function with the $\tau_3 \cong 1$ s and $\Delta E_3^0/\Delta E^0 = 100\%$. When the comments on the results of Rechnitz and Kugler[28] are considered (see Table 2), the only cause of the retardation of the GE response in this case is the diffusional change in the composition of the layer of liquid near the electrode.

As already stated in connection with Eqn.(5), the approach resulting in Eqn.(13) can be used as a purely empirical procedure[2,17-20]. The present author now believes that at least τ_3 has a theoretical justification [criteria defined by Eqns. (8a) and (9a)]; τ_2 and τ_1 can be treated by analogy. The quantities ΔE_i^0 are still empirical, although it is evident that $(RT/F)\ln(\Delta c/c_1)$ makes a large contribution to ΔE_3^0.

Attempts to derive Eqn.(13) theoretically have been described in the literature. For example, in relation to the F^--selective electrode with an LaF_3 membrane (which is sometimes regarded as an anionic analogue of GE), an equation has been derived[40] with two exponential components; however, one of these was attributed to diffusion and the other to a surface reaction. The corresponding experiment was carried out over the range 1–44 min.

Among empirical and semiempirical equations describing experimental data with a high degree of accuracy, there is a hyperbolic expression for the time variation[2,40]; in some time intervals it is more convenient to employ the dependence on $t^{1/2}$. These equations have been compiled by Buck[35].

III. TRANSITION FROM RESPONSE TO ONE CATION TO THE RESPONSE TO ANOTHER

1. Classification of Phenomena and Experimental Results

In the given case it is necessary to take into account the involvement of at least two and frequently three potential-determining cations in the electrode reaction and one of the cations can have a multiple charge.

In the previous section the response to only one cation I^+ was as a rule considered. The presence of an "interfering" ion for a specified ratio of the concentration of I^+ and J^+ did not affect the equilibrium potential of the GE in the region of its I^+ function. This section deals with the dynamics of the GE potential and with the form of the kinetic curves in cases where the presence of the cation J^+ (or J^{2+}) has the following effects: (1) does not affect the equilibrium potential in the region of the I^+ function but does affect the dynamics of its attainment[14,16,22,28,37,38,41-43]; (2) causes a deviation from the I^+ function and a transition to the "mixed" $I^+ + J^+$ function[28,38,41,43-48]; (3) causes a transition to the full J^+ function[19,21,47,49-61].

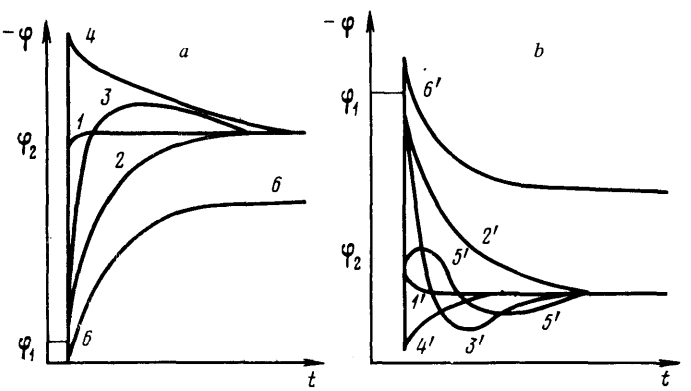


Figure 1. Schematic representation of dynamic curves for two cases: for transient processes in the region of I^+ function in the presence of J^+ or on transition to (from) the mixed $I^+ + J^+$ function: *a*) dilution with respect to I^+; *b*) concentration with respect to I^+; for transient processes with almost complete replacement of I^+ by J^+ in solution: *a*) when the stationary selectivity of the GE with respect to I^+ is higher than with respect to J^+; *b*) when the selectivity is lower. Curves 5′, 6, and 6′ refer solely to the second case—see Bobrov and Rudenko[54] and Belyustin et al,[19] respectively.

The first two cases are frequently encountered in practical applications of GE and the last is of great theoretical interest. The phenomena associated with the first two cases have been studied using pH titration GE made from lithium and sodium glasses for the pairs of ions H^+–Na^+,[14,16,41,44-48] H^+–Mg^{2+},[16] and H^+–Li^+;[45,47] series based on the increasing influence of M^+ and M^{2+}, determined from the height of the extremum on the ϕ–t curve (see Fig.1 above) have been published for GE

with metal ion functions made from NaAl-1118 [23,37,42,43,49] and NaAl-2704 [28,38] glasses for the pairs of ions Na^+–K^+, [22,37,42,49] Na^+–M^+ ($NH_4^+ < Cs^+ < Rb^+$, K^+), and Na^+–M^{2+} ($Mg^{2+} \leq Co^{2+}$, Ni^{2+}, $Zn^{2+} < Ca^{2+} < Mn^{2+} < Sr^{2+} < Cd^{2+} < Cu^{2+} < Ba^{2+} < Pb^{2+}$).

The third case—transition from the full H^+ function to the postulated M^+ function in an alkaline solution ($M^+ = Li^+$, Na^+, or K^+)—obtains in the study of GE made from glasses based on the Na_2O–CaO–SiO_2 system[47], pH titration lithium glasses[47], and the model lithium and sodium silicate glasses Li-27, LiB,[50] Na-16, Na-25,[51] and Na-20 [52–54] (the numerous studies by Bobrov and coworkers on the dynamics of the potential of GE made from non-silicate glasses are not considered here; they have been surveyed elsewhere[57,58]). For GE with a predominant response to metal ions, the transiton

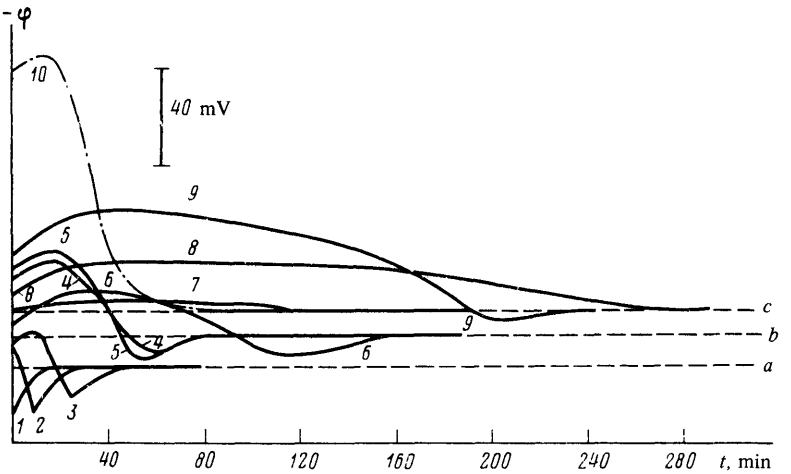


Figure 2. Dynamics of the potential of a GE of Na-20 glass in a buffer solution at pH 6,86 after treatment in a solution of the same pH and then in 1 *N* NaOH; GE subjected to a preliminary treatment for 3–4 min in a 1 : 1 HF + HCl solution at pH −0,6 *a*)–*c*) stationary potential levels corresponding to soaking for 1,2–3, and 7 days in a solution at pH 6.86 at 17–20 °C; duration of treatment (in days) in solution at pH 6,86: *1*) 0; *2*) 2/24; *3*) 5/24; *4*) and *5*) 2; *6*) 3; *7*) 10–7; duration of treatment (in days) in 1 *N* NaOH solution: *1*)–*4*), *6*), and *8*) 1; *5*) 9; *7*) 3/24; *9*) 7; *10*) 1/24 (90 °C) and 1 (17 °C). The figure has been constructed on the basis of the data of Bobrov and Rudenko[54] with the authors' permission.

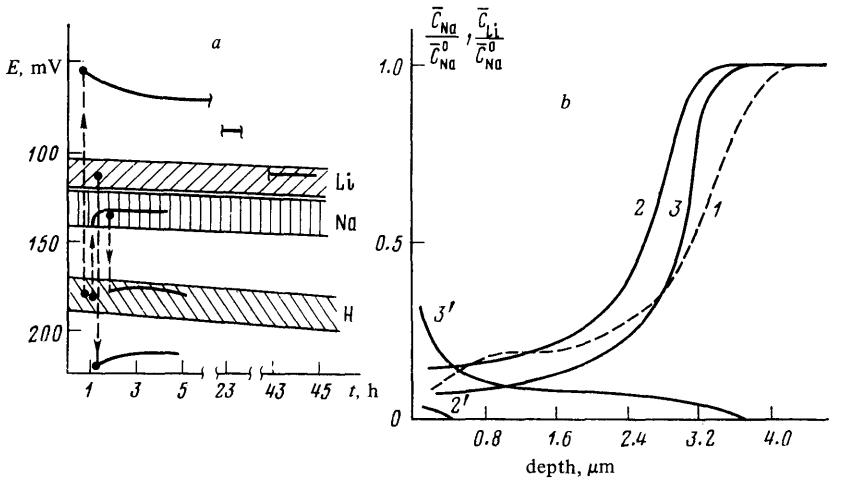


Figure 3. Dynamics of the potential of a GE of NaAl-2704 glass soaked for eight days in 0.1 *N* HCl, NaCl, or LiCl with replacement of one solution by another (*a*) and the corresponding distribution of the concentrations of Na (curves *1*–*3*) and Li (curves *2'* and *3'*) in the surface layers of the glass (*b*) after soaking the latter for 8 days in 0.1 *N* HCl and subsequent treatment in 0.1 *N* LiCl for different periods (days): *1*) 0; *2*) and *2'*) 1; *3*) and *3'*) 3. The shaded bands (representing the experimental scatter of data for a series of electrodes) correspond to stationary levels of potential obtained after prolonged soaking in 0.1 *N* HCl (H), NaCl (Na), or LiCl (Li).[59]

from the region of the H^+ function to that of the M^+ function has been studied using LiAl,[19,55] LiAlGe,[56] NaBAl, NaAl–2704, and NaAl-1118 [29] glasses. For GE of this type in neutral and alkaline solutions containing Na^+ or K^+, the transient phenomena, in which the involvement of the H^+ ion is not postulated, were studied using glasses with low (NaBAl) and high (NaAl–1118, LiAl) Na^+-specificities[19,21,59–61], and also NaAl-2704 [19,21] glass. Transitions of the type $(tris)^+ \rightleftharpoons M^+$ ($M^+ = Na^+$, Li^+, Ag^+, NH_4^+, Rb^+, Cs^+, or K^+) and $(tris)^+ \rightleftharpoons M^{2+}$, where $(tris)^+$ is the cation of the base tris(hydroxymethyl)-aminomethane and M^{2+} has the significance indicated above, have been studied using the NaAl-1118 glass.

The most characteristic observed feature of the kinetic curves considered in this section is their non-monotonic variation: there are extrema on the $\phi-t$ curves (although this is not obligatory). Fig.1 illustrates schematically the types of curves obtained experimentally in the studies mentioned above. Examples of real curves are presented in Figs.2 and 3 (see opposite).

The absolute height of the extrema reaches 60 mV in individual cases[43], although it is usually smaller. The duration of the transient processes in mixed solutions is between several seconds (in this case they can have a "solution" origin as in studies[16,28,38,43] dealing with M^{2+}, except Ba^{2+} and Pb^{2+} in Ref.43) and 30–60 s.[41–49] In the complete transition from one function to another the duration of the processes is between several minutes and tens of minutes and hours[19,21,50–56,61]. A drift continuing for days is frequently noted[31,50–58].

The principal components of the above processes are the exchange reactions

$$Li^+(glass) + I^+(soln) \rightleftharpoons I^+(glass) + L^+(soln) \qquad (14a)$$

or

$$I^+(glass) + J^+(soln) \rightleftharpoons J^+(glass) + I^+(soln) \qquad (14b)$$

(where L^+ is the "intrinsic" mobile cation of the glass), which lead to the breakdown of the constancy of the activity of the L^+ or I^+ cations in the glass ($\bar{a}_l$ or $\bar{a}_i$) which is a necessary condition for the Nernst equation to hold for the L^+ or I^+ function.

The ion-exchange process can be complicated by non-ion-exchange processes involving the hydration of the glass, its corrosion, etc., which lead to the formation of layers with a structure different from that of the bulk of the glass. Diffusion through such layers or their very formation are believed[41,43–48,50–58] to be a factor which determines the dynamics of the potential both for a response to a single ion and in the cases considered here.

2. Theoretical Treatment

The kinetic relations described for the potential can be explained in terms of the modern theory of the membrane GE potential, mentioned in the introduction[4,21] and modified by the hypothesis of surface layers differing in their structure from the bulk of the glass membrane[62].

The unmodified theory dealt with an ion-exchange membrane separating solutions, designated by single and double primes, containing cations I^+ and J^+ having the activities a_i', a_j', a_i'', and a_j'', the concentrations $\bar{c}_i$ and $\bar{c}_j$ within the membrane, and the mobilities $\bar{u}_j$ and $\bar{u}_i$. If the ratio of the ionic activity coefficients within the membrane $\bar{\gamma}_j/\bar{\gamma}_i$, the ratio of the mobilities $\bar{u}_j/\bar{u}_i$, and the activities of the ions in the solution of one side of the membrane (for example, that designated by a double prime) are assumed to be constant, then the overall membrane potential is described by an equation of type (3) [taking into account Eqn.(2)].

The possible dependence of ϕ on t subject to these limitations has been discussed[63,66] and it has been concluded that, for two ions involved in exchange and reciprocal diffusion, the relation will cease to hold after the attainment of equilibrium at the interfaces between the membrane and the solutions designated by single and double primes even when the variation of the concentration profiles within the membrane is a continuous process. The point is that for two ions, the values of $\bar{u}_j/\bar{u}_i$ and the transport numbers $\bar{t}_i$ and $\bar{t}_j$ are single-valued functions of the limiting concentrations and the independence of ϕ of t after the attainment of equilibrium is observed even for $\bar{u}_j/\bar{u}_i \neq$ const.[62,64], while the membrane phase can be non-ideal under these conditions ($\gamma_j/\gamma_i \neq$ const.). For more than two exchanging ions bearing charges of the same sign, the independence of ϕ of t can be observed only for an ideal membrane ($\bar{\gamma}_i, \bar{\gamma}_j = 1$) and subject to the conditions $\bar{u}_k/\bar{u}_1 =$ const.[64,65] (here k denotes any ion and 1 denotes the first cation).

The theory, derived for any ion-exchange membrane, has been extended to a glass membrane with modified surface layers and a fixed thickness in which current is transported by a single cation L^+. All the changes in the surface layers were reduced to ion exchange despite the fact that the occurrence of stresses[64] and hydration (solvation), hydrolytic, silanol group condensation, etc. reactions in such membranes have been known for a long time. Furthermore, all these reactions can lead to the breakdown of the above conditions ensuring the independence of ϕ from t as a result of a change in the structure of the membrane as a function of time and space.

Savage and Isard[26] pointed to hydration as a possible cause of the time variation of the GE potential. Shul'ts and Ivanovskaya[7,67] considered the influence of non-aqueous solvents on the GE potential and its dynamics. Isard[62] took into account the available experimental data for the structure and properties of the surface layers of glasses[68–72] (the present author could add to these the data in Refs.18, 46 to 48, 73–83, etc.), and linked them to the observations made on the dynamics of the GE potential (a number of studies of are quoted[21,26,41]). He arrived at an important conclusion: if the surface hydrated (leached) layer of glass is homogeneous and there are no concentration gradients (there is no diffusion potential), then equilibrium is established between the surface layer, the solution, and the bulk of the glass and the final potential has the value that it would have if there were no surface layer. The same conclusion was arrived at by Shul'ts[84] as early as 1960, which served as a basis for a number of studies in which a relation was found between the chemical composition of the initial glass and its electrode properties[85–87].

When the solution is changed rapidly, concentration gradients may arise in the outer part of the surface layer of the glass and an "external diffusion" potential can be established (the same diffusion potential for the outer layer has also been reported by Baucke[83]). These gradients are gradually "dissipated" and new concentration levels are established throughout the leached layer up to the inner gradient layer, where the "internal" potential acquires a new value. A similar explanation has been given by Hozumi and Akimoto[43].

The above considerations are largely qualitative. A quantitative treatment of the dynamics of the GE potential on transiton from one function to another has been given by Morf[66] on the basis of the Doremus[64] two-layer model of the glass membrane. Doremus considered a glass membrane consisting of two homogeneous components I and II with different ratios $(\bar{u}_j/\bar{u}_i)^I$ and $(\bar{u}_j/\bar{u}_i)^{II}$ and exchange constants K_{ij}^I and K_{ij}^{II} at the interfaces with the solutions designated by

single and double primes respectively in equilibrium with this membrane. He obtained the following expression for the overall membrane potential:

$$\varphi = \frac{RT}{F}\left[\ln\frac{a_i' + K_{ij}^{I}(\bar{u}_j/\bar{u}_i)^{I}a_j'}{a_i'' + K_{ij}^{II}(\bar{u}_j/\bar{u}_i)^{II}a_j''} + \ln\frac{\bar{c}_i^{I,II} + \frac{K_{ij}^{II}}{K_{ij}^{I}}\left(\frac{\bar{u}_j}{\bar{u}_i}\right)^{II}\bar{c}_j^{I,II}}{\bar{c}_i^{I,II} + \left(\frac{\bar{u}_j}{\bar{u}_i}\right)^{I}\bar{c}_j^{I,II}}\right], \quad (15)$$

where $\bar{c}_i^{I,II}$ and $\bar{c}_j^{I,II}$ are the concentrations of ions in the immediate vicinity of the inner interface between components I and II on the side of I. The ratio K_{ij}^{II}/K_{ij}^{I} reflects the difference between the standard chemical potentials of the ions in I and II. At this interface there is an interfacial potential jump. In the derivation of Eqn.(15) the same assumptions were made as in the derivation of Eqn.(3) but separately for each component I and II.

If $(\bar{u}_j/\bar{u}_i)^{I}K_{ij}^{I} = (\bar{u}_j/\bar{u}_i)^{II}K_{ij}^{II}$ and phases I and II are ideal, then, for an initially homogeneous membrane, we obtain $\phi \neq \phi(t)$ following the attainment of equilibrium at the interfaces. If the phases are non-ideal, then the maintenance of such independence requires that the activity coefficients in different phases should be identical functions of concentration [identical values of the "thermodynamic factor" n in the equality $(\bar{u}_j/\bar{u}_i)^{I}(K_{ij}^{I})^{1/n} = (\bar{u}_j/\bar{u}_i)^{II}(K_{ij}^{II})^{1/n}$]. If this is not so, then $\phi = \phi(t)$ when the concentration changes at the inner interface.

Suppose that component I is a hydrated surface layer of the glass in the I^+-form and component II is the bulk of the glass. When the membrane is immersed in a solution designated by a single prime, containing J^+, the J^+ ions will begin to diffuse through I to II, but $\phi = \text{const.}$ as long as the diffusion occurs within I. When J^+ reaches the inner interface between I and II at a sufficient concentration, the potential will begin to change and will vary with time until the attainment of equilibrium at this interface.

Morf[66] adopted Eqn.(15) as the initial expression. The inner solution (designated by a double prime) is constant; then, omitting the single prime, we obtain from Eqn.(15):

$$\varphi = \varphi^0 + \frac{RT}{F}\ln\left[a_i + K_{ij}^{I}\left(\frac{\bar{u}_j}{\bar{u}_i}\right)^{I}a_j\right] + \frac{RT}{F}\ln\left\{\left[\bar{c}_i^{I,II} + \frac{K_{ij}^{II}}{K_{ij}^{I}}\left(\frac{\bar{u}_j}{\bar{u}_i}\right)^{II}\bar{c}_j^{I,II}\right]\Big/\left[\bar{c}_i^{I,II} + \left(\frac{\bar{u}_j}{\bar{u}_i}\right)^{I}\bar{c}_j^{I,II}\right]\right\}. \quad (16)$$

Morf retained the assumptions adopted by Doremus and added the following ones: (a) the diffusion of ions through I is slower than the attainment of equilibrium on the outer interface but faster than the diffusion in II; (b) the overall concentration of cations in the surface layer I is constant: $\bar{c}_i^{I} + \bar{c}_j^{I} = c^{OI} = \text{const.}$; (c) $\bar{u}_i^{I} = \bar{u}_j^{I} = \bar{u}^{I}$. The latter assumption greatly reduces the generality of the derivation, but cannot be avoided. It implies in fact that the diffusion potential in the surface layer is assumed to be zero and all the changes in the potential as a function of time are attributed to the change of the interfacial potential at the inner interface—a procedure used in a number of studies[2,15,39].

The solution of the diffusional equation for the concentration at this interface $\bar{c}_i^{I}$ at any instant is found in the form

$$\bar{c}_i^{I} = \bar{c}_{1,i}^{I} + (\bar{c}_{2,i}^{I} - \bar{c}_{1,i}^{I})\,f(t), \quad (17)$$

where $f(t) = 0$ when $t = 0$ and $f(t) = 1$ when $t \to \infty$. Here $\bar{c}_{1,i}$ and $\bar{c}_{2,i}$ are the initial and final concentratons corresponding to equilibrium with solutions *1* and *2*, where the ionic activities are $a_{1,i}$, $a_{1,j}$ and $a_{2,i}$, $a_{2,j}$. The form of $f(t)$ is determined by an equation of type (7) containing a parameter τ defined by an equation of type (8a).

For the case under consideration, the general equation of the ϕ–t relation is as follows [we now go over to Morf's notation for I and II: I = s (surface) and II = m (membrane)]:

$$\varphi = \varphi^0 + \frac{RT}{F}\ln[a_{1,i} + K_{ij}^{pot}(m)\,a_{1,i}] + \frac{RT}{F}\ln\left[\frac{a_{2,i} + K_{ij}^{pot}(m)\,a_{2,i}}{a_{1,i} + K_{ij}^{pot}(m)\,a_{1,i}}f(t) + \frac{a_{2,i} + K_{ij}(s)\,a_{2,i}}{a_{1,i} + K_{ij}(s)\,a_{1,i}}[1 - f(t)]\right]. \quad (18)$$

Here K_{ij}^{pot} and K_{ij} have the same signficance as in Eqn.(2). Analysis of Eqn.(18) shows that, for $t < 0$, the equilibrium potential is specified by the initial solution ($a_{1,i}$, $a_{1,j}$) and by the properties of the bulk of the membrane; for $t = 0$ (the instant of the completion of the change of solution), the response of the surface itself to the change in activities is added to this; when $t \to \infty$, a potential determined by the properties of the final solution and the bulk of the membrane is established.

For intermediate values of t, Eqn.(18) predict curves of the following type when $a_j = a_{1,j} = \text{const.}$ and a_i is variable (Fig.1):

(a) Curves *1* and *1'* when the surface and the bulk of the glass are selective with respect to I:

$$K_{ij}^{pot}(m) \ll 1,\ K_{ij}(s) \ll 1;$$

(b) Curves *2* and *2'* when the surface is selective with respect to J^+ and the bulk of the glass is selective with respect to I^+:

$$K_{ij}^{pot}(m) \ll 1,\ K_{ij}(s) \gg 1;$$

(c) Curves *3* and *3'* or *4* and *4'* when the surface is selective with respect to I^+ and the bulk of the glass is selective with respect to J^+:

$$K_{ij}^{pot}(m) \gg 1,\ K_{ij}(s) \ll 1^{66}.$$

Eqn.(15) also has a number of corollaries which are important for the understanding of properties of GE such as the asymmetric potential, the specific solvent effect, and other phenomena associated with the variation of the standard potential ϕ^0 and its drift (without affecting the Nernst function). To make the system concrete, we shall put $I^+ = H^+$ and $J^+ = Na^+$ in Eqn.(15); suppose that the existence of regions I and II reflects the asymmetry of the properties of the glass membrane arising either in the preparation of the GE or as a result of the action of solutions designated by single and double primes on each side. The asymmetry is manifested in the potential, as long as one of the components (I and II) has not been "worked through" and as long as equilibrium is not established at the inner interface between I and II. We shall assume that phase I consists of the entire modified surface layer of glass in contact with the solution designated by a single prime and phase II is the bulk of the membrane and the modified surface layer on the other side. Then $\bar{c}_H^{I,II} = 0$ and we have from Eqn.(15)

$$\varphi = \frac{RT}{F}\ln\frac{a_H' + K_{HNa}^{I}(\bar{u}_{Na}/\bar{u}_H)^{I}a_{Na}'}{a_H'' + K_{HNa}^{II}(\bar{u}_{Na}/\bar{u}_H)^{II}a_{Na}''} + \frac{RT}{F}\ln\frac{K_{HNa}^{II}(\bar{u}_{Na}/\bar{u}_H)^{II}}{K_{HNa}^{I}(\bar{u}_{Na}/\bar{u}_H)^{I}}. \quad (19)$$

This equation was first derived[7,67] to account for the specific influence of the non-aqueous solvent on the GE potential and has been used[88,89] to describe the asymmetric GE potential (ϕ_{as}). Indeed, in the region of the H^+ function, when $a'_H \gg K_{HNa}^{I}(\bar{u}_{Na}/\bar{u}_H)^{I}a'_{Na}$, $a''_H \gg K_{HNa}^{II}(\bar{u}_{Na}/\bar{u}_H)^{II}a''_{Na}$, and $a'_H = a''_H$, we have

$$\varphi_{as,H} = \frac{RT}{F}\ln\frac{K_{HNa}^{II}(\bar{u}_{Na}/\bar{u}_H)^{II}}{K_{HNa}^{I}(\bar{u}_{Na}/\bar{u}_H)^{I}}. \quad (19a)$$

In the region of the Na^+ function, the opposite inequalities hold, and when $a'_{Na} = a''_{Na}$, we have

$$\varphi_{as,\,Na} = 0. \qquad (19b)$$

We shall extend the approach developed in relation to a one-sided leached layer in a number of studies[62,64,66] and others, to a real leached layer having for a number of reasons an inhomogeneous structure (we assume, as before, that $I^+ = H^+$ and $J^+ = Na^+$). This inhomogeneity is modelled by a sequence of n layers differing in the values of $(\bar{u}_{Na}/\bar{u}_H)^{(k)}$ and in the standard chemical potentials of the ions (and hence in the values of $K^{(k)}_{HNa}$ and the interfacial potential jumps; here k is the number of the layer).

If all the surface layers have been equilibrated with one another and with the solution with respect to the H^+ and Na^+ ions, then, according to Eqns.(15) and (18), the potential is determined by the equilibrium between the solution and the nth layer adjoining the bulk of the membrane and tentatively retaining its structure and properties. When the situation in solution is altered, a new equilibrium is established slowly as the reciprocal diffusion front passes the interfaces between the layers and equilibria are established at the latter. Suppose that equilibrium has been established at $k-1$ interfaces and that the concentration profile changes in the kth layer without reaching its interface with the $(k+1)$th layer. We then have an expression for the overall potential of the type of Eqns.(15) and (16):

$$\varphi^{(k)} = \varphi^0 + \frac{RT}{F}\ln\left[a_H + K^{(k)}_{HNa}(\bar{u}_{Na}/\bar{u}_H)^{(k)}a_{Na} + \frac{\bar{c}^{(k)}_H + \frac{K^{(k+1)}_{HNa}}{K^{(k)}_{HNa}}\left(\frac{\bar{u}_{Na}}{\bar{u}_H}\right)^{(k+1)}\bar{c}^{(k)}_{Na}}{\bar{c}^{(k)}_H + (\bar{u}_{Na}/\bar{u}_H)^{(k)}\bar{c}^{(k)}_{Na}}\right]. \qquad (20)$$

Suppose that for some reason [the condensation of ≡SiOH (see below) groups, the interaction with OH^-, etc.] we have $c^{(k)}_H \to 0$. We then obtain in the region of the H^+ function

$$\varphi^{(k)}_H = \varphi^0 + \frac{RT}{F}\ln\frac{K^{(k+1)}_{HNa}(\bar{u}_{Na}/\bar{u}_H)^{(k+1)}}{K^{(k)}_{HNa}(\bar{u}_{Na}/\bar{u}_H)^{(k)}} + \frac{RT}{F}\ln a_H. \qquad (20a)$$

In the region of the Na^+ function subject to the same condition, we have

$$\varphi^{(k)}_{Na} = \varphi^0 + \frac{RT}{F}\ln\left[K^{(k+1)}_{HNa}(\bar{u}_{Na}/\bar{u}_H)^{(k+1)}\right] + \frac{RT}{F}\ln a_{Na}. \qquad (20b)$$

We may note that, when there is a rapid alteration of the H^+ or Na^+ concentration in solution, the extent of the corresponding response is determined by the closeness to unity of the H^+ or Na^+ transport number in the first layer of the glass in equilibrium with the solution [see Eqn.(1)].

In Eqns.(20a) and (20b) terms which are constant under the conditions where the reciprocal diffusion front passes the kth layer are added to the potential ϕ^0. The time during which constant values of the potential are retained at the intermediate "quasi-stationary" level depends on the thickness of the layer $\delta^{(k)}$ and the reciprocal diffusion coefficient $D^{(k)}_{HNa}$. The $(k+1)$th layer is then in equilibrium with the subsequent layers and the parameters K_{HNa} and $(\bar{u}_{Na}/\bar{u}_H)$ characterising it can be replaced by the parameters of the nth layer and can be introduced into the expression for ϕ^0. We then obtain from Eqn.(20a)

$$\varphi^{(k)}_H = (\varphi^0)' - \frac{RT}{F}\ln\left[K^{(k)}_{HNa}(\bar{u}_{Na}/\bar{u}_H)^{(k)}\right] + \frac{RT}{F}\ln a_H. \qquad (21)$$

When the reciprocal diffusion front reaches the nth layer, the potential reaches a stationary level and no longer changes, provided that no structural changes take place within this layer.

Differences between the structure and properties of the layers can arise when the GE is soaked in solution, as a result of ion-exchange processes such as hydration, corrosion, hydrolysis ⇋ condensation (hydroxylation ⇋ dehydroxylation) by the reaction

$$\equiv Si{-}O{-}Si\equiv + H_2O \rightleftarrows 2 \equiv Si{-}OH, \qquad (22)$$

the sorption of acid by the outer layer from a concentrated solution, etc.

Presumably the low-temperature condensation of the ≡Si–OH groups, observed by infrared spectroscopy[74,75,77] for the surface layers of many silicate glasses after leaching with acid and leading to an increase of their chemical stability towards a number of reagents, including HF solutions[78], results simultaneously in an increase of the selectivity of the H^+ function of the GE, i.e. in a decrease of $K^{pot}_{HNa} = K_{HNa}\cdot(\bar{u}_{Na}/\bar{u}_H)$. Hydrolysis has the opposite effect. It then follows from Eqn.(22) that, on condensation in the kth layer, a $\phi^{(k)}$ potential in the region of the H^+ function should shift towards positive values and on hydrolysis the shift should be towards negative values. We shall now quote several examples.

In Wikby's study[46] glass electrodes made from $NaCa\text{-}21_4O6_2$ glass were hydrated for a long time in a 10^{-4} M NH_4HCO_3 solution at pH 7. The electrodes were then transferred to an etching solution (0.1 M HCl + 0.3% HF). A potential of approximately 340 mV was established initially and was then maintained for several tens of minutes, whereupon it changed abruptly to approximately 250 mV and then remained constant. The first, quasi-stationary level corresponds to equilibrium with the leached layer, in which considerable condensation was observed for this glass[74,75,77], and the second, stationary level corresponds to equilibrium with the internal ion-exchange layer adjoining the bulk phase.

Bobrov and coworkers[52,54] noted a shift of the stationary potential of GE made from Na-20 glass in a negative direction when the electrodes were soaked in an acid or neutral solution, which was regarded as the result of an internal increase of the alkalinity of the liquid within the pores. Consequently, under these experimental conditions, it was possible to postulate the maintenance of equilibrium with respect to H^+ ions between the solution and the internal ion-exchange layer adjoining the bulk phase. In this layer there is a possibility of the hydrolysis of the ≡Si–O–Si≡ bonds, leading to an increase of K^{pot}_{HNa}.

Even more striking negative shifts of ϕ were observed after treating the glasses in alkaline solutions (Fig.2), which leads not only to a partial dissolution of the outer layer but also to its loosening and an increase of the overall concentration of ionogenic groups in the residual layer. Then $\phi_{quasi\text{-}st} < \phi_{st}$ when the GE is transferred from alkali to an acid solution. As H^+ diffuses into the bulk phase, the change of potential is described by curve 5′ (Fig.1). The entire multiplicity of curves with extrema can be accounted for similarly (Figs.1 and 2).

We shall note separately the initial sharp extrema on curves of type 4 and 4′ (Fig.1) and also curves of type 6 and 6′. The latter were observed experimentally[19] after a rapid replacement of dilute (10^{-2}–10^{-3} M) $Na^+ \rightleftarrows K^+$ solutions for GE made of NaAl-1118, NaBAl, and LiAl-1608 glasses. Judging from the time required for their manifestation (several seconds for curves 6 and 6′ and several minutes for curves

4 and *4'*), these phenomena are associated with non-stationary processes involving the reciprocal diffusion of ions of different mobilities in the stagnant liquid layer and the adjoining porous surface layer of glass as well as the kinetics of the attainment of the interfacial concentration.

In order to describe such phenomena, it is convenient to solve beforehand Eqn.(12) for mixed solutions. It is also possible that the general causes of the type described above in relation to a porous layer of glass, differing markedly in structure and properties from deeper layers, can also operate in this instance.

For GE made of glasses with a predominately metal ion function, which do not tend to form deep leached layers[79,81], the duration of the transient processes is also small, particularly when two ions are involved, one of which is the "intrinsic" ion of the glass. Thus in GE made of NaBAl glass, soaked in NaCl solutions, the transient process after the replacement of NaCl by HCl in 1 s is completed in approximately 30 s (curves of type *2'* and *3'* in Fig.1), while in the opposite replacement the transient process lasts 2–3 min (curves of type *3* and *4*).[19] For GE made of NaAl-2704 glass, soaked in 0.1M HCl for 1,3, and 8 days, there is a transition to the Na^+ function in 0.1M NaCl in less than 1 h (curves of type *2* in Fig.1; see also Fig.3*a*). The opposite transition is faster (curves of type *2'* in Fig.1 after 1 and 3 days and of type *3'* after 8 days) and is sharper (Fig.3*a*).

Specific features have been noted in the transiton from the H^+ function to the response to an alkali metal ion which is not the intrinsic (L^+) ion of the glass: $H^+ \to Na^+$ for the LiAl glass[19]; $H^+ \to K^+$ [59] and $H^+ \to Li^+$ for the NaAl-2704 glass (Fig.3*a*). As a rule, curves of type *4* are obtained with a rapid attainment of a certain level of potential. However, in subsequent observations (after hours and days)[59] it was found that this level is quasi-stationary. After 24 h in the case of $H^+ \to K^+$ there is a transition to another layer which no longer changes; for $H^+ \to Li^+$, another quasi-stationary layer is established after 24 h and after a further 24 h a final (stationary) level is reached, which is also attained when the GE is soaked in the LiCl solution alone. At each level the K^+ or Li^+ function of the GE is manifested approximately. In both cases the potential at the stationary level is more positive than at the quasi-stationary level.

The attainment of the stationary level of potential coincides in time (approximately 40 h) with the attainment by the Li^+ ions of the internal interface between the leached layer and the bulk phase at a depth of 3 μm (Fig.3*b*). The use of these parameters for the calculation of D_{LiNa} by Eqn.(8a) leads to reasonable values $D_{LiNa} = 2.5 \times 10^{-13}$ cm^2 s^{-1}, which agree well with the values calculated from concentration profiles after treating the NaAl-2704 glass with LiCl solutions[90]. The reverse transition from the K^+ or Li^+ function to the H^+ function is also accompanied by the attainment by the potential of a more positive quasi-stationary level than the stationary level (curves of type *4'* for $Li^+ \to H^+$ in Fig.1 and of type *3'* for $K^+ \to H^+$).[59]

The relative positions of the stationary levels correspond to the series of equilibrium specifities[21] after prolonged soaking of the GE in solutions of the corresponding ions. The distribution of the quasi-stationary levels depends on the time of the observation and, for the same time, on the solution concentration[19].

When an attempt is made to explain theoretically the phenomena described, complications arise due to the involvement of three ions in the process. In this case there is no unambiguous relation between the mobility ratio or the ionic transport numbers in the glass, on the one hand, and the ionic concentrations at the interface, on the other. However, we suggest that this case can be reduced in most instances to the previous one, i.e. it is possible to neglect the contribution of the third potential-determining ion to the sum of the transport numbers at the given interface between the layers. Thus, when the mutual diffusion of metal cations in a glass with an increased Al_2O_3 content, in equilibrium with neutral or alkaline salt solutions, is considered, it is possible to neglect the contribution of H^+.[79]

On being soaked in HCl, a glass with a low Al_2O_3 content, for example, NaAl-2704, tends to form a leached layer. When the GE soaked in HCl is transferred to an LiCl solution, at the beginning of the process one can neglect the contribution of Na^+ and the quasi-stationary potential levels may be assumed to correspond to the reciprocal diffusion $H^+ \rightleftharpoons L^+$. As already mentioned, the establishment of a stationary level of potential at the end of the process corresponds to the attainment by Li^+ ions of the ion-exchange layer adjoining the bulk of the glass, where the reciprocal diffusion $Li^+ \rightleftharpoons Na^+$ is of decisive importance (Fig.3*b*).[59]

IV. CONCLUSION

On the basis of the experimental data examined and the theoretical studies, it is possible to formulate the following picture of the dynamics of the attainment of the potentials of glass electrodes after a stepwise alteration of the concentration of the potential-determining cation in aqueous solution.

1. In the region of the response by the electrode to the "intrinsic" cation of the glass or the exchange function with respect to a given cation I^+ of a "prepared" GE, it is possible to assume that the activity of this cation in the surface layer of the glass is constant and the response time is limited not by the transfer of the charge through the glass/solution interface but by both the diffusion of the electrolyte through the liquid diffusion layer arising near the GE surface and by the mutual diffusion of the ions within the pores and the walls in the outer loosened (hydrated) layer of glass (or by one of the processes indicated). The potential–time curves for the case under consideration have a complex exponential form and consist (when the accuracy of the measurements is to within 1 mV) of not more than three components with characteristic relaxation times $\tau_3 \leq 1$, $\tau_2 \cong 10$, and $\tau_1 \cong 100$ s when the duration of the concentration jump is ≤ 1 s. The contribution of the fastest process, corresponding to diffusion in the liquid layer near the electrode, to the overall change in the potential is usually greater than 50% and frequently 85–100%.

The values of τ_i are resonably predicted by the formula $\tau_i = m\delta_i^2/D_i$, where δ_i is the thickness of the diffusion layer, D_i the reciprocal diffusion coefficient, and m a multiplier ($m = 1$, 0.5, or $4/\pi^2$ in different models of the diffusion layer).

2. In the concentration jump in a mixed solution containing, apart from I^+, an "interfering" cation J^+ in the range of the ratios of the I^+ and J^+ concentrations where the constancy of the activity of I^+ ($\bar{a}_i$) in the surface layer of the glass is virtually unaffected in the stationary state, i.e. the I^+ function is retained, there is a possibility of the retardation of the attainment of a steady potential or of the presence of an extremum on the potential–time curve caused either by the reciprocal diffusion of the electrolyte ions in the diffusion layer of the liquid or by the time-dependent breakdown of the condition $\bar{a}_i = \text{const}$. in the outer surface layer of the glass (the time-dependent sensitivity of this layer to the cation J^{z+}).

3. In the concentration jump in the region of the transition from the I^+ function to the J^+ function of the GE in a mixed solution of I^+ and J^+ or in a pure solution of J^+ the dynamics of the attainment of a steady potential is determined by the low rate of the attainment of the boundary conditions in the ion-exchange reciprocal diffusion of cations in the surface layers of the glass differing in their structure from the bulk of the glass membrane. This structure is established during the preliminary preparation of the GE in a I^+ solution and is the result of non-ion-exchange corrosion, hydration, the hydrolysis of $\equiv Si-O-Si\equiv$ linkages, the condensation of $\equiv SiOH$ groups, the sorption of acid molecules in acid solutions, etc.

Against this background, the main result of the process is a decrease of $\bar{a}_i$ due to the substitution of I^+ ions by J^+ ions and an increase of $\bar{a}_j$ to a constant value. This is accompanied by a change in the phase and diffusion potentials in the glass.

When the boundary conditions are established, the overall GE potential reaches a definite level—in minutes if the native surface interacts with the new solution and a layer with the structure of the bulk phase is formed and in tens of minutes if an altered surface layer exists beforehand. In the latter case this layer can persist for a long time—hours and days (quasi-stationary potential) until the migration of the reciprocal diffusion front into the bulk of the glass results in the attainment of a layer with a different structure and properties, such as K_{ij} and $\bar{u}_j/\bar{u}_i$, i.e. until the boundary conditions change again. The potential can then change more until the attainment of another quasi-stationary level. This continues until the I^+ ions reach the internal ion-exchange diffusion layer having the structure of the bulk phase. A stationary potential level is then established. This level can vary over a very long time (days and weeks) owing to secondary corrosion, condensation, hydration, etc. processes.

At each quasi-stationary level and at the stationary level a I^+ function of the GE, close to the theoretical Nernst function, can obtain, provided that the transport number t_i in the layer in equilibrium with the solution is close to unity.

At the beginning of the process, immediately after the concentration jump, a non-monotonic variation of the potential—time (seconds, minutes) curve is frequently observed owing to the difference between the mobilities and the exchange current of the mutually diffusing ions in the boundary layer of the electrode and in the glass pores, and also as a consequence of the possible large difference between the properties of the surface layer of the glass itself, established by the preliminary treatment, and the properties of the deeper layers.

The semiquantitative theoretical description of the transient curves for the transition from one electrode function to another has been based on the hypothesis of interfaces between the glass layers mentioned above, differing in structure, the exchange constants, and ionic mobilities, and hence of potential jumps at such interfaces and of diffusion-dependent limitations within the layers. The explanation given in the literature for two homogeneous layers has been extended in this review to a large number of layers.

REFERENCES

1. "Ion-Selective Electrode Reviews, Pergamon Press, Oxford–Paris–New York–Frankfurt, 1979, Vol.1.
2. A.Shatkay, Anal.Chem., **48**, 1039 (1976).
3. M.M.Shultz, in "Ion-Selective Electrodes, Conference, Budapest, 1977", Akad.Kyado, Budapest, 1978. p.539.
4. O.K.Stefanova, M.M.Shul'ts, E.A.Materova, and B.P.Nikol'skii, Vestnik Leningrad.Gos.Univ., No.4, 93 (1963).
5. J.Kuta and E.Yeager, in "Techniques of Electrochemistry", (Edited by E.Yeadger and A.J.Salkind) (Translated into Russian), Izd.Mir, Moscow, Vol.1, p.270.
6. R.G.Bates "Electrometric pH Determinations" (Translated into Russian), Izd.Khimiya, Leningrad, 1972, p.283.
7. I.S.Ivanovskaya, Candidate's Thesis, Leningrad State University, Leningrad, 1968.
8. A.Disteche and M.Dubuisson, Rev.Sci.Instr., **25**, 869 (1954).
9. M.W.Geerlings, in "Plant and Process Dynamic Characteristics, Proc.Conf.Soc.Instr.Technol, Cambridge, 1956" (Translated into Russian), Inostr.Lit., Moscow, 1960, p.130.
10. W.H.Beck, J.Caudle, A.K.Convington, and W.F.K.Wynne-Jones, Proc.Chem.Soc., 110 (1963).
11. A.E.Bottom and A.K.Covington, J.Electroanal.Chem., **24**, 251 (1970).
12. G.Johansson and K.Norberg, J.Electroanal.Chem., **18**, 239 (1968).
13. N.Lakshminarayanaiah, "Membrane Electrodes" (Translated into Russian), Izd.Khimiya, Leningrad, 1979, p.292.
14. V.M.Mokhov and L.M.Leikviishvili, Symposium, "Doklady I Respublikanskoi Nauchno-Tekhnicheskoi Konferentsii po Metrologii, Tbilisi, 1970" (Reports at the Ist All-Republic Science and Engineering Conference on Metrology, Tbilisi, 1970), p.143.
15. P.L.Markovic and J.O.Osburn, Amer.Inst.Chem. Engineers J., **19**, 504 (1973).
16. H.Z.Hershkovitch, T.J.McAvoy, and A.I.Liapis, Canad.J.Chem.Eng., **56**, 346 (1978).
17. M.M.Shul'ts, A.A.Belyustin, I.V.Valova, I.S.Ivanovskaya, and N.V.Peshekhonova, Symposium, "Tezisy Dokladov IV Vsesoyuznogo Simpoziuma po Elektricheskim Svoistvam i Stroeniyu Stekla" (Abstracts of Reports at the IVth All-Union Symposium on the Electrical Properties and Structure of Glass), Izd. Akad.Nauk Arm.SSR, Erevan, 1977, p.173.
18. M.M.Shultz, A.A.Belijustin, V.S.Bobrov, I.M.Bushueva, and N.V.Peshekhonova, in "Proceedings of the XIth International Congress on Glass, Prague", 1977, Vol.3, p.197.
19. A.A.Belijustin, I.V.Valova, I.S.Ivanovskaja, in "Ion-Selective Electrodes, Conference, Budapest, 1977", Akad.Kyado, Budapest, 1978, p.235.
20. A.A.Belyustin and I.V.Valova, Fiz.i Khim.Stekla, **6**, No.4, 449, 456 (1980).
21. G.Eisenman, Adv.Anal.Chem.Instr., 4, 213 (1965).
22. S.M.Friedman, Meth.Biochem.Anal., **10**, 71 (1962).
23. S.M.Friedman and F.K.Bowers, Anal.Biochem., **5**, 471 (1963).
24. G.Mattock and R.Uncles, Analyst, **87**, 977 (1962).
25. G.Mattock, Analyst, **87**, 930 (1962).
26. J.A.Savage and J.O.Isard, Phys.Chem.Glasses, **3**, 147 (1962); **7**, 60 (1966).
27. G.A.Rechnitz, in "Glass Electrodes for Hydrogen and other Cations, Principles and Practice", (Edited by G.Eisenman), M.Dekker, New York, 1967, p.322.
28. G.A.Rechnitz and G.C.Kugler, Anal.Chem., **39**, 1682 (1967).
29. R.P.Buck and I.Krull, J.Electroanal.Chem., **18**, 387 (1968).

30. A.A.Kiprianov, A.M.Pisarevskii, A.A.Belyustin, V.V.Kondrat'ev, and M.M.Shul'ts, Fiz.i Khim.Stekla, **5**, 476 (1979).
31. G.A.Rechnitz and H.F.Hameka, Z.anal.Chem., **214**, 252 (1965).
32. K.Vetter, "Electrochemical Kinetics" (Translated into Russian), Izd.Khimiya, Moscow, 1967, p.136.
33. R.P.Buck, CRC Crit.Rev.Anal.Chem., **5**, 323 (1976).
34. R.P.Buck, Anal.Chem., **48**, 23R (1976).
35. R.P.Buck, in "Ion-Selective Electrodes, Conference, Budapest, 1977", Akad.Kyado, Budapest, 1978, p.21.
36. W.S.Morf, E.Linder, and W.Simon, Anal.Chem., **46**, 1596 (1975).
37. S.M.Friedman, in "Glass Electrodes for Hydrogen and other Cations. Principles and Practice", (Edited by E.Eisenman), M.Dekker, New York, 1967. p.442.
38. G.A.Rechnitz, in "Ion-Selective Electrodes" (Translated into Russian), Izd.Mir, Moscow, 1972, p.307.
39. R.P.Buck, J.Electroanal.Chem., **18**, 363 (1968).
40. R.C.Hawkins, P.Corriveau, S.A.Kushneriuk, and P.Y.Wong, Anal.Chim.Acta, **102**, 61 (1978).
41. B.Karlberg, J.Electroanl.Chem., **42**, 115 (1973).
42. S.M.Friedman, J.D.Jamieson, M.Nakashima, and C.L.Friedman, Science, **130**, 1252 (1959).
43. K.Hozumi and N.Akimoto, Bunseki Kagaku, **25**, 228 (1976).
44. B.Karlberg, J.Electroanal.Chem., **42**, 127 (1973).
45. B.Karlberg, J.Electroanal.Chem., **49**, 1 (1974).
46. B.Karlberg and A.Wikby, Acta Chem.Scand., **27**, 1885 (1973).
47. A.Wikby and B.Karlberg, Electrochim.Acta, **19**, 323 (1974).
48. A.Wikby, Electrochim Acta, **19**, 329 (1974).
49. G.Eisenman, in "Glass Microclectrodes" (Edited by M.Lavallée, O.F.Schanne, N.C.Hebert), J.Wiley, New York-London-Sydney-Toronto, 1969, p.32.
50. V.S.Bobrov, N.V.Rozhdestvenskaya, and M.M.Shul'ts, Zhur.Prikl.Khim., **48**, 1034 (1975).
51. V.S.Bobrov and L.P.Kalmykova, Zhur.Prikl.Khim., **50**, 781 (1977).
52. V.S.Bobrov and L.F.Rudenko, Zhur.Prikl.Khim., **50**, 1474 (1977).
53. V.S.Bobrov, T.A.Solov'eva, and L.F.Rudenko, Zhur.Prikl.Khim., **51**, 751 (1978).
54. V.S.Bobrov and L.F.Rudenko, Zhur.Prikl.Khim., **52**, 2493 (1979).
55. V.S.Bobrov and L.A.Matsievskaya, Zhur.Prikl. Khim., **50**, 2669 (1977).
56. V.S.Bobrov, V.V.Murashova, and M.M.Shul'ts, Zhur.Prikl.Khim., **50**, 1257 (1977).
57. V.S.Bobrov, Zhur.Prikl.Khim., **50**, 1997 (1977).
58. V.S.Bobrov, Zhur.Prikl.Khim., **51**, 2237 (1978).
59. A.A.Belyustin, M.M.Shul'ts, N.V.Peshakhonova, L.I.Ivanova, A.L.Shugalova, V.V.Mogileva, and I.S.Ivanovskaya, Dokl.Akad.Nauk SSSR, **240**, 1376 (1976).
60. A.A.Belyustin and I.V.Valova, Symposium, "Biofizika Membran" (The Biophysics of Membranes), Kaunas, 1973, p.70.
61. R.P.Buck, J.H.Boles, R.D.Porter, and J.A.Margolis, Anal.Chem., **46**, 255 (1974).
62. J.O.Isard, Phys.Chem.Glasses, **17**, 1 (1976).
63. F.Helfferich, "Ionenaustauscher" (Translated into Russian), Inostr.Lit., Moscow, 1962, p.376.
64. R.H.Doremus in "Glass Electrodes for Hydrogen and other Cations. Principles and Practice", (Edited by G.Eisenman), M.Dekker, New York, 1967, p.101.
65. G.Eisenman, in "Ion-Selective Electrodes" (Translated into Russian), Izd.Mir, Moscow, 1972, p.11.
66. W.E.Morf, Analyt.Letters, **10**, 87 (1977).
67. M.M.Shul'ts and I.S.Ivanovskaya, Electrokhimiya, **93**, 576 (1967).
68. Z.Boksay, G.Bouquet, and S.Dobos, Phys.Chem. Glasses, **8**, 140 (1967).
69. A.Wikby, J.Electroanal.Chem., **33**, 145 (1971); **38**, 429, 441 (1972); **39**, 103 (1972).
70. F.G.K.Baucke, J.Non-Cryst.Solids, **14**, 65 (1974).
71. H.Scholze, Glastechn.Ber., **35**, 105 (1962).
72. F.Steuerwald and R.Corbach, Tonind.-Ztg.keram. Rdsch., **96**, 227 (1972).
73. B.Csakvari, Z.Boksay, and G.Bouquet, Anal.Chim. Acta, **56**, 279 (1971).
74. R.Corbach, Dissertation, TU Berlin, D83, 1973, A 1217.
75. H.Scholze, D.Helmreich, and I.Bakardjiev, Glastechn. Ber., **48**, 237 (1975).
76. H.Scholze and I.Bakardjiev, Glastechn.Ber., **50**, 281 (1977).
77. H.Scholze, Fiz.i.Khim.Stekla, 2, 105 (1976).
78. I.S.Ivanovskaya, A.A.Belyustin, M.M.Shul'ts, and T.P.Vorob'eva, Fiz.i.Khim.Stekla, **1**, 156 (1975).
79. A.A.Belyustin, I.S.Ivanovskaya, M.M.Shul'ts, and T.P.Vorob'eva, Fiz.i.Khim.Stekla, **1**, 358 (1975).
80. R.H.Doremus, J.Non-Cryst.Solids, **19**, 137 (1975).
81. V.V.Mogileva, I.S.Ivanovskaya, A.A.Belyustin, and M.M.Shul'ts, Fiz.i.Khim.Stekla, **4**, 465 (1978).
82. V.V.Mogileva, I.S.Ivanovskaya, A.A.Belyustin, and M.M.Shul'ts, Fiz.i.Khim.Stekla, **4**, 473 (1978).
83. F.G.K.Baucke, in "Ion-Selective Electrodes, Conference, Budapest, 1977", Akad.Kyado, Budapest, 1978, p.215.
84. M.M.Shul'ts, Vestnik Leningrad.Gos.Univ., No.22 40 (1960).
85. M.M.Shul'ts, Vestnik Leningrad.Gos.Univ., No.4 174 (1963).
86. B.P.Nicolsky, M.M.Shultz, A.A.Belijustin, and A.A.Lev, "Glass Electrodes for Hydrogen and other Cations. Principles and Practice", (Editied by G.Eisenman), M.Dekker, New York, 1967, p.174.
87. B.P.Nikol'skii, M.M.Shul'ts, and A.A.Belyustin, Symposium, "100 Let Periodicheskogo Zakona Khimicheskikh Elementov" (100 Years of the Periodic Law of the Chemical Elements), Izd.Nauka, Moscow, 1969, p.318.
88. V.V.Dolidze, Candidate's Thesis, Kharkov State University, Kharkov, 1968.
89. V.A.Dolidze, in "Ion-Selective Electrodes, Conference, Budapest, 1977", Akad.Kyado, Budapest, 1978, p.57.
90. M.M.Shul'ts, A.A.Belyustin, V.V.Mogileva, and I.S.Ivanovskaya, Dokl.Akad.Nauk SSSR, 241, 155 (1978).

Leningrad State University

Translated from *Uspekhi Khimii*, 49, 1904 - 1936 (1980) U.D.C. 541.183.12

Inorganic Ion-exchange Materials Based on Insoluble Antimony(V) Compounds

F.A.Belinskaya and E.A.Militsina

Studies of inorganic ion exchangers based on insoluble compounds of antimony(V) are reviewed [polymeric antimonic acid and its numerous derivatives containing one or two multivalent elements (P, Zr, Nb, Ti, Te, etc.)]. Different approaches to the discussion of their composition, structure, and ion-exchange properties are analysed. Examples of the preparation and of the characteristics of different types of exchanger are given, and their possible practical applications are outlined.
212 references.

CONTENTS

I. Introduction 933
II. Polymeric antimonic acids 933
III. Synthesis and properties of mixed cation exchangers derived from antimonic acid 939
IV. Applications of cation exchangers 947

I. INTRODUCTION

The scientific and technological need for selective ion-exchange materials with a high stability towards heat and radiation was responsible for the interest shown in the 1950's in inorganic ion exchangers and for the extensive studies which began at that time of the ion-exchange properties of various sparingly soluble inorganic compounds. Among the most important of the modern inorganic ion exchangers are the insoluble oxygen compounds of quinquevalent antimony: polymeric antimonic acid and its derivatives, including (in addition to antimony) one or two multivalent elements such as P, Zr, Nb, Ti, Te, etc.

Many papers have been published on the synthesis, properties, and applications of these cation exchangers, because of their unusually high selectivity (which allows many important practical problems to be solved by ion exchange methods). Previously published reviews of inorganic ion exchangers[1-5], including Sb(V) compounds, do not mention the advances made in the last few years. Furthermore, none of the foreign reviews deals adequately with the work done in the Soviet Union.

The aim of this review was to fill this gap by generalising the results of research on ion exchangers based on Sb(V) compounds, both published and still in progress in the ion exchange laboratory of the physical chemistry department of Leningrad State University. Thus we aim to bring to the reader's attention not only problems which have been solved but also controversial questions on the synthesis of these materials and on different approaches to studies of their composition, structure, and ion-exchange properties. When discussing the characteristics of different types of ion exchanger we shall specially emphasise their advantages, their shortcomings, and their possible practical applications.

II. POLYMERIC ANTIMONIC ACIDS

The study of the ion-exchange properties of polymeric antimonic acids (hydrated Sb(V) oxides, Sb(V) hydroxide, hydrated antimony pentoxide, hydrates of antimony pentoxide) began almost simultaneously in several countries. The earliest widely available publications appeared in 1965–1969. These include the work of Lefebvre[6], Lefebvre and Gaymard[7], Abe and Ito[8,9], Baetsle and Huys[10], and Girardi and Sabbioni[11]. In the Soviet Union the ion-exchange properties and the structure of antimonic acids began to be studied in 1965, and the first publications appeared in 1967–1969.[12,13]

This work made clear the high exchange capacity of antimonic acid (up to 5 mg-equiv g^{-1} or 20 mg-equiv cm^{-3}), its ability to undergo ion exchange in acid solutions, and its selectivity towards Sr^{2+}, Ba^{2+}, Cd^{2+}, Pb^{2+}, Ag^{+}, Na^{+}, and K^{+} ions. However, even at that early stage different points of view on the origin of the ion-exchange properties of these materials and on the composition and structure of polymeric antimonic acid began to emerge: in particular, it was shown that the selectivity is very sensitive to the method of preparation.

The fundamental aspects of the preparation of sparingly soluble ("precipitated") antimonic acids and antimonates were first examined during the previous century. Since then there have been many changes in our understanding of the nature of these compounds. It is now generally accepted[14-21] that monomeric antimonic(V) acid—the starting material for the preparation of the insoluble forms—is a strong monobasic complex acid (hexahydroxoantimonic acid $H[Sb(OH)_6]$), which can exist in solution for a short time but is converted by condensation (in 2 or 3 days) into a precipitate of polymeric antimonic acid[18,19-22]. The salts of $H[Sb(OH)_6]$ (the hexahydroxoantimonates) also show a tendency towards polymerisation[23-25].

The state of antimony(V) in solution and the mechanism of the ageing processes of antimonic acid and antimonate solutions have been studied in detail[26-35]. Some substances were found to be a "stabilising" effect on solutions of antimonic acid (H_2O_2, oxo-compounds[19,36,37], and arsenious acid[38]), whereas other substances (such as KCl[19,36]) accelerate the precipitation.

It is therefore essential in the synthesis of insoluble antimonic acids (and especially in the preparation of mixed sorbents) to fix a large number of parameters in order adequately to characterise the initial solution: its concentration and pH, method of preparation, conditions and time of storage, presence of other substances, etc.

1. Preparation of Amorphous Antimonic Acid

Amorphous antimonic acid (AAA) can be prepared by the following methods:

a) by adding solutions of mineral acids (HCl, HNO_3) to solutions of the so-called "acid potassium or sodium pyroantimonates"†[10,13,23,39,40–43];

b) by hydrolysing $SbCl_5$ with water, chlorine water, or a dilute solution of NH_4OH;[13,23,42–44,47];

c) by treating $SbCl_3$ with oxidising agents such as HNO_3 or HNO_3 + HCl,[44,48–50] or H_2O_2,[24,45,51] and diluting the solution with a large volume of water;

d) by dissolving metallic antimony in *aqua regia* and evaporating the solution with repeated additions of nitric acid[43,52,53];

e) by dissolution of Sb_2O_3 in *aqua regia*[54] followed by hydrolysis;

f) by dissolving freshly precipitated antimonic acid and removing the solvent by freezing[44];

g) by a recently developed ion exchange method[55]. A solution of $K[Sb(OH)_6]$ is passed through the hydrogen form of a strongly acid cation exchanger in order to give a solution of $H[Sb(OH)_6]$,[18,19] which is then frozen or slowly evaporated, and the residue is dried over P_2O_5[13,42] or $CaCl_2$.[57,58]

Production of the amorphous acid is assisted by a low hydrolysis temperature, short time of contact between the precipitate and the mother liquor (4 h,[43] or 1 day[42]), and a low drying temperature[44,56]. These same factors favour the production of an amorphous product with a high solubility[44].

Washing AAA precipitates with water causes dispersion of the solid, increasing as the electrolyte is removed by the wash liquid. In order to minimise the loss of antimonic acid and to obtain a more stable product Abe and Ito[43,59] recommend washing the precipitate with cold water and separating it from the wash liquid by centrifuging. Colin and Lefebvre[56] froze the solution of antimonic acid prepared by ion exchange and treated the residue with alcohol at −4 °C. The granular material thus obtained was rapidly filtered and dried at 25 °C. Loss of antimony during washing of the AAA can be reduced still further[13] by introducing an additional drying stage (after partial removal of the chloride ions).

The composition of the AAA can vary over a wide range. Immediately after precipitation the value of n in the empirical formula $Sb_2O_5.nH_2O$ (which defines the composition of the samples) can be as high as 29–30,[43,47] but the water is rapidly lost. Relatively stable AAA samples, amorphous to X-rays, may contain between 3 and 8 molecules of water per molecule of Sb_2O_5 (reported values include $n = 5–8$,[13,42] $n = 4–5$,[43] and $n = 3$[57,58]).

Amorphous antimonic acid is not a stable product. It is spontaneously converted into crystalline antimonic acid on storage. When dry samples are kept at room temperature the first indications of crystallinity are observed after 3 months, and crystallisation is complete after 1.5–2 years[13,42].

† The term "pyroantimonate", which reflects the early, erroneous belief that antimony (like phosphorus) can form meta-, ortho-, and pyroantimonic acids and salts, is still used in textbooks as well as in research publications. Doubts concerning the validity of this analogy were expressed even in the last century (see, for example, Ref.44). More recent work has shown that the "pyroantimonates" are really hexahydroxoantimonates of the type of $M(I)[Sb(OH)_6]$,[15,16,20,21] or their partial condensation products[45,46].

2. Preparation of Crystalline Antimonic Acid

Crystalline antimonic acid (CAA) can be prepared by the methods used in the preparation of AAA. Crystallisation of the antimonic acid can be induced either in the mother liquor (by allowing very long ageing times, by increasing the temperature of the mother liquor, or by increasing the concentration of mineral acid[32,43,54,59,60,61]), or it can be induced by heat treatment of the precipitate (separated from the solution).

For example, Abe and Ito[43,59] prepared samples showing a high degree of crystallinity by hydrolysing $SbCl_5$ in a large volume of water and allowing the precipitate to stand in the mother liquor at 30 °C for 20 days. The time could be shortened to 4 h by raising the temperature to 60 °C and increasing the concentration of mineral acid present during the hydrolysis.

The preparation conditions of CAA by thermal dehydration of the amorphous acid and the optimum drying conditions for the crystalline acid are more complex. The usually recommended procedure[13,42,62] involves drying the amorphous phase for 2–3 days at 110–180 °C, i.e. in the temperature range corresponding to reversible sorption of water according to thermal analysis data[13,42,59,61]. The CAA samples obtained in this way are white powders or free-flowing granules of composition $Sb_2O_5.nH_2O$ (where $n = 3–4$), showing no tendency to peptisation; under the electron microscope they appear as cubic crystals ~0.1 μm in size[13]. At lower temperatures the crystallisation is slower, and at higher temperatures structural changes are possible (reduction of Sb(V) to Sb(III)), leading to changes in the ion-exchange properties of the material.

We should note that in many laboratories the CAA samples (including the hydrated antimony pentoxide marketed by the Italian Carlo Erba firm) are prepared by heat treating the amorphous material at 270 °C.[11,54,61] These samples have good mechanical properties[54], but they appear to have undergone some thermal changes (yellow colour[54,61], lower intensity of the odd-index X-ray reflections[13,61,69], weight losses at 900–1000 °C smaller than those of samples which have not been heat treated[54,61]).

In addition to AAA and CAA, we can prepare glassy antimonic acid by dissolving freshly precipitated antimonic acid in hot water and rapidly evaporating and cooling the solution[43,57–59].

The choice of crystallisation conditions and temperature for the preparation of CAA is determined mainly by the views of individual workers on the composition, structure, and mode of operation of the ion-exchange groups and on the processes which accompany thermal decomposition. We shall therefore discuss some of the most important results obtained in physicochemical studies of antimonic acid.

3. Results of Physicochemical Studies of the Structure of Antimonic Acids

Physicochemical studies of the oxygen compounds of Sb(V) can be arbitrarily divided into two periods. The first was concerned mainly with the composition of Sb(V) oxides, and it included some early applications of X-ray diffraction methods. The second period has been concerned with the ion exchange and catalytic properties of the Sb(V) oxides. It has coincided with the extensive introduction of new methods of analysis (differential thermal analysis, high-temperature X-ray diffraction, i.r. spectroscopy, etc.).

Work done during the first period could not establish whether the hydrates formed by Sb_2O_5 have a fixed or an indeterminate composition. The reported dehydration and thermal decomposition products included the hydrates $Sb_2O_5.nH_2O$ with $n = 3$, 2, and 1 (by analogy with the phosphoric acids), and also $n = 6$, 5, $4\frac{1}{2}$, 4 (see Ref.47), or $n = 6$, 4, 3, 2, 1.5,[63] or anhydrous Sb_2O_5, Sb_3O_6OH, Sb_6O_{13}, Sb_2O_4, and Sb_2O_3.

The initial oxide $Sb_2O_5.nH_2O$ and the products obtained by baking it at 800 °C (with formation of Sb_2O_4) have similar crystal structures (pyrochlore type, *Fd3m* space group[64-67]). X-ray data for the hydrates ($n = 3$, 1) and for the heat treatment products are given in the ASTM tables, although the existence of definite hydrates and of some of the heat treatment products is still being debated.

Thus, Sb_3O_6OH[64] was not detected by some workers[43,68], and was categorically excluded by others[69]. In place of Sb_6O_{13},[70] the compound $Sb_2O_{4.35}$ (of almost identical composition) has been suggested[69]. Doubts on the existence of anhydrous Sb_2O_5 have been expressed[64,71].

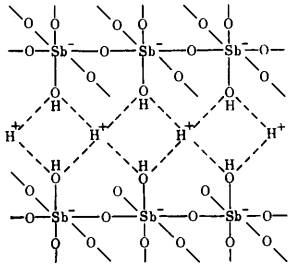
Natta and Baccareda[66,67], when reporting their X-ray diffraction results for $Sb_2O_5.3H_2O$, $Sb_2O_5.H_2O$, Sb_2O_5, and Sb_2O_4, pointed out that the compound which they had denoted Sb_2O_5 contained not less than one mole of water per mole of Sb_2O_5. However, this reservation was ignored by later workers and the original results[66,67] are still referred to anhydrous Sb_2O_5 [43,57,58,68,71].

A more recent comparison of the diffraction patterns and microwave resonance spectra of commercial samples of "anhydrous" Sb_2O_5[69] has shown that all these materials either contain water or show evidence of thermal decomposition (since all the samples dried at high temperatures contain Sb(III), including the Sb_2O_5 discussed in Ref.72). Only in the initial CAA of composition $Sb_2O_5.4H_2O$ (which had not been dried at high temperature) was the whole of the antimony in the Sb(V) form. Heating the CAA to 700 °C does not alter the crystal lattice type (pyrochlore, *Fd3m* space group), but the relative intensity of the reflections with odd indices is decreased by the treatment, suggesting structural rearrangements involving the cations. A decrease in the intensity of the odd reflections has been observed even in CAA held at 150 °C for 2 h.[69] It is thought that materials of reproducible composition cannot be produced by heat treatment up to 700 °C, and the breaks observed on the TG curves are ascribed to changes in the rate of dehydration and decomposition processes.

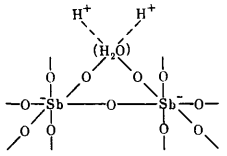
Other workers, however, interpret[73-76] the breaks in the TG curves (and the corresponding extrema on the DTG curves) as evidence for the formation at these temperatures of stable pyrochlore phases of composition $H_xSb(III)_tSb(V)_{16}.O_{56}$ (the composition of the elementary cell). Transitions between the phases are accompanied by the loss of O_2 and H_2O, and by reduction of some of the Sb(V) to Sb(III), the Sb(III) being transferred from a B position to an A position of the $A_2B_2X_7$ pyrochlore structure. The latter effect accounts for the decreased intensity of the odd reflections in the diffraction patterns. The number of pyrochlore phases stable up to 820–840 °C corresponds to the number t of Sb(III) cations which can be accommodated in the first coordination sphere of the $Sb(V)O_{6/2}$ octahedra without infringing the electrical neutrality of the pyrochlore structure as a whole. These views on the thermal decomposition processes deserve to be taken seriously and to be developed further.

Even the first studies of the ion-exchange properties of CAA led to rejection of the formula $Sb_2O_5.nH_2O$ and showed the need to establish a correlation between the exchange capacity of the ions and the structure of the CAA. Thus, in 1965 Lefebvre[6] examined the ion-exchange properties of crystalline CAA (in particular, the equivalent exchange of H^+ and Ag^+), and they compared the composition of the Ag^+ form ($AgSbO_3.0.5H_2O$) with that of the original CAA ($Sb_2O_5.4H_2O$) by using the formula $HSbO_3.yH_2O$ for the CAA. In 1972 Jolivet and Lefebvre[77] arrived at the formula $H(H_2O)SbO_3.0.5H_2O$, which reflects the non-equivalence of the water molecules, by studying exchange on CAA and antimonates.

Abe and Ito[43,59,78] proposed the following formulae for CAA and AAA:



CAA: $H_2Sb_2O_5(OH)_2$



AAA: $Sb_2O_5 \cdot nH_2O$

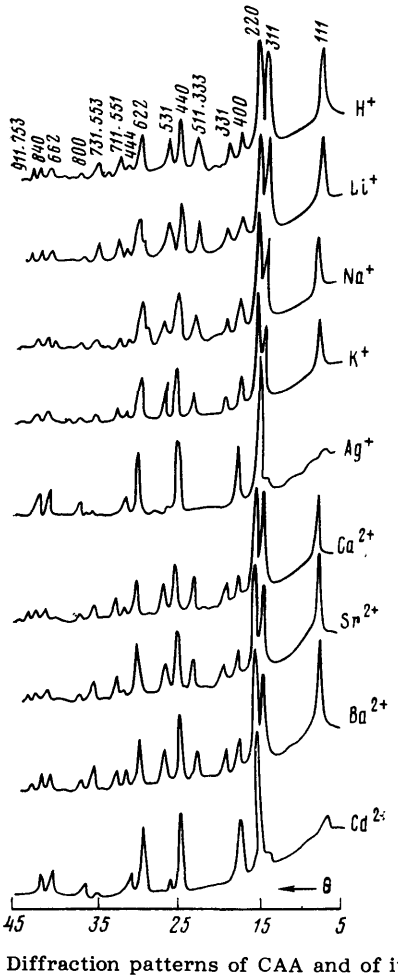


Figure 1. Diffraction patterns of CAA and of its salt forms[13,62].

They showed[59] that the exchangeable H^+ ions (like the Na^+ ions in the $Na[Sb(OH)_6]$ structure) are surrounded by six oxygen atoms. The H^+ ions in this structure can attach

themselves to H_2O, forming H_3O^+ ions. SbOH groups are postulated only in the CAA, following an i.r. spectral study[59] in which absorption bands assigned to Sb—O vibrations (750 cm^{-1}) and to sorbed water (1630 and 3350 cm^{-1}) were observed in all the samples, whereas bands at 1280 and 2430 cm^{-1} (assigned to vibrations of the SbOH group) were found only in the CAA. This conclusion is surprising, since SbOH groups would be expected to appear first in the AAA (the partial condensation product of $H[Sb(OH)_6]$).

The first attempt to correlate the ion-exchange properties and the structural features of CAA was reported in 1968 by Baetsle and Huys[10], who studied partly crystallised samples of CAA. Starting from the composition $Sb_2O_5.4H_2O$ and the experimentally determined density (4.27 g cm^{-3}), and assuming a lattice constant $a = 10.3$ Å, they concluded that the elementary cell contains 14 antimony atoms. They proposed an elementary cell structure of composition $[H_3Sb_3O_5.(OH)_8]_3.H_5Sb_5O_6(OH)_{18}$. This CAA structure accounts for the equality of the maximum exchange capacity to the concentration of Sb, and for the *S*-shaped isotherms (the nine strongly acidic exchange points of the trimers are assumed to be non-equivalent to the five weakly acidic points of the pentamer).

One weakness of the model[10] is its reliance on the measured densities of finely divided materials to calculate the number of Sb atoms in the elementary cell. Experimentally measured densities in these materials are usually lower than the true value (see, for example, Ref.79): this should lead to an erroneously low value of the number of Sb atoms in the elementary cell (14 instead of 16). We note that the CAA structure proposed by Baetsle and Huys[10] is still accepted by many workers[5,80].

In 1969 Novikov and coworkers[13] demonstrated that all the following materials had identical Debye diffraction patterns: the initial CAA, its sodium form, a synthetic sample of $NaSbO_3$ (prepared by heating $Na[Sb(OH)_6]$ at 480 °C), and the product obtained by treating $NaSbO_3$ with acid (i.e. antimonic acid prepared independently from $NaSbO_3$). Diffraction patterns for the hydrogen form and some salt forms of CAA, confirming the conclusions from the Debye patterns, are shown in Fig.1[62,81–83]. We note the regular decrease in the relative intensity of the odd-order reflections as the scattering power of the counter-ion is increased, and the almost complete disappearance of these reflections for the heaviest counter-ions (Ag^+ and Cd^{2+})#.

All these compounds belong to the pyrochlore structure type ($Fd3m$ space group). According to published data, the Sb(V) atoms in this structure can occupy only the 16(*c*) positions of the elementary cell, and the Sb(III) atoms must be partly or fully accommodated in the 16(*d*) positions[64–67]. Since the maximum exchange capacity for Ag^+ (in mg-atom g^{-1}) is equal to the Sb content (in mg-equiv g^{-1}) we may conclude that the whole of the antimony in CAA is in the Sb(V) form. Using the coordinates of the Sb(V) [16(*c*)] and O atoms (48*f*)[85,86] we constructed a model of the CAA anion skeleton[83]§ consisting of corner-sharing $[SbO_{6/2}]^-$ octahedra

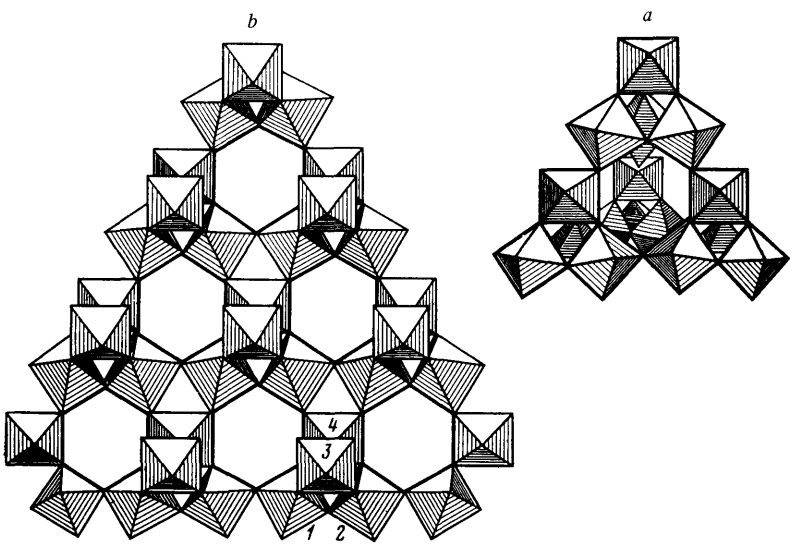


Figure 2. Structure of the anion skeleton of CAA: (*a*) elementary cell, (*b*) schematic representation of two types of (111) plane formed by $[SbO_{6/2}]^-$ octahedra.

The effect of the difference in scattering power between A and B ions in compounds with the pyrochlore structure and in CAA is discussed in Refs.61 and 84. The similarity between the losses of reflections by ion exchange and by heat treatment[13,69,73,75,76] confirms that the counter-ions and Sb(III) occupy identical positions in the CAA structure.

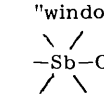
§ The pyrochlore structure was described by Belov[87] as a derivative of the fluorite structure. Interest in compounds with the pyrochlore structure has increased in recent years (see, for example, Refs.88 and 89). A detailed description of the structure is given in Ref.90.

carrying an excess of negative charge. This charge is compensated by the exchangeable cations (counter-ions) H^+ (or H_3O^+), Na^+, Sr^{2+}, Ag^+, etc.

The elementary cell of the anion skeleton is shown in Fig.2, with two types of (111) plane. The CAA structure can be built up in different ways. One is to arrange in layers the two types of (111) plane shown in Fig.2*b*. The lower plane forms a system of hexagonal "windows", the upper plane is more open. The next plane is similar to the first, but its "windows" are in a staggered configuration with respect to the lower plane, and so on. The CAA structure can also be built up from layers of parallel columns of octahedra: octahedra *1* and *2* in Fig.2*b* belong to one of these columns, *3* and *4* belong to a column of the next layer. In each layer the columns are perpendicular to those of the next layer. We can choose as the building block the group of four octahedra (*1*, *2*, *3*, and *4* in Fig.2*b*) joined to form an empty octahedron.

As Fig.2 shows, the anion skeleton of CAA has an open-lattice structure. At the centre of the elementary cell we find a hole connected to the neighbouring holes by four hexagonal rings ~3 Å in diameter. Six of the faces of each $[SbO_{6/2}]$ octahedron are in contact with six different holes, the other two with an empty octahedron. The counter-ions and the water can be accommodated at the centre of the hexagonal windows [16(*d*)] or at the centre of the holes [8(*b*)].

By assuming the simplest, uniform distribution of the Sb^{5+} and O^{2-} charges over all the bonds[91] we can calculate the excess of negative charge at the centre of the hexagonal "windows" or at the centre of the holes. Each oxygen bridge

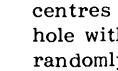


$-Sb-O-Sb-$ contributes an excess charge of $\delta = z_O + n_O\, z_{Sb}/n_{Sb} = -2 + 2(5/6) = -1/3$, where z_O, n_O and z_{Sb}, n_{Sb} are the valence and the coordination number of O and Sb respectively in the anion skeleton. Since each window is formed by six bridges and each bridge contributes to the formation of two windows, each hexagonal ring will carry a charge of -1. On the other hand if we assume that the counter-ions are located at the centre of holes formed by four hexagonal windows (each contributing to two holes) the same calculation gives a charge of -2 for the hole. It follows that singly-charged cations are easily accommodated at the centre of the windows [16(*c*)], as in typical pyrochlores. This leaves room at the centre of the hole [8(*b*)] for the sorbed water. The compositions $NaSbO_3.0.5H_2O$ and $H_3O.SbO_3.0.5H_2O$ are exactly consistent with this distribution of counter-ions on the assumption that H_3O^+ plays the role of a counter-ion. When the skeleton contains doubly charged counter-ions the most suitable locations for these ions are the centres of the holes (as in $RbNbTeO_6$,[90] in which Rb occupies a hole with a charge of -1), or alternatively the M^{2+} ions are randomly distributed at the centres of hexagonal windows, filling alternate windows as in normal pyrochlore structures.

The assumption that H_3O^+ can be treated as a counter-ion in CAA is confirmed by i.r. spectral results[92].

In addition to the strong ν_{Sb-O} absorption band (770 cm^{-1}) the CAA samples give two absorption bands in the region of the OH_n bending vibrations: a wide band with a maximum at 1640 cm^{-1}, assigned to bending vibrations of adsorbed water, and a stronger, narrow band at 1705 cm^{-1}, assigned to H_3O bending vibrations[93]. Deuteration of the CAA shifts both these bands towards lower frequencies (the isotopic shift of the 1705 cm^{-1} band is $\delta(OH)/\delta(OD) = 1.34$). The absorption band at 1705 cm^{-1} is absent in the Na^+ form of CAA, but it reappears when this is converted into the H^+ form. From these results, and from the absence of the absorption bands at 1030–1300 cm^{-1} (assigned to δ_{Sb-OH} vibrations[20,21]), we may conclude that the SbOH group does not exist in CAA and the counter-ions are H_3O^+.[92] Data on the thermal decomposition of antimonic acid are consistent with this conclusion[13].

However, other workers[58,59] failed to observe an absorption band at 1704 cm^{-1} in the i.r. spectra of CAA, and at the same time they found two absorption bands at 1030–1300 cm^{-1} which they assigned to vibrations of the OH group in bridging



Sb–O–Sb groups (1290 cm^{-1}) and to SbOH end-groups (1140 cm^{-1}). Conversion into the Ag^+ form suppresses the 1290 cm^{-1} band, and treatment of the initial CAA sample with hydrofluoric acid suppresses the 1140 cm^{-1} band. From these results the authors conclude[58,59] that the protons of the SbOH bridging groups are responsible for the exchange, and that the SbOH end-groups do not take part in exchange.

Lukina and coworkers[94,95] concluded, from an analysis of i.r. spectra, that both SbOH and H_3O^+ are present in CAA. We must assume that the CAA samples used in that work had an unusual degree of condensation and crystal size, and hence an atypical ratio of surface $[Sb(OH)_{6-x}O_{x/2}]^-$ to bulk $[SbO_{6/2}]^-$ complex groups: this is suggested by the observed i.r. spectra.

The fact that the maximum exchange capacity of AAA and CAA is equal to the Sb content (whatever the degree of condensation or the crystallinity[42]) provides additional evidence that the surface and the bulk complex groups carry a charge of -1, and that the SbOH end-groups do not take part in the exchange: the traditional dissociation of these groups, often invoked to explain the ion-exchange properties of hydroxides, does not apply in this case[42,96].

4. Ion-exchange Properties of Antimonic Acid

The ion-exchange properties of CAA have been fairly fully characterised. Even in acid solutions the exchange capacity for Ag^+, Na^+, Sr^{2+}, Pb^{2+}, and Cd^{2+} ions is already quite high. Thus, the absorption (in mg-equiv g^{-1}) from 0.01 and 0.1 *N* solutions under static conditions (with a 1 : 100 ratio of weight of exchanger to volume of solution) is found to be[13,97]

$$\left.\begin{array}{c} Ag^+ > Na^+ > K^+ > Li^+ > Cs^+ \\ 5.06 \quad 2.22 \quad 1.28 \quad 0.26 \quad 0.04 \\ Pb^{2+} > Cd^{2+} > Sr^{2+} \geqslant Ba^{2+} > Ca^{2+} > Mg^{2+} \geqslant Ni^{2+} \\ 5.10 \quad 3.72 \quad 2.52 \quad 2.42 \quad 1.14 \quad 0.16 \quad 0.10 \end{array}\right\} \text{0.1 } N \text{ solutions},$$

$$\left.\begin{array}{c} Cd^{2+} > Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} > Ni^{2+} \\ 3.37 \quad 2.76 \quad 2.05 \quad 0.97 \quad 0.09 \quad 0.07 \end{array}\right\} \text{0.01 } N \text{ solutions}.$$

The absorption of Ag^+ and Pb^{2+} ions under these conditions reaches its maximum value, equal to the exchange capacity (and therefore to the Sb content) of the material.

Since the distribution coefficient (K_d) for the sorption of many cations from dilute solutions can be as high as 10^4, detailed studies of the dependence of K_d on the concentration and nature of the background electrolyte have been carried out (HNO_3, HCl, $HClO_4$, CH_3COOH, NH_4OH, HF, etc.)[10,11,97–99,61].

Exchange isotherms and titration curves give complementary information and offer the fullest description of the ion-exchange properties of CAA. Titration curves for CAA have been obtained with the following solutions: NaOH[6,7,9,13]; KOH, LiOH, $(CH_3)_4NOH$, and CsOH[82]; $Ba(OH)_2$, $Ca(OH)_2$, and $(CH_3)_4NOH$ in the presence of $MgCl_2$ and $NiCl_2$.[83] Isotherms for the exchange of H^+ ions by Na^+,[7,97,100] K^+,[97,100] Li^+,[10,97] Rb^+,[100] Cs^+,[101] Ag^+,[77,97,100] Mg^{2+}, Ni^{2+}, Cd^{2+}, Ca^{2+},[83,97] Sr^{2+},[10,50,101] Ba^{2+},[10,83,97] and La^{3+}[10] have been reported. Isotherms for exchange on CAA in H^+–M^{z+} systems (where $M^{z+} = Ag^+$, Na^+, Li^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, and Ni^{2+})[97] are compared in Fig.3 for a total concentration of

exchanging ions of 0.1 *N*. Almost all the isotherms are *S*-shaped, intersecting the diagonal of the square at different values of $\gamma_{M^{z+}}$ (the equivalent fraction in the solid phase). Various workers have pointed out that isotherms measured at different total concentrations of exchanging counter-ions are identical[10,101].

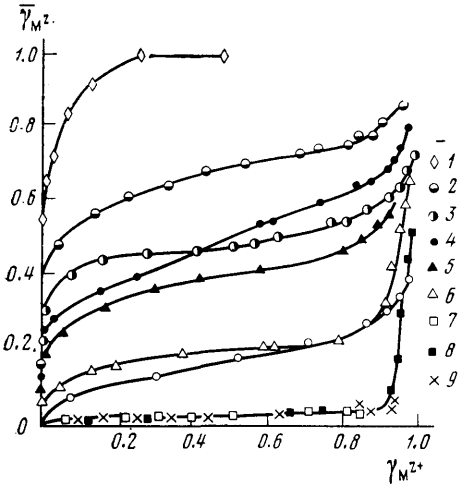


Figure 3. Isotherms for the H^+–M^{z+} exchange on CAA[83,97]: *1*) Ag^+, *2*) Cd^{2+}, *3*) Ba^{2+}, *4*) Sr^{2+}, *5*) Na^+, *6*) K^+, *7*) Ni^{2+}, *8*) Li^+, *9*) Mg^{2+}.

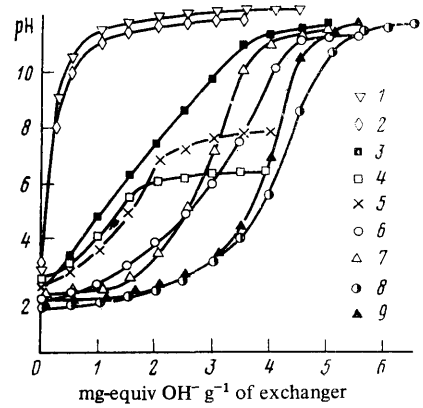


Figure 4. Titration curves of CAA for different solutions[13,82,97]: *1*) CsOH, *2*) $(CH_3)_4NOH$, *3*) LiOH, *4*) $(CH_3)_4NOH$ with Ni^{2+}, *5*) $(CH_3)_4NOH$ with Mg^{2+}, *6*) $(CH_3)_4NOH$ with Ca^{2+}, *7*) KOH, *8*) $Ba(OH)_2$, *9*) NaOH.

Fig.4 shows the titration curves of crystalline antimonic acid with 0.1 *N* solutions of LiOH, NaOH, KOH, CsOH, $Ba(OH)_2$, and $(CH_3)_4NOH$ in the presence of a 1 *N* background of the chloride of the corresponding metal. Since the $(CH_3)_4N^+$ cation is not sorbed (the titration curve for the $(CH_3)_4NOH$ solution being almost identical to the blank titration) we can use this solution for titrations in the presence of 1 *N* $CaCl_2$, $MgCl_2$, and $NiCl_2$, and characterise the sorption of the Ca^{2+}, Mg^{2+}, and Ni^{2+} ions at high pH values (up to the precipitation of the corresponding hydroxide). The titration curves which characterise the ion exchange in the region $2 < pH < 12$ (the non-buffering range of the alkali chosen for the titration and of the acid produced by the exchange) also differ according to the nature of the cation being exchanged. Thus, the titration curve of LiOH suggests that CAA is a polyfunctional cation exchanger, that of NaOH is consistent with a monofunctional cation exchanger, and the *S*-shaped isotherm for the H^+–Na^+ exchange again indicates polyfunctionality of the exchanger.

At first sight polyfunctionality appears inconsistent with the uniform structure of the CAA and with the location of all the counter-ions in identical positions. However, the high charge density of the polymer skeleton¶ and the interconnection between neighbouring holes and six-membered rings through the antimony–oxygen octahedra (see preceding section, p.937, left column) ensure that the replacement of one counter-ion by any other ion affects the bond energy of the other counter-ions. The number of these energetically non-equivalent exchange steps can be estimated by examining the CAA structure (Fig.2). Since each $[SbO_{6/2}]^-$ octahedron of the polymer skeleton contributes to the formation of six windows, at the centre of which the counter-ions are located, the replacement of all the singly charged cations of one kind by singly charged cations of another kind can occur in six energetically non-equivalent stages (each stage having a capacity of $\Gamma^0/6$). If the singly charged cations are replaced by doubly charged cations the number of these non-equivalent stages is three (each corresponding to a capacity of $\Gamma^0/3$). Hence the exchange isotherms (and titration curves) should be interpreted as sums of isotherms (or titration curves) whose shape is determined by the partial exchange constants. The number of these partial exchange constants varies by discrete amounts and depends on the charge of the exchanging cations.

An important aspect of the practical use of CAA is the reversibility and equivalence of the exchange of ions on this material. Contradictory views are held on this problem. Thus, some workers[6,82,83,100,102] find that the exchange is reversible, and that equivalence is preserved. On the other hand complete elution of selectively sorbed ions (Na^+, Sr^{2+}) is difficult or impossible[54,76,103,104]. This problem can be solved by correctly choosing the eluent[98,102]. Thus, Na^+ ions can be eluted by 2 *M* NH_4OH (but not by 10 *N* HNO_3);[98] 1 *M* HNO_3 is recommended for the desorption of Mg^{2+} and Ba^{2+}, and 3 *M* HNO_3 for the desorption of Sr^{2+} and Ca^{2+}.[102] Ag^+ and Pb^{2+} ions are recommended as universal displacers[10], though it is difficult subsequently to remove them from the exchanger (for example, Ag^+ ions can only be removed by converting them into an ammine complex[81]).

No less important is the dependence of the selectivity of CAA and AAA on the preparative conditions and on the degree of crystallinity of the samples[13,42,43,54,60,61,105]. An increase in selectivity and a decrease in the absorption of salts from solutions is observed as the crystallinity is increased from AAA to CAA[43,60,105]. The titration curves of AAA and of its crystallisation products (Fig.5) show a gradual shift from the curve for the monomeric $H[Sb(OH)_6]$ to that for the fully crystallised acid. The maximum exchange capacity (achieved in alkaline solutions) is the same for all the samples, and

¶ In contrast to the aluminosilicates, in which the charge of the anion skeleton is carried by $[AlO_{4/2}]^-$ groups alternating with neutral $[SiO_{4/2}]^0$ groups, in CAA the lattice is composed entirely of charged $[SbO_{6/2}]^-$.

equal to the amount of antimony present, but at lower pH values the capacity for Na^+ of the crystalline samples may be lower than that of the amorphous samples.

Systematic studies of the effect of crystal size on the ion-exchange properties of CAA have not yet been reported. It is stated[68] that the size of the primary crystalline blocks in CAA can vary over wide limits (from 150 to 3200 Å) depending on the preparative conditions. We can expect the sorption properties of small CAA crystals to be more similar to those of the monomeric acid $H[Sb(OH)_6]$ than to those of fully developed crystals. Neglect of the surface groups $[Sb(OH)_{6-x}O_{x/2}]^-$ is justified only when the crystal size is not less than 5×10^2 Å (the size of a cubic crystal containing five elementary cells of the CAA structure along each cube edge).

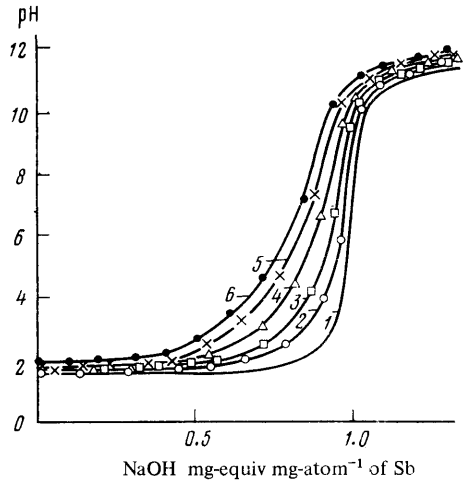


Figure 5. Titration curves of different samples with NaOH solutions: *1*) $H[Sb(OH)_6]$,[18] *2*) freshly prepared AAA and its crystallisation products, *3*) after 5 months, *4*) after 10 months, *5*) after 1.5 year, *6*) after 2 years[42].

Heat treatment of the H^+ form of CAA above 200 °C causes reduction of the Sb(V): as a result, some of the counter-ion sites are occupied by Sb(III), and the exchange capacity decreases. The thermal stability of AAA is lower than that of CAA,[13,105] and therefore samples which have been heat treated (for example, those dried at 270 °C) cannot be said to be identical to samples which have not been heat treated in comparisons of the ion-exchange properties and of the selectivity of these materials. The observed differences in properties suggests useful methods of thermally modifying CAA as an ion exchanger.

III. SYNTHESIS AND PROPERTIES OF MIXED CATION EXCHANGERS DERIVED FROM ANTIMONIC ACID

Ion-exchange properties are found not only in antimonic acid but also in various insoluble oxygen compounds of antimony(V) whose structure includes one or two multivalent elements (P, Si, Zr, Ti, etc.). There is no unique terminology for these materials, but they are often called antimonates. By analogy with the salts of heteropolyacids we shall call them phosphoantimonate, silicoantimonate, titanoantimonate (etc.) cation exchangers, stressing the ability of both constituents (Sb(V) on the one hand and P, Si, Zr, Ti, etc. on the other hand) to form a polymeric skeleton. The role of the second element in the structure of the antimonic acid is not always clear, but there can be no doubt of its influence on the selectivity of the material. At the time of writing, 17 types of these mixed cation exchangers are known.

1. Phosphoantimonate Cation Exchanger (PSb, Phosphoantimonic Acid, Antimony Phosphate)

This cation exchanger was prepared by Abe and Ito by mixing solutions of antimony pentachloride (or pentafluoride) and of phosphoric acid and heating the mixture for 16 h at 80 °C.[106,107] The $\overline{Sb}/\overline{P}$ atomic ratio in the solid phase decreases sharply as the concentration of H_3PO_4 is increased (which also lowers the rate of formation of the precipitate). At H_3PO_4 concentrations of 0.3–0.4 *M* the $\overline{Sb}/\overline{P}$ ratio is approximately 2, and a glassy product is obtained[108]. Glassy materials with different $\overline{Sb}/\overline{P}$ ratios can be prepared also by adding NH_4OH to a mixed solution of $SbCl_5$ and H_3PO_4 in hydrochloric acid[109–112]. Changes in the Sb/P ratio in solution from 0.5 to 8 give samples with $\overline{Sb}/\overline{P}$ ratios between 1.31 and 9.3.[112] Increasing the amount of phosphorus in solution during the synthesis does not yield an even greater concentration of phosphorus in the solid phase. Instead of NH_4OH, we can use NaOH, NH_4Cl, or HNO_3 as precipitants[113,114]. Phosphoantimonate cation exchangers have been prepared with reagents of various concentrations: 8 *M* $SbCl_5$,[113,114] 1 *M* and 10 *M* H_3PO_4,[109] 1 *M* and 0.01 *M* H_3PO_4,[114] and 0.25–4.0 *M* H_3PO_4.[113]

A granular product is obtained either by drying the precipitate in a thermostat[106–113] or by freezing it (at −10 °C[114] or at −6 °C[115]). When the dried material is mixed with water the larger granules disintegrate into smaller granules[108,109], but if the sample is first stored for 1 week in air at room temperature and then in a desiccator it can be mixed with water without change in granule size[108].

A series of papers by Lefebvre and coworkers[116–121] describes a detailed study of the products of the interaction of $SbCl_5$ and H_3PO_4, and of the properties of the resulting compounds.

The phosphoantimonate cation exchanger consists of transparent, heavy (density 2.66–3.22 g cm^{-3} for samples with an atomic ratio $\overline{Sb}/\overline{P} = 1.3–9.3$[112]), glassy granules[108,109] which can be amorphous to X-rays[111,112] or show a crystalline structure[115] (for $\overline{Sb}/\overline{P} \geq 2$).

The ion-exchange properties of phosphoantimonate cation exchangers have been characterised by potentiometric titration curves[106,109–115,122,124], by measurements of the absorption of cations bearing different charges[97,111,112], by isotherms for the exchange of hydrogen ions by alkali metal[97,112,125,126], alkaline-earth[97,112,125], and cadmium ions[127], and by the distribution coefficients of alkali metal ions[114,128] and of barium and lanthanum[97]. Studies of the rate of ion-exchange processes are described in Refs. 112, 114, and 122.

The high chemical stability of PSb cation exchangers in solutions of acids and salts has been stressed[97,108]. Partial dissolution of the samples occurs in hot water[108] and at pH > 8;[97] it is pointed out[108] that the materials are more stable in NH_4OH solutions than in NaOH solutions. The chemical stability depends markedly on the drying temperature of the sample: samples dried at 60 °C are more soluble than those dried at 100 °C.[108]

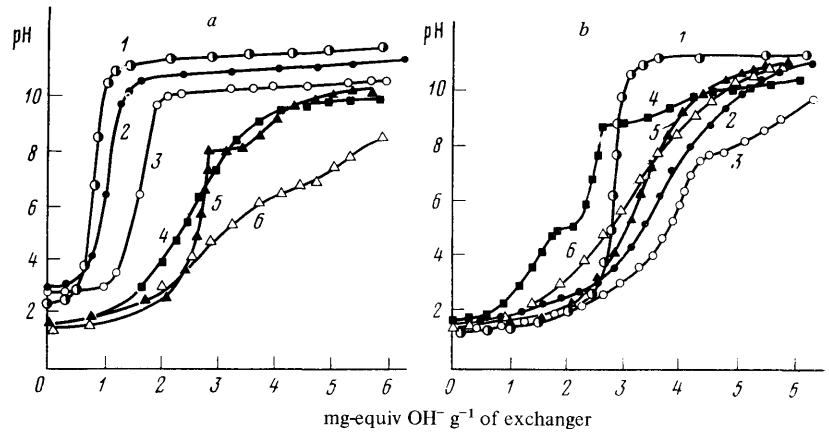


Figure 6. Titration curves of PSb for different solutions: *1*) $Ba(OH)_2$, *2*) $Sr(OH)_2$, *3*) $Ca(OH)_2$, *4*) LiOH, *5*) NaOH, *6*) KOH; (*a*) sample of composition $\overline{Sb}/\overline{P} = 1.35$, (*b*) sample of composition $\overline{Sb}/\overline{P} = 6.8$.

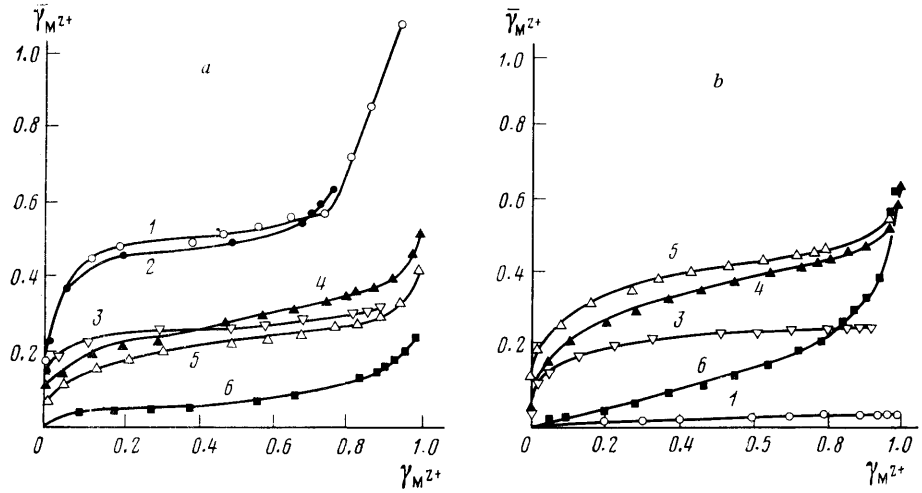


Figure 7. Isotherms for the H^+–M^{z+} exchange on PSb:[97,125] (*a*) sample with $\overline{Sb}/\overline{P} = 6.73$, (*b*) sample with $\overline{Sb}/\overline{P} = 1.64$; *1*) Ca^{2+}, *2*) Sr^{2+}, *3*) Cs^+, *4*) Na^+, *5*) K^+, *6*) Li^+.

Drying the gels at 100 and 200 °C shortens the time needed to prepare these materials without significantly affecting their ion-exchange properties[122]. Increasing the drying temperature of the granules lowers the ion exchange capacity, by a negligible amount for temperatures up to 140 °C[108] but more markedly in the range 100–260 °C (depending on the $\overline{Sb}/\overline{P}$ ratio in the sample), with complete loss of exchange capacity at 800 °C.[122] Hence there must be some doubt about the claim[123] that PSb samples with good exchange capacity can be prepared by drying the gel at 300–700 °C.

The most detailed study of the ion-exchange properties of PSb samples as a function of the $\overline{Sb}/\overline{P}$ ratio is described in Refs.112, 124, and 125. The titration curves of PSb samples with different alkalis and a constant 1 *N* salt background are shown in Fig.6 (for LiOH, NaOH, KOH, $Ca(OH)_2$, $Ba(OH)_2$, and $Sr(OH)_2$). We see that the shape of the curve and its distance from the pH axis depend not only on the nature of the exchanging cation (as in the case of CAA) but also on the $\overline{Sb}/\overline{P}$ ratio of the sample.[112,124] For each sample we can distinguish a number of pH regions of different selectivity. As a result, statements of the functionality of PSb cation exchangers (monofunctional or multifunctional) may be contradictory[106,115]. The type and shape of the exchange isotherms (Fig.7) also depend on the nature of the cation and on the $\overline{Sb}/\overline{P}$ ratio. The titration curves and the exchange isotherms (as well as the absorptions of different ions from 0.1 *N* solutions of their chlorides or of $AgNO_3$) can be used to demonstrate the effect of the phosphorus content on the selectivity of PSb.[97,111,112] Samples in which the P content is relatively small ($\overline{Sb}/\overline{P} = 9.3$) are like CAA in absorbing Ca^{2+} and Sr^{2+} more selectively than Mg^{2+}, Ni^{2+}, Co^{2+}, and triply charged or singly charged ions. High phosphorus contents ($\overline{Sb}/\overline{P} = 1.3$) favour selectivity towards singly charged cations, and the absorption of doubly or triply charged cations becomes negligible[111,112].

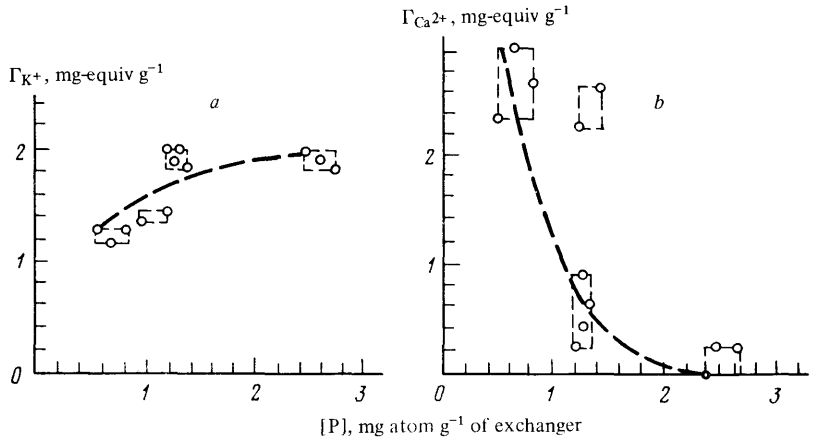


Figure 8. Plots of the absorption Γ_{K^+} (*a*) and $\Gamma_{Ca^{2+}}$ (*b*) against the phosphorus content of PSb samples[112]. Sorption from 0.1 *N* solutions of the chlorides. Data for PSb samples synthesised from nominally identical solutions are indicated by the rectangles.

A closer study of the dependence of the absorption (ΓM^{z+}) on the phosphorus content (Fig.8) shows that this is the predominant (but not the only) effect on the selectivity of the material. Other factors tending to influence ΓM^{z+} include the number of functional groups in the sample (which is equal to the concentration of antimony), and their accessibility to the counter-ions. This structural characteristic of the PSb samples can be evaluated qualitatively from differential thermal analysis results[112]. This method can be used to calculate the amount of free water and of structural water in the PSb sample and to highlight differences between samples of similar composition ($\overline{Sb}/\overline{P}$) prepared under identical conditions[112]. The combined effect of all three factors determines the position of the sample within the rectangles arbitrarily drawn in Fig.8 as well as the relative positions of the rectangles.

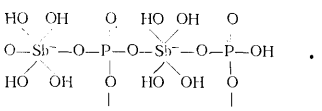
The highest affinity of the phosphoantimonate cation exchangers is for silver ions[97,108,110–112,118,126]. The selectivity of the PSb increases as the loading of the exchanger phase with metal ions decreases[112,125] and as the concentration of the solution decreases[97,112,114]. Several workers report high values of the distribution coefficients of alkali metal ions[114,128] and of Ba[97].

A study[108] of the reversibility of ion exchange in a PSb sample ($\overline{Sb}/\overline{P} = 2$) showed that both sorption and displacement go to completion in the H^+–NH_4^+, K^+–NH_4^+, and Ag^+–NH_4^+ systems. The hydrogen ions are quantitatively replaced by potassium ions; the sorbed K^+ ions are not washed out by 3 *N* solutions of HCl or HNO_3, but they are easily eluted by 1 *M* NH_4NO_3.[108]

Oxidation–reduction processes can take place on PSb cation exchangers. Treatment of PSb samples with a 0.2 *N* solution of $SnCl_2$ in 1 *N* HCl produces sorption of Sn^{2+}, accompanied by conversion of some of the Sb(V) in the solid phase into Sb(III) with formation of Sn(IV).[129] A Mössbauer study[129] of the Sn forms revealed the presence of two types of Sn(II), differing in the ionicity of their bond with the ionogenic group (52% and 26% respectively). The appearance of Sb(III) in the cation exchanger causes a decrease in the total exchange capacity for Na^+ ions and in the absorption of doubly and triply charged cations[129].

Abe and Ito believe[106] that antimony-containing, strongly acidic groups analogous to $H[Sb(OH)_6]$ are responsible for the ion-exchange properties of PSb.

Studies of phosphoantimonate cation exchangers by ion exchange, differential analysis, and i.r. spectroscopy[111,112,130] have led to the following structure, in which the polymer chains consist of interconnected antimony–oxygen octahedra (the building blocks of CAA) and phosphorus–oxygen tetrahedra:



The hydrogen ions which compensate the charge on the $[SbO_{x/2}(OH)_{6-x}]^-$ octahedra and the hydrogen ions of the phosphate groups are involved in the ion exchange process[112,130]. The dependence of the selectivity of the phosphoantimonate cation exchangers on the phosphorus content stems from the decrease in the density of fixed charges produced by the phosphorus, which enters the structure as the non-exchanging $\equiv PO_4$ group[111,112].

More recently, Lefebvre and coworkers[119,120] proposed a PSb structure in which the basic elements are groups of three $[SbO_{6/2}]^-$ octahedra associated with one $\equiv PO_4$ (or $=HPO_4$) tetrahedron and which is consistent with all the above considerations.

In contrast, Tikavyi and Bratennikova[115] suggest that the phosphorus in the PSb structure is present as HPO_4^{2-} and $H_2PO_4^-$ groups, but Astaf'eva and coworkers[113] support the $=HPO_4$ structure.

2. Silicoantimonate Cation Exchanger (SiSb, Silicoantimonic Acid, Antimonosilicic Acid, Antimonosilicic Cation Exchanger)

The SiSb cation exchanger is prepared by joint polycondensation of the hydrolysis products of $SbCl_5$ and Na_2SiO_3[62,131–133]. The resulting gel is allowed to remain in the mother liquor for 1–2 days before being washed and dried. In contrast to PSb, in SiSb the $\overline{Sb}/\overline{Si}$ ratio can be varied over wide limits (0.29–17.67).[133] The diffraction patterns of SiSb are similar to those of CAA, but the peaks are more diffuse in the case of SiSb. Raising the temperature (to 150 °C) and increasing the drying time (to 200 h) has no effect on

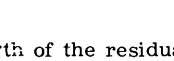
the degree of crystallinity. The similarity between the diffraction patterns of SiSb and CAA suggests that the structure of SiSb is determined by the antimony[62,133].

Unlike the normal CAA material, SiSb does not form a powder but consists of mechanically strong white granules of irregular shape. Its chemical stability is very high, as shown by the absence of any indication of dissolution during the measurement of titration curves or of exchange isotherms. SiSb is decomposed only by concentrated HCl at the boiling point.

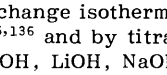
Samples of SiSb can be characterised by the absorption from 0.1 *N* or 0.01 *N* solutions of various salts[97,134], by their exchange isotherms (H^+–Li^+, Na^+, K^+, Ba^{2+}, Sr^{2+}, Cd^{2+}),[97, 135,136] and by titration curves obtained with different alkalis (KOH, LiOH, NaOH, $Ba(OH)_2$)[135]: the equivalence and the reversibility of the exchange have been demonstrated. Over a wide range of pH values and of solution compositions the exchange capacity (as in CAA) is correlated only with the antimony content of the samples. Increasing the pH raises the exchange capacity to its maximum value, corresponding to the amount of Sb in the sample. At pH 9–10 the SiSb titration curves show a second horizontal section, corresponding to weakly acid groups[135,136].

The exchange isotherms for samples with low concentrations of silicon ($\overline{Sb}/\overline{Si} = 13.8$) are almost indistinguishable from those for CAA[97,135,136]. On the other hand in samples with $\overline{Sb}/\overline{Si} = 2.34$ and 0.51 (Fig.9*a* and 9*b*) the isotherms are shifted within the $\bar{\gamma}_M = f(\gamma_M)$ square. The selectivity towards Ca^{2+}, Sr^{2+}, and Ba^{2+} is improved, especially at low concentrations, and there is a small increase in the absorption of Li^+, Mg^{2+}, and Ni^{2+} ions (whose absorption is very slight on CAA), but the shape of the H^+–Cd^{2+} exchange isotherms is almost unaffected.

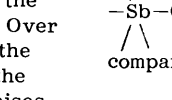
By comparing the diffraction patterns, exchange isotherms, and titration curves of CAA and SiSb we conclude that the silicon may be present as $[SiO_{4/2}]^0$ or $[SiO_{6/2}]^{2-}$ groups. In the former case the silicon should not contribute to the exchange capacity, but in the second case the exchange capacity of the sample should be greater than the antimony content. By using Pauling's electrostatic valency rule we can show[134–136] that in the first case the bond between the proton and the oxygen bridges in the SiSb structure should be weaker (i.e. the acidic properties should be enhanced), and in the second case the bond should be stronger (the strength of the residual O^{2-} bond in the



and



groups should be 1/6 and 1/2 respectively, as compared with 1/3 for the



group in CAA).

Since the ion-exchange properties of SiSb also indicate a slight weakening of the bond between the polymer skeleton and the H^+ counter-ion, and a small increase in capacity in the alkaline region, it has been suggested[133,135] that the $[SiO_{4/2}]^0$ and $[SiO_{6/2}]^{2-}$ groups can exist together in SiSb.

Further studies of SiSb cation exchangers are reported in Refs.99, 137, and 138. Super-equivalent sorption on SiSb was observed in a study of the sorption of Na^+ (using radioactive tracers) in the pH range 0–1.5, and of the sorption of Na^+, Sr^{2+}, Cd^{2+}, and Hg^{2+} from nitric acid solutions at pH 3.5.[99,137,138]. There is a report of irreversible sorption of the Sr^{2+} ion[99], which cannot be eluted from SiSb either by 7–10 *N* HNO_3 or by concentrated salt solutions. The protonogenic groups in SiSb are thought to be[138] "the hydroxyl

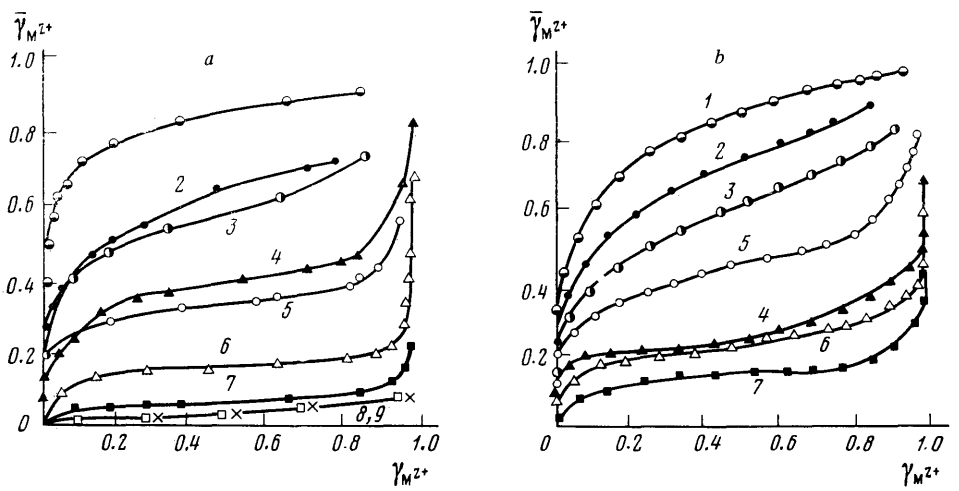


Figure 9. Isotherms for the H^+–M^{z+} exchange on SiSb[97,135,136]: (*a*) sample with $\overline{Sb}/\overline{Si} = 2.43$, (*b*) sample with $\overline{Sb}/\overline{Si} = 0.51$; *1*) Cd^{2+}, *2*) Sr^{2+}, *3*) Ba^{2+}, *4*) Na^+, *5*) Ca^{2+}, *6*) K^+, *7*) Li^+, *8*) Ni^{2+}, *9*) Mg^{2+}.

groups in –SbOH and –SiOH, and also H_2O molecules attached by coordination bonds to neighbouring SbO_6 octahedra".

Since many of the published papers[99,137,138] fail to state exactly the conditions under which the samples were prepared, and to describe the methods of analysis and the methods of measuring exchangeable and non-exchangeable sorption, it is not easy to discuss the discrepancies between their results and ours.

3. Silicophosphoantimonates (SiPSb, Phosphoantimonosilicate (PASC) Cation Exchangers)

The samples are prepared by mixing solutions of $SbCl_5$, Na_2SiO_3, and H_3PO_4; the precipitate is washed with water to pH 4–6 or with acetone, dried in a thermostat at 60 °C, converted into the hydrogen form by treating it with 1 *N* HCl, washed with water until free from Cl^- ions, and air-dried[139–143]. Approximately 50 samples were prepared in our laboratory[143], and used to investigate the relationship between the composition of the solid phase and that of the solutions used for the synthesis. In each sample the combined phosphorus and silicon contents were found to be strictly determined, and directly proportional to the concentration of antimony in the sample[143] (Fig. 10*a*). The concentrations of silicon and phosphorus vary in opposite senses (Fig. 10*b*).

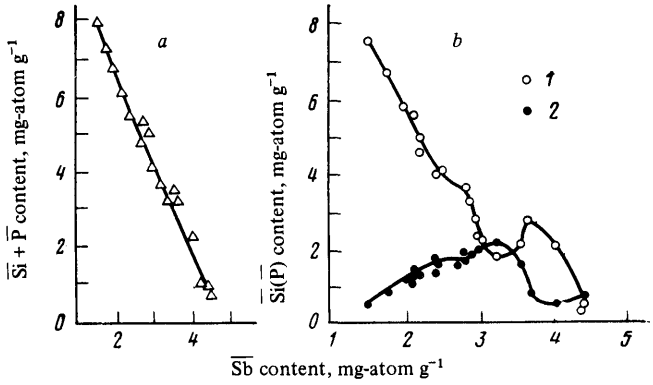


Figure 10. Variation of the $\overline{Si}(\overline{P})$ and $(\overline{Si} + \overline{P})$ content with amount of $\overline{Sb}$ in SiPSb samples[143]: (*a*) $\overline{Si} + \overline{P}$; (*b*), *1*) $\overline{Si}$, *2*) $\overline{P}$.

The compositions of the SiPSb samples and those of the samples in the binary systems (SiSb and PSb) were plotted in a composition triangle[143] (see Fig. 11). We can see that the concentration of silicon in the SiPSb samples can vary over wide limits, but the phosphorus concentration can vary only over a narrow range, and both these ranges apply to the binary systems as well. The SiPSb samples consist of mechanically strong granules of irregular shape and density between 2.0 and 3.2 g cm^{-3} (measured pyknometrically in CCl_4 at 20 °C).[143]

The SiPSb cation exchangers are chemically very stable[143]. According to the potentiometric titration curves obtained with different alkalis, these exchangers are polyfunctional[144].

The variation of the absorption of M^{z+} (at different pH values) with composition suggests that in the acid and the neutral region the H^+–M^{z+} exchange takes place at the antimony–oxygen ionogenic groups, whereas in the alkaline region (pH ≥ 9) phosphorus-containing groups are involved (as well as the antimony–oxygen groups) in the exchange of singly-charged ions. The silicon–oxygen groups take part in the exchange of doubly charged cations[144].

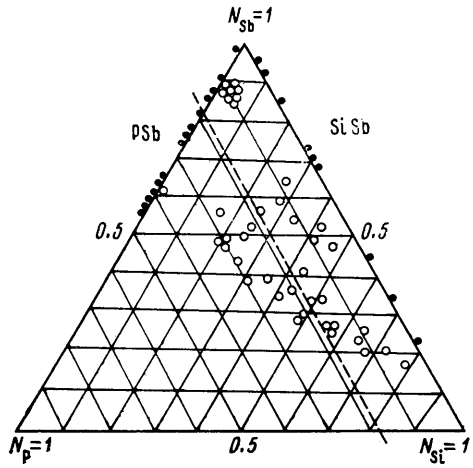


Figure 11. Composition triangle for SiPSb, SiSb, and PSb samples[143]. *N* is the atom fraction of the element in the solid phase (the ratio of the concentration in mg-atom g^{-1} of one of the components $\overline{Sb}$, $\overline{Si}$, or $\overline{P}$ to the sum of the concentrations).

Like the other types of antimony-containing cation exchanger the SiPSb samples are most selective towards Ag^+ ions, and the Γ_{Ag^+} value corresponds to the antimony content. Addition of silicon favours the sorption of doubly and triply charged cations, whereas an increase in the concentration of phosphorus has the opposite effect. Above a critical phosphorus concentration (1.5–2.0 mg-atom g^{-1}, shown in Fig. 11 as a broken line) the sorption of multiple-charged cations decreases, and below this concentration multiple-charged cations can be sorbed (but Γ_M depends on the concentration of antimony and silicon: an increase in the concentration of antimony favours the sorption of Sr^{2+} and Cd^{2+}, and an increase in the concentration of silicon favours the sorption of La^{3+}).[145,146]

The sorption of ions on SiPSb samples takes place by an ion exchange mechanism in which equivalence is preserved[145,146]. The shape of the exchange isotherms (as in the case of the related SiSb and PSb samples) depends on the composition of the material and on the nature and charge of the counter-ion[127,146] (Figs. 12*a* and 12*b*).

Non-equivalent sorption of singly charged and doubly charged cations has been observed[47,94,99,147,148] in a study of SiPSb (Sb : P = 8 : 1; 4.5 wt.% Si).

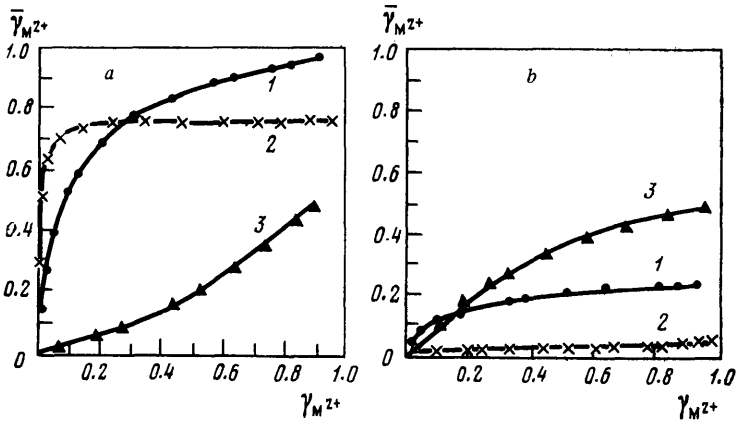


Figure 12. Isotherms for the H^+–M^{z+} exchange on SiPSb samples[127,146]: (*a*) sample with $\bar{Sb} : \bar{Si} : \bar{P} = 2.18 : 4.49 : 1.24$, (*b*) sample with $\bar{Sb} : \bar{Si} : \bar{P} = 3.52 : 2.17 : 1.71$; *1*) Sr^{2+}, *2*) La^{3+}, *3*) Na^+.

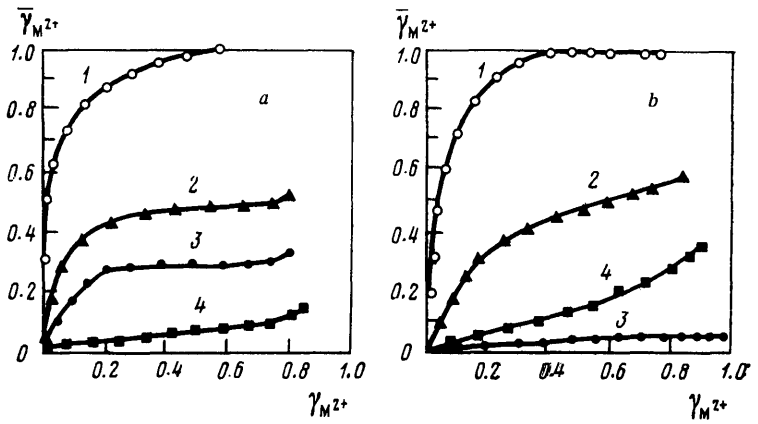


Figure 13. Isotherms for the H^+–M^{z+} exchange on TeSb[151]: (*a*) sample with $\bar{Sb}/\bar{Te} = 5.76$, (*b*) sample with $\bar{Sb}/\bar{Te} = 1.93$; *1*) Ag^+, *2*) Na^+, *3*) Sr^{2+}, *4*) Li^+.

4. Telluroantimonate Cation Exchanger (TeSb)

The exchanger was prepared by mixing solutions of 1 *M* $SbCl_5$ (in 3 *M* HCl) and 0.5 *M* H_2TeO_4.[149–151] Varying the Sb/Te ratio in solution during the synthesis allows the ratio in the solid samples to be varied in the range $\bar{Sb}/\bar{Te} = 1.93$–6.23, but the total concentration of tellurium and antimony is almost constant in all the samples (4.98–5.19 mg-atom g^{-1})[151]. The selectivity is again greatest towards Ag^+ ions, and the sorption of Ag^+ is practically equal to the concentration of antimony in the sample. As the tellurium concentration increases the absorption values for alkali metal ions (Li,Na, K) increase somewhat, but those for the alkaline earth metals (Mg, Sr, Ba) and for Cd fall off sharply, reaching zero at tellurium concentrations Te ≥ 1 mg-atom g^{-1}. Triply charged ions are not sorbed on the majority of these samples[127,150,151]. Thus the effect of tellurium on the selectivity is similar to that of phosphorus, but it can be observed at much lower concentrations[151].

Measurements of the exchange isotherms in the H^+–Ag^+, H^+–Li^+, H^+–Na^+, and H^+–Sr^{2+} systems revealed that—depending on the composition of the sample (i.e. on $\bar{Sb}/\bar{Te}$) and on the nature of the exchanging counter-ion—the sorption of M^{z+} can be predominant over the whole range of solution compositions (in the H^+–Ag^+ system), or the sorption of H^+ can be predominant (in the H^+–Li^+ system, and also in the H^+–Sr^{2+} system for the $\bar{Sb}/\bar{Te} = 1.93$ sample), or a selectivity reversal can take place, with an *S*-shaped exchange isotherm (H^+–Na^+ on both samples and H^+–Sr^{2+} on the sample with $\bar{Sb}/\bar{Te} = 5.73$, see Figs. 13*a* and 13*b*).[151]

The potentiometric titration curves obtained with 0.1 *N* solutions of NaOH and KOH showed that as the pH increases from 2 to 12 the capacity of the samples (Γ, mg-equiv M^+ g^{-1}) varies from 2.3 to 4.6 for the H^+–Na^+ exchange and from 2 to 4.5 for the H^+–K^+ exchange: $\Gamma_{K^+} < \Gamma_{Na^+}$ for all samples[151]. At high pH values (>10) the capacity for Na^+ of all samples exceeds the antimony content, the difference increasing with the tellurium content[151].

This work led to the conclusion that both the antimony and the tellurium are accommodated in the cation exchanger structure with six oxygen atoms as nearest neighbours. The tellurium replaces antimony isomorphously, and the structure is similar to that of polymeric antimonic acid. The protons which compensate the charge on the antimony–oxygen

octahedra and those of the tellurium-containing groups are both involved in the ion exchange process[150,151].

5. Zirconium Antimonate (ZrSb)

The ZrSb samples were prepared by adding an NH_4OH solution to a mixed solution of $ZrOCl_2$ and $SbCl_5$ in hydrochloric acid[152-155], or by mixing solutions of zirconium oxide chloride and of potassium pyroantimonate[156,157] or of antimonic acid prepared by ion exchange[156]. Samples with the following $\overline{Sb}/\overline{Zr}$ ratios were obtained: 2,[152] 0.53–4.1,[154] and 0.99–1.14.[157]

The most detailed studies of the preparation, structure, and of the physicochemical and ion-exchange properties of the ZrSb cation exchanger were reported by Lapitskii and Tikavyi[154,155,158-161]. The ZrSb samples consist either of white, glassy granules, suitable for operation in a column[154,157], or of friable, chalky particles[154]. The chemical stability of ZrSb was studied in several laboratories[152,154,157]. Raising the drying temperature of the samples lowers their ion-exchange capacity[153,157], and when ZrSb is heated to 300 °C its selectivity towards singly charged cations increases[155,159].

The cation exchange capacity of ZrSb increases with the antimony content[154,157,161]. Samples with $\overline{Sb}/\overline{Zr}$ ratios of 0.53 and 0.55 showed anion exchange properties: their capacity towards chlorine, determined from the potentiometric titration curves, was 0.75 and 0.95 mg-equiv g^{-1} respectively.[154]

The kinetics of the exchange of H^+ ions by Cs^+ and Rb^+ ions have been studied in detail[162] on a sample with an $\overline{Sb}/\overline{Zr}$ ratio of 1.03. The rate-determining step in the exchange of these ions was found to be diffusion in solution (in the case of 0.02 *M* and 0.05 *M* solutions) and diffusion in the grains for solution concentrations ≥ 0.1 *M*.[162] The kinetics of ion exchange on ZrSb are discussed also in Refs. 154 and 157.

The unusual alkali metal selectivity sequence ($Na^+ > Rb^+ > K^+$) of a sample with $\overline{Sb}/\overline{Zr} = 2$ was first noted by Phillips and Kraus[152]. Abe and Ito point out[156] that a more conventional selectivity sequence is obtained with samples in which the ratio is $\overline{Sb}/\overline{Zr} < 1$, whereas samples with $\overline{Sb}/\overline{Zr} > 1$ contain enough antimonic acid to display an abnormally high selectivity towards Na^+ ions. Similar explanations are given in Refs. 155 and 158. The following selectivity sequence is given[157] for a ZrSb sample with $\overline{Sb}/\overline{Zr} = 1.03$:

	Ba^{2+}	$>Ca^{2+}\geqslant Mg^{2+}\simeq Na^+$		$>K^+>NH_4^+\simeq Li^+$			
Γ, mg-equiv g^{-1}	1.85	1.24	1.21	1.20	1.09	0.74	0.73

Exchange isotherms have been measured in H^+–M^+ systems ($M^+ = Li^+$, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Ag^+, Tl^+) with three ZrSb samples ($\overline{Sb}/\overline{Zr} = 0.55$, 3.05, and 4.1).[155,158] The selectivity of the cation exchanger towards these ions was found to increase as the antimony content increases and as the equivalent fraction of the ions in the exchanger decreases. The sample with the ratio $\overline{Sb}/\overline{Zr} = 4.1$ had the highest affinity for the Ag^+ and Tl^+ ions.

Contrasting views have been expressed on the structure and on the functional groups of ZrSb.[155,163] Mathews and Tandon[163] describe zirconium antimonate as the polymeric condensation product of antimony and zirconium hydroxides. On the basis of DTA and TGA data they assign to the $\overline{Sb}/\overline{Zr} = 1.03$ sample the formula $ZrO_2.0.5Sb_2O_5.5.1H_2O$. The number of water molecules shown in this formula describes the total content of water of crystallisation and water of constitution. The formula weight contains only one exchangeable proton (in the Sb–OH hydroxyl group[163]). Singly charged ions (Rb^+ and Cs^+) are sorbed by an ion exchange mechanism, unlike the doubly and triply charged ions (whose sorption is thought[157,163] to involve a more complicated mechanism).

From these results, and using the criteria for the monofunctionality of the cation exchanger discussed above, the authors conclude[162,163] that ZrSb is polyfunctional, either because it contains more than one type of functional group or because the single functional group $[Sb(OH)_6]^-$ is connected to the exchanger skeleton in different ways. However, no data on the structure of the ZrSb exchanger or on the constitution of the $[Sb(OH)_6]^-$ group are given in these papers.

Lapitskii and Tikavyi[155,160,161] treat zirconium antimonate as a polymeric compound of variable composition, consisting of $[SbO_6]^-$ antimony–oxygen octahedra attached to zirconium atoms. By comparing the i.r. spectra of antimony and zirconium hydroxides with those of the hydrogen and the sodium form of ZrSb (whose absorption bands are assigned according to Balicheva and Roi[57,58]) these workers conclude that the cation exchanger structure includes bridging hydroxyl groups



(Sb–O–Zr) whose proton can be exchanged reversibly for different counter-ions[155,161]. It is suggested[155] that, in addition to the proton from the bridging hydroxyl groups, oxonium ions H_3O^+ are also involved in ion exchange on ZrSb, but their absorption band (1710 cm^{-1} according to Yukhnevich[93]) does not appear in the spectra reported by these workers[155,160].

6. Tin Antimonate (Sn(II)Sb, Sn(IV)Sb)

An ion exchanger containing Sb(V) and Sn(II) was synthesised by Abe and Ito[164] by mixing solutions of stannous chloride and potassium pyroantimonate. Increasing the Sb/Sn(II) ratio in the solution increases the $\overline{Sb}/\overline{Sn}$(II) ratio in the samples from 0.25 to 5. All the samples are stable towards water and mineral acids, but only the samples with a high $\overline{Sb}/\overline{Sn}$ ratio are stable in alkaline solutions. The potentiometric titration curves suggest weakly acidic properties. As we have shown[129], reduction of Sb(V) to Sb(III) with formation of Sn(IV) can be expected in the Sn(II)–Sb(V) system.

Several papers on the preparation and ion-exchange properties of tin(IV) antimonate have been published[156,165,166,167]. The Sn(IV)Sb samples were prepared by mixing $SnCl_4$ solutions with solutions of $SbCl_5$[165] or of potassium pyroantimonate[166], or of antimonic acid[166]. The samples obtained by precipitation with antimonic acid are found to have a higher exchange capacity and greater mechanical strength than those prepared by precipitation with potassium pyroantimonate[166].

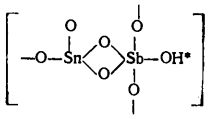
The exchanger is stable in water and in mineral acids (less so in hydrochloric than in nitric and in sulphuric acid), and its stability in these media is higher than that of TiSb.[165] When these samples are heated their capacity decreases: by 21.6% at 100 °C and by 50% at 500 °C.[165] Studies of the chemical and thermal stability of these materials are reported also in Ref. 166.

The capacity of an Sn(IV)Sb sample with $\overline{Sb}/\overline{Sn}$(IV) = 5.10 towards NH_4, alkali metal, and alkaline earth metal ions decreases in the sequence[166]

NH_4^+	$>Ba^{2+}>Na^+\geqslant Ca^{2+}>Mg^{2+}>K^+>Li^+>Rb^+>Cs^+$								
1.94	1.76	1.60	1.55	1.18	1.09	0.88	0.72	0.56	

Measurements of the distribution coefficient have shown that this exchanger has a high affinity for the Hg^{2+}, Pb^{2+}, and Ag^+ ions[166]; the cations Zr^{4+}, Hf^{4+}, Th^{4+}, La^{3+}, Ce^{3+}, Y^{3+}, Sm^{3+}, Nd^{3+}, and Pr^{3+} are fully sorbed at pH 0–6.[165]

Qureshi and coworkers[165] treat Sn(IV) antimonate as an individual compound for which they propose the formula



The hydrogen ion of the Sb–OH group, indicated by an asterisk, takes part in ion exchange.

On the other hand, Mathew and Tandon[166] consider their cation exchanger as a mixture of oxides in which Sb–OH groups only can take part in exchange. They point out that only Rb^+ and Cs^+ are sorbed by an ion exchange mechanism: other ions (Tl^+, Ca^{2+}, Zn^{2+}, Tl^{3+}) are sorbed by a different mechanism[166].

7. Titanoantimonate Cation Exchanger (TiSb, Titanium Antimonate)

This exchanger is prepared by adding a solution of NH_4OH to a solution of $TiCl_4$ and $SbCl_5$ in hydrochloric acid[168–170], or by mixing solutions of titanium tetrachloride and of potassium pyroantimonate (or of hexahydroxoantimonic acid).[171] Samples with different $\overline{Sb}/\overline{Ti}$ ratios have been obtained (0.3–3.6,[168,169] 1.0–1.10,[171] and 0.16–4.7[170]), some of which showed weak crystallinity while others were amorphous to X-rays.

The material consists of mechanically strong, semi-transparent granules suitable for packing in columns[168–171]; however, the TiSb samples obtained from solutions of potassium pyroantimonate are less suitable for column operation and have a lower capacity than the samples prepared from antimonic acid solutions[171].

The TiSb cation exchanger is chemically stable in solutions of mineral acids and alkalis[97,168–172]. Its stability is higher than that of TiAs, TiMo, and TiSe, and it is also more thermally stable than these compounds[4,172], retaining its exchange capacity up to 300 °C.[171] The properties of TiSb (with $\overline{Sb}/\overline{Ti} = 1.04$) are unaffected by a dose of 4×10^7 Rad of γ-radiation[171]. The exchange of ions bearing different charges (Cs^+, Hg^{2+}, Tl^+) on TiSb obeys the law of mass action[173].

Fairly large differences in exchange capacity are reported by different workers for samples of similar composition: for $\overline{Sb}/\overline{Ti} = 1$, $\Gamma_{Na^+} = 0.73$,[169] for $\overline{Sb}/\overline{Ti} = 1.04$, $\Gamma_{Na^+} = 1.71$,[171] and for $\overline{Sb}/\overline{Ti} = 1.4$, $\Gamma_{Na^+} = 1.5$ mg-equiv g^{-1}.[170]

The selectivity of TiSb varies between samples of the same material[168–171]. Qureshi and Kumar[168] ascribe this variation to holes of different size, whose relative numbers are determined by the precipitation conditions rather than by the composition ($\overline{Sb}/\overline{Ti}$) of the sample.

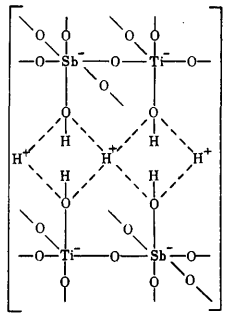
According to some workers[168–171] the potentiometric titration curves of TiSb samples are typical of a monofunctional cation exchanger. On the other hand, other workers[97,124,170] consider TiSb to be a bifunctional exchanger, its potentiometric titration curves (for a 0.1 *N* NaOH solution and samples of different $\overline{Sb}/\overline{Ti}$ composition) lying between those of CAA and titanium hydroxide[124].

The ion-exchange capacity of TiSb samples towards ions with different charges increases with pH.[170] The sorption of silver ions is good on all the TiSb samples. However, unlike other cation exchangers containing antimony (such as PSb,[97,111] SiPSb,[144] TeSb[151]), this material has a capacity for Ag^+ ions not equal to its antimony content[170].

The selectivity towards cations carrying multiple charges increases with the titanium content of the samples[170]:

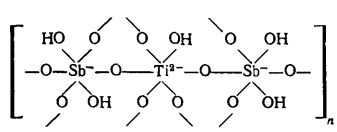
$\overline{Sb}/\overline{Ti} = 2.4$, $Ag^+ > Ba^{2+} > Na^+ > La^{3+}$;
$\overline{Sb}/\overline{Ti} = 1.4$, $Ag^+ > Na^+ > Ba^{2+} > La^{3+}$;
$\overline{Sb}/\overline{Ti} = 0.16$, $Ag^+ > La^{3+} > Na^+ > Ba^{2+}$.

Contradictory results have been published on the structure and on the functional groups of the titanoantimonate cation exchanger. Qureshi and Kumar[168] treat the material as the product of simultaneous condensation of titanium and antimony hydroxides, and they propose a structural formula in which Sb and Ti have oxygen coordination numbers of 5 and 4 respectively. However, in their next paper[169] they assign to the Sb atom its characteristic coordination of 6, but the Ti atom has a coordination of 5:



Gill and Tandon[174] propose the formula $TiO_2 \cdot \frac{1}{2}Sb_2O_5 \cdot 4H_2O$, and they conclude from the i.r. spectra of as-prepared and of baked samples that OH^- groups are responsible for the ion-exchange properties of the material (without specifying whether those groups are attached to Sb or Ti atoms).

Using the concepts on the structure of inorganic cation exchangers developed in Ref. 96 we can describe TiSb as a polymer consisting of alternate $[SbO_{x/2}(OH)_{6-x}]^-$ and $[TiO_{y/2}(OH)_{6-y}]^{2-}$ [124,170] (or $[TiO_{y/3}(OH)_{6-y}]^{-(2-y/3)}$) octahedra:

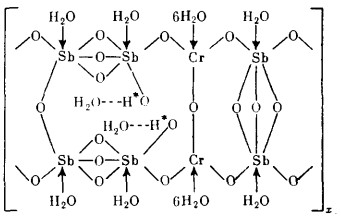


The hydrogen ions which compensate the charge on these octahedra take part in the exchange of counter-ions.

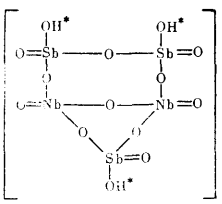
8. Other Mixed Cation Exchangers

Other mixed ion exchangers based on oxygen compounds of antimony have been prepared, mainly by Qureshi and coworkers: NiSb and CoSb,[175] AlSb,[176] FeSb,[165,177,178] CrSb,[179,180] CeSb,[173,174,181] ThSb,[165,182,183] TaSb,[184] NbSb,[185,186] AsSb,[187] and WSb[188]. However, these compounds (described as antimonates of the stated metals) have not been studied as fully as the sorbents discussed above. By mixing solutions of M^{z+} salts and of $SbCl_5$, or potassium pyroantimonate, orantimonic acid, samples with different $\overline{Sb}/\overline{M^{z+}}$ ratios have been prepared. Like the other sparingly soluble antimony compounds, these are found to be chemically very stable. Their capacity decreases as the drying temperature is increased, and increases with the pH of the solution. Each sorbent has a characteristic selectivity towards certain ions: for example, CeSb[181] has a high affinity for Hg^{2+} ions, and NbSb[185] for Mg^{2+} ions.

When the structure of these compounds and the functional groups responsible for their exchange properties are mentioned it is usually assumed that the exchangeable ions are the protons of hydroxyl groups, without specifying whether these groups are attached to Sb or to M atoms[174,184]; alternatively, Qureshi and his coworkers rely on the analogy between antimony and phosphorus compounds, and they suggest the following formulae: for NiSb and CoSb,[185] $M(OH)_2M_3(HSb_2O_7)$; for FeSb,[165] $FeSbO_4.\frac{3}{4}H_2O$; for CrSb,[179] $Cr_2O_3.3Sb_2O_5.22H_2O$, i.e.



and for NbSb[185]



The protons of the SbOH groups (labelled with an asterisk) take part in ion exchange on NbSb and CrSb.

These formulae are unacceptable, since it is well known that antimony differs from phosphorus in not forming tetrahedral oxygen groupings either in solid compounds or in solutions (see, for example, the recent work on the stereochemistry of antimony compounds[86], on the state of antimony in solutions[18,28-35,38], and on the i.r. spectra of antimony compounds[20,21,57,58,130,155,160,162,163]).

9. Modified Sorbents

The term "modified" refers to sorbents supported or precipitated on an inert carrier. The preparation and ion-exchange properties of phosphoantimonic acid (PSb) supported on silica gel have been described[189], and also those of the same exchanger supported on SKT and BAU active carbons[190-192]. The silica gel (or carbon) is steeped in a hydrochloric acid solution of $SbCl_5$ (or a mixed solution of $SbCl_5$ and H_3PO_4), and the resulting material is hydrolysed with water or NH_4OH solution. By baking the finely ground inorganic sorbent (for example, CAA, SiSb, or SiPSb) with polytetrafluoroethylene at 375 °C porous blocks are obtained: these are very convenient for use in columns[193,194]. The capacity (referred to antimony content) is somewhat decreased by this treatment, and the selectivity is slightly affected, but the kinetic characteristics of the material are greatly improved.

A method for preparing heterogeneous compositions from a suspension in acetone of finely divided cation exchanger and the F-26 soluble fluorine-containing polymer has been developed[110,124,195]. By varying the geometric shape of the composition (membranes, tubes, filaments, gauzes, etc.) it is possible to vary the conditions of the sorption process over wide limits, to achieve high flow rates, to control the free volume of the column, to apply an electric field, etc.

Modification of the exchangers yield granulated materials, convenient for column operation, with improved kinetic characteristics and enhanced dynamic exchange capacity, without (as a rule) significant loss of selectivity.

IV. APPLICATIONS OF CATION EXCHANGERS

The high selectivity of sorbents based on oxygen compounds of Sb(V) defines the practical applications of these materials. The most widely used so far is "hydrated antimony pentoxide", marketed by the Italian firm Carlo Erba; the use of the silicoantimonate cation exchanger as a medicinal preparation has also been described. The application of the other sorbents described in this review is still at the stage of practical recommendations by the authors, based on laboratory tests. These recommendations include the possible applications listed below.

CAA: to purify highly radioactive acid solutions from decay products, and to separate ^{137}Cs and ^{90}Sr;[10] to remove Sr^{2+} from dilute nitric acid solutions[50]; to separate alkali[98,196] and alkaline-earth metal ions[197]; to purify lithium chloride solutions from sodium and potassium[198]; to separate Cd^{2+} (or Sr^{2+}, Ba^{2+}) from Ca^{2+} (or Mg^{2+}, Ni^{2+}), and Ca^{2+} from Mg^{2+} (or Ni^{2+}), and for the selective concentration of elements to be sorbed (Cd^{2+}, Sr^{2+}, Ba^{2+}, Ag^+)[13,63,97]; to extract Na radioisotopes from biological samples during neutron activation analysis[11,103,199-203]. The use of antimonic acid activated at 150 and 500 °C in gas chromatography (for the separation of n-butane, n-pentane, n-hexane, n-heptane, and n-octane) has been described[204]. Antimonic acid supported on silica gel or active carbon[104,191,192] is recommended for the removal of Na^+ from solutions of mineral acids[104], and for purifying Li^+, K^+, and Cs^+ salts from Na^+ impurities[190].

SiSb: for the extraction of Cd^{2+}, Sr^{2+}, and Ba^{2+} ions from mixed solutions[134], and for the separation of Cd^{2+} (or Sr^{2+}, Ba^{2+}) ions from Ca^{2+} (or Mg^{2+}, Ni^{2+}), and of Ca^{2+} ions from Mg^{2+} (or Ni^{2+})[134]; SiSb is known as the medicinal preparation "Polisur'min", used in cases of contamination with radiostrontium[205-207].

PSb: for the chromatographic separation of alkali metal ions[128]; to separate the short-lived sodium isotope from large quantities of magnesium and aluminium[208]; to extract strontium from natural waters[209]. Membranes made of PSb have a high electrical conductivity[110,124], and have been used to partition the cathode space in the electrolytic refining of metals[210]; filaments made from PSb have been used for sorbing potassium from biological fluids[195,211].

Because of their high specificity towards Cd^{2+} the cation exchangers SiSb, PSb, and SiPSb have been recommended[127] for the medical treatment of poisoning by cadmium salts. A method of using modified sorbents (CAA, SiSb, SiPSb) for the rapid extraction of sodium from the condensate of boiling water reactors[194] and in the analysis of effluent waters from atomic power stations[193] has been developed.

ZrSb: for the separation of alkali metal ions[152,156]; for the separation of Hg^{2+} from Zn^{2+}, Cd^{2+}, Pb^{2+}, and Bi^{3+}; of Ca^{2+} from Mg^{2+}; of Sr^{2+} from Rb^+, Cs^+, and Ba^{2+}; of Ba^{2+} from La^{3+}; of In^{3+} from Fe^{3+}, Ga^{3+}, and La^{3+}; of Ag^+ from Tl^+.[157]

SnSb: for the following separations. Mg^{2+}–Sr^{2+}, Cd^{2+}, Cu^{2+}, Al^{3+}, La^{3+};[165] Zn^{2+}–Cd^{2+}, Hg^{2+}–Bi^{3+}, Cs^+–UO_2^{2+}, UO_2^{2+}–ZrO_2^{2+}; Th^{4+}–La^{3+}; Th^{4+}–ZrO_2^{2+}; Mn^{2+}–Fe^{3+}; Mg^{2+}–Ca^{2+}; Zn^{2+}–Hg^{2+}–Cd; Al^{3+}–Fe^{3+}–UO_2^{2+}.

TiSb: for the separation of various cations[168,169]. The material can be used to fabricate ion-exchange membranes[124]; filaments made from TiSb compositions are recommended for

the sorption of calcium from complex solutions including biological fluids[212].

Separations of various ions on the following sorbents have been reported:

$NbSb^{186}$: Mg^{2+} — Sr^{2+}, Ba^{2+}, Hg^{2+}, Al^{3+}, Ga^{3+}, Fe^{3+}, La^{3+}, Th^{4+}.
$FeSb^{177}$: Mg^{2+} — Sr^{2+}, Al^{3+} — Ga^{3+}, Y^{3+} — La^{3+}, Th^{4+} — Sm^{3+}, Mg^{2+} — Cd^{2+} — Sm^{3+}.
$AlSb^{176}$: Th^{4+} — UO_2^{2+}, Mg^{2+} — Ca^{2+}, Mg^{2+} — Sr^{2+}, Ni^{2+}—Cu^{2+}—Ag^{+}, Mo^{6+}—Ti^{4+}—W^{6+}.
$CeSb^{181}$: Hg^{2+}—Cd^{2+}, Zn^{2+}, Pb^{2+}, Tl^{+}; Cu^{2+}—Mn^{2+}, Fe^{3+}—Al^{3+}, Zr^{4+}—Th^{4+}.
$ThSb^{183}$: Mg^{2+}—Zn^{2+}, Mg^{2+}—Cd^{2+}, Mg^{2+}—Cu^{2+}, Zn^{2+}—Cd^{2+}, Ni^{2+}—Cu^{2+}, Co^{2+}—Cu, Mn^{2+}—Cu^{2+}.
$TaSb^{184}$: VO^{2+}—Fe^{3+}—Ti^{4+}, VO^{2+}—Al^{3+}—Ti^{4+}, UO_2^{2+} — Ti^{4+}.
$NiSb^{176}$: Bi^{3+}—Cu^{2+}, Cd^{2+}, Al^{3+}, Fe^{3+}, Hg^{2+}, Zn^{2+}, Mn^{2+}, VO^{2+}, Mg^{2+}, Ba^{2+}, Ca^{2+}, Sr^{2+}, Co^{2+}, Pb^{2+}, Y^{3+}.

The high affinity of CrSb for the following ions has been stressed[180]: Ag^{+}, Tl^{+}, Hg^{2+}, Co^{2+}, Pb^{2+}, Ca^{2+}, Sr^{2+}, Fe^{3+}, Bi^{3+}, Al^{3+}, La^{3+}, and Zr^{4+}.

---o0o---

To conclude this review we should point out that cation exchangers based on antimony(V) compounds are scientifically important as well as having great practical value. Crystalline antimonic acid is one of the few "hydrated oxides" for which a simple correlation between composition, structure, and ion-exchange properties has been demonstrated.

Antimony also plays a structure-determining role in many mixed cation exchangers: when symptoms of crystallinity are detected in these materials the X-ray reflections are usually those of CAA. However, the structure of mixed cation exchangers and the role of the second element (added to the antimonic acid polymeric skeleton during the synthesis) are still the subject of debate. The structures proposed by some workers for the mixed sorbents are incompatible with modern views on the crystal chemistry of the oxygen compounds of antimony(V). For example, the coordination number of Sb(V), which is almost invariably 6, is taken[168] to be 5, and by analogy with phosphorus the group $-\mathrm{Sb}(=\mathrm{O})-$ is postulated[175,186]; the soluble form of antimonic acid is written[175] $H_4Sb_2O_7$, and so on. Differences in the coordination number of Sb(V) lead to different interpretations of the nature of the active groups: either in terms of the dissociation of the SbOH groups[168,180,186], which is not typical of the chemistry of antimony, or in terms of exchange with the outer-sphere ligands of the $[SbO_{6/2}]^-$ complex groups[96]. Hence, structural studies of Sb-containing compounds (including those of variable composition) are still needed.

Because of the discrepancies between the ion-exchange characteristics of sorbents of the same type studied in different laboratories, greater attention must be paid to the state of the starting materials in the solutions from which the sorbent is synthesised, especially in the preparation of mixed sorbents, for which it is not always clear whether the product is a single-phased or a multi-phased (micro-heterogeneous) system.

REFERENCES

1. E.I.Kazantsev, V.S.Pakholkov, Z.Yu.Kokoshko, and O.N.Chupakhin, "Ionoobmennye Materialy, Ikh Sintez i Svoistva" (Ion-exchange Materials: Their Synthesis and Properties), Sverdlovsk, 1964.
2. E.A.Materova, F.A.Belinskaya, E.A.Militsina, and P.A.Skabichevskii, Symposium "Ionnyi Obmen" (Ion Exchange), Izd.Leningrad.Univ., 1965, p.3.
3. C.B.Amphlett, "Inorganic Ion Exchangers", Topics in Inorganic and General Chemistry, Monograph 2, Amsterdam, Elsevior, 1964 (Translated into Russian), Izd.Mir, Moscow, 1966, p.145.
4. M.Qureshi, S.Z.Qureshi, J.P.Gupta, and H.S.Rathore, Separation Sci., **7**, 615 (1972).
5. V.Veselý and V.Pekarek, Talanta, **19**, 219 (1972).
6. J.Lefebvre, Compt.rend., **260**, 5575 (1965).
7. J.Lefebvre and F.Gaymard, Compt.rend., **260**, 6911 (1965).
8. M.Abe and T.Ito, J.Chem.Soc.Japan, Pure Chem. Sect., **86**, 1259 (1965).
9. M.Abe and T.Ito, J.Chem.Soc.Japan, Pure Chem. Sect., **87**, 1174 (1966).
10. L.H.Baetsle and D.Huys, J.Inorg.Nuclear Chem., **30**, 639 (1968).
11. F.Girardi and E.Sabbioni, J.Radioanalyt.Chem., **1**, 169 (1968).
12. B.G.Novikov, Symposium "Konferentsiya Molodykh Uchenykh-khimikov Posvyashchennaya 50-letiyu Sovetskoi Vlasti" (Young Chemists' Conference to Celebrate the 50th Anniversary of Soviet Rule), Izd.Leningrad. Univ., 1967, p.20.
13. B.G.Novikov, F.A.Belinskaya, and E.A.Materova, Vestnik Leningrad.Univ., Ser.Fiz.Khim., **2**, 97 (1969).
14. L.Pauling, J.Amer.Chem.Soc., **55**, 1895 (1933).
15. J.Beintema, Proc.Acad.Sci.Amsterdam, **39**, 625 (1936).
16. J.Beintema, Rec.Trav.chim., **56**, 931 (1938).
17. N.Schrewelius, Z.anorg.Chem., **238**, 241 (1938).
18. D.V.S.Jain and A.K.Banerjee, J.Inorg.Nuclear Chem., **19**, 177 (1961).
19. S.H.Gate and E.Richardson, J.Inorg.Nuclear Chem., **23**, 257 (1961).
20. H.Siebert, Z.anorg.Chem., **301**, 161 (1959).
21. H.Siebert, Z.anorg.Chem., **301**, 316 (1959).
22. J.B.Senderens, Bull.Soc.chim.France, **21**, 47 (1899).
23. G.Jander, Kolloid.Z., **23**, 122 (1918).
24. G.Jander and W.Brüll, Z.anorg.Chem., **158**, 321 (1926).
25. A.Lottermoser, Z.Elektrochem., **33**, 514 (1927).
26. G.Jander and H.Y.Ostmann, Z.anorg.Chem., **315**, 241 (1962).
27. G.Jander and H.J.Ostmann, Z.anorg.Chem., **315**, 250 (1962).
28. J.Lefebvre and H.Maria, Compt.rend., **256**, 1982 (1963).
29. J.Lefebvre and H.Maria, Compt.rend., 256, 2400 (1963).
30. J.Lefebvre and H.Maria, Compt.rend., 256, 3121 (1963).
31. J.Lefebvre and H.Maria, Compt.rend., **256**, 4219 (1963).
32. J.Lefebvre and J.Lemerle, Compt.rend., **267**, 604 (1968).
33. J.Lefebvre and J.Lemerle, Compt.rend., **268**, 1125 (1969).

34. J.Lefebvre and J.Lemerle, Compt.rend., **268**, 1760 (1969).
35. J.Lefebvre and J.Lemerle, Compt.rend., **273**, 1201 (1971).
36. S.H.Gate and E.Richardson, J.Inorg.Nuclear Chem., 23, 265 (1961).
37. J.Mazières and J.Lefebvre, Rev.Chim.Mineral., **10**, 457 (1973).
38. J.Lemerle, Thesis, Paris, 1971.
39. E.Fremy, Ann.Chim.Phys., **23**, 405 (1848).
40. A.Geuther, J.Prep.Chem., 4, 438 (1871).
41. C.P.Conrad, Chem.News, **40**, 197 (1879).
42. B.G.Novikov, E.A.Materova, and F.A.Belinskaya, Zhur.Neorg.Khim., 20, 1566 (1975) [Russ.J.Inorg. Chem., No.6 (1975)].
43. M.Abe and T.Ito, Bull.Chem.Soc.Japan, **41**, 333 (1968).
44. A.E.Delacroix, Bull.Soc.chim.France, 22, 1049 (1899).
45. I.N.Lisichkin, A.V.Kerimbekov, N.A.Kerimbekova, and O.Ya.Manashirov, Zhur.Neorg.Khim., **16**, 2133 (1971) [Russ.J.Inorg.Chem., No.8 (1971)].
46. T.G.Balicheva and N.I.Roi, Zhur.Neorg.Khim., 17, 2959 (1972) [Russ.J.Inorg.Chem., No.11 (1972)].
47. G.Jander and A.Simon, Z.anorg.Chem., **127**, 68 (1923).
48. J.B.Senderens, Bull.Soc.chim.France, **21**, 47 (1899).
49. A.E.Delacroix, Bull.Soc.chim.France, **25**, 288 (1901).
50. C.Konečný and V.Kourim, Radiochem.Radioanalyt. Letters, **2**, 47 (1969).
51. I.N.Lisichkin and G.I.Gorshtein, Zhur.Prikl.Khim., **24**, 176 (1972).
52. F.Henz, Z.anorg.Chem., 37, 4 (1903).
53. E.Groschufft, Z.anorg.Chem., 103, 179 (1918).
54. G.Török and J.F.Diehl, Radiochim.Acta, **15**, 96 (1971).
55. J.Lefebvre, Compt.rend., **260**, 5575 (1965).
56. J.M.Colin and J.Lefebvre, Compt.rend., **268**, 1760 (1969).
57. T.G.Balicheva and N.I.Roi, Izv.Akad.Nauk SSSR, Neorg.Materialy, **9**, 277 (1973).
58. T.G.Balicheva and N.I.Roi, Symposium "Problemy Sovremennoi Khimii Koordinatsionnykh Soedinenii" (Problems in Modern Coordination Chemistry), Izd.Leningrad.Univ., 1974, No.4, p.231.
59. M.Abe and T.Ito, Bull.Chem.Soc.Japan, **41**, 2366 (1968).
60. S.Cahuzac and Lefebvre, Compt.rend., **C267**, 1127 (1968).
61. I.N.Bourrelly, Thesis, Paris, 1976.
62. B.G.Novikov, Thesis, Leningrad, 1972.
63. E.I.Kolesnikova, Thesis, Kazan', 1957.
64. K.Dilström and A.Westgren, Z.anorg.Chem., **235**, 153 (1937).
65. U.Dehlinger and R.Glocker, Z.anorg.Chem., **165**, 41 (1927).
66. G.Natta and M.Baccareda, Z.Kristallogr., **85**, 271 (1933).
67. G.Natta and M.Baccareda, Gazzetta, **66**, 308 (1936).
68. V.V.Molodtsova, D.V.Tarasova, V.A.Dzis'ko, L.G.Karakchiev, I.P.Olen'kova, and A.V.Shkarin, Kinetika i Kataliz, **13**, 1258 (1972).
69. D.J.Stewart, O.Knop, C.Ayasse, and F.W.D.Woodhams, Canad.J.Chem., **50**, 690 (1972).
70. A.Simon, Z.anorg.Chem., **165**, 31 (1927).
71. A.Simon and E.Thaler, Z.anorg.Chem., **161**, 113 (1927).
72. The American Society for Testing Materials, Powder Diffraction File, 1973.
73. V.G.Trofimov, A.I.Sheinkman, and G.V.Kleshchev, Zhur.Strukturnoi Khim., **14**, 275 (1973).
74. G.V.Kleshchev, V.G.Trofimov, D.G.Kleshchev, and A.I.Sheinkman, Kristallografiya, **21**, 832 (1976).
75. V.N.Konev, D.G.Kleshchev, A.I.Sheinkman, and G.V.Kleshchev, Symposium "Fizika Metallov i Ikh Soedinenii" (Physics of Metals and Their Compounds), Izd.Ural'sk.Politekh., Sverdlovsk, 1979, p.178.
76. A.E.Vanin, V.N.Konev, D.G.Kleshchev, A.I.Sheinkman, and G.V.Kleshchev, Symposium "Fizika Metallov i Ikh Soedinenii" (Physics of Metals and Their Compounds), Izd.Ural'sk.Politekh., Sverdlovsk, 1979, p.183.
77. J.P.Jolivet and J.Lefebvre, Rev.Chim.Mineral., **9**, 845 (1972).
78. M.Abe, J.Chem.Soc.Japan, Ind.Chem.Sect., **70**, 2226 (1967).
79. G.A.Il'inskii, "Opredelenie Plotnosti Mineralov" (Measurement of the Density of Minerals), Izd. Nauka, Leningrad, 1975.
80. F.Kepák, Chem.Listy, 72, 1121 (1978).
81. B.G.Novikov, F.A.Belinskaya, and E.A.Materova, Vestnik Leningrad.Univ., **22** (4), 100 (1976).
82. B.G.Novikov, F.A.Belinskaya, and E.A.Materova, Vestnik Leningrad.Univ., **4** (1), 29 (1971).
83. B.G.Novikov, F.A.Belinskaya, and E.A.Materova, Vestnik Leningrad.Univ., **4** (1), 35 (1971).
84. Yu.A.Pyatenko, Symposium "Novye Dannye o Mineralakh SSSR" (New Data on Minerals of the Soviet Union), Izd.Nauka, Moscow, 1966, p.119.
85. Internationale Tabellen zur Bestimmung von Kristallstrukturen, 1, 367 (1935).
86. G.B.Bokii and M.A.Porai-Koshits, "Prikladnoi Kurs Rentgenostrukturnogo Analiza" (Applied X-ray Structural Analysis), Izd.Moskov.Univ., 1951, p.104.
87. N.V.Belov, "Mineralogicheskii Sbornik L'vovskogo Geologicheskogo Obshchestva" (Mineralogy Symposium of the L'vov Geological Society), 1950, No.4, p.21.
88. Yu.A.Pyatenko, A.A.Voronkov, and Z.V.Pudovkina, "Mineralogicheskaya Kristallokhimiya Titana" (Mineralogical Crystal Chemistry of Titanium), Izd.Nauka, Moscow, 1976.
89. I.P.Olen'kova and L.M.Plyasova, Zhur.Strukturnoi Khim., **19**, 1040 (1978).
90. H.Nyman and S.Andersson, J.Solid State Chem., **26**, 123 (1978).
91. L.Pauling, "The Nature of the Chemical Bond" (Translated into Russian), Goskhimizdat, Moscow–Leningrad, 1947.
92. B.G.Novikov, T.G.Balicheva, F.A.Belinskaya, and E.A.Materova, Vestnik Leningrad.Univ., 22, 110 (1969).
93. G.V.Yukhnevich, Zhur.Neorg.Khim., **6**, 231 (1961) [Russ.J.Inorg.Chem., No.1 (1961)].
94. A.G.Lukina, E.F.Speranskaya, and R.K.Drachevskaya, Symposium "Prikladnaya i Teoreticheskaya Khimiya" (Applied and Theoretical Chemistry), Alma-Ata, 1974, No.5, p.30.
95. A.G.Lukina, E.F.Speranskaya, and R.K.Drachevskaya, Symposium "Prikladnaya i Teoreticheskaya Khimiya" (Applied and Theoretical Chemistry), Alma-Ata, 1974, No.5, p.43.
96. F.A.Belinskaya, Vestnik Leningrad.Univ., **4** (1), 94 (1974).

97. F.A.Belinskaya, E.A.Materova, E.A.Militsina, L.A.Karmanova, B.G.Novikov, and N.S.Grigorova, Symposium "Ionity i Ionnyi Obmen" (Ion-exchange Materials and Ion Exchange), Izd.Nauka, Leningrad, 1975, p.14.
98. M.Abe, Bull.Chem.Soc.Japan, **42**, 2683 (1969).
99. B.N.Laskorin, L.I.Bondarenko, V.V.Strelko, T.S.Kul'bich, and V.I.Denisov, Dokl.Akad.Nauk SSSR, **229**, 1411 (1976).
100. M.Abe, J.Inorg.Nuclear Chem., **41**, 85 (1979).
101. C.Konečný and I.Hartl, Z.phys.Chem., **256**, 17 (1975).
102. M.Abe, Bull.Chem.Soc.Japan, **52**, 1386 (1979).
103. L.G.Nagy, G.Tőrők, and G.Foti, "Proceedings of the International Conference on Colloid and Surface Science", Budapest, Vol.1, 1975, p.33.
104. R.Caletka, C.Konečný, and M.Šimkova, J.Radioanalyt.Chem., **10**, 5 (1972).
105. J.M.Colin, Thesis, Paris, 1971.
106. T.Ito and M.Abe, Bull.Chem.Soc.Japan, **34**, 1736 (1961).
107. T.Ito and M.Abe, Jap.P.4054 (1960).
108. T.Ito and M.Abe, Denki Kagaku, **33**, 175 (1965).
109. F.A.Belinskaya, E.A.Materova, O.P.Shubalova, L.A.Karmanova, and O.M.Bulaeva, Symposium "Ionnyi Obmen" (Ion Exchange), Izd.Leningrad. Univ., 1965, p.43.
110. F.A.Belinskaya, E.A.Materova, O.P.Shubalova, A.S.Astashenko, L.A.Karmanova, and E.A.Militsina, Symposium "Sintez i Svoistva Ionoobmennykh Materialov" (Synthesis and Properties of Ion-exchange Materials), Izd.Nauka, Moscow, 1968, p.65.
111. E.A.Materova, F.A.Belinskaya, and E.A.Militsina, Izv.Akad.Nauk SSSR, Neorg.Materialy, **5**, 1943 (1969).
112. E.A.Militsina, Thesis, Leningrad, 1974.
113. V.N.Astaf'eva, R.B.Dushin, V.N.Krylov, and A.A.Pospelov, "Issledovanie Mekhanizma Ionnogo Obmena na Amorfnom Neorganicheskom Sorbentem Fosfate Sur'my Metodom Infrakrasnoi Spektroskopii" (Study of the Mechanism of Ion Exchange on the Amorphous Inorganic Sorbent Antimony Phosphate by Infrared Spectroscopy), Izd.Radiev.Inst., RI-21, Leningrad, 1974.
114. V.N.Krylov, V.N.Astaf'eva, V.P.Timakov, and A.M.Trofimov, Trudy Ural'sk.Politekh.Inst., Sverdlovsk, 1975, No.224, p.88.
115. V.F.Tikavyi and A.N.Bratennikova, Izv.Akad.Nauk BelorussSSR, Ser.Khim.Nauk, **4**, 82 (1974).
116. J.P.Jolivet and J.Lefebvre, Bull.Soc.chim.France, 2409 (1975).
117. J.P.Jolivet and J.Lefebvre, Bull.Soc.chim.France, 2415 (1975).
118. J.P.Jolivet and J.Lefebvre, Bull.Soc.chim.France, 2420 (1975).
119. J.P.Jolivet and J.Lefebvre, Bull.Soc.chim.France, 27 (1977).
120. J.P.Jolivet and J.Lefebvre, Bull.Soc.chim.France, 34 (1977).
121. J.P.Jolivet and J.Lefebvre, Bull.Soc.chim.France, 43 (1977).
122. F.A.Belinskaya, E.A.Militsina, and T.N.Runeva, Izv.Akad.Nauk SSSR, Neorg.Materialy, **12**, 1631 (1976).
123. K.F.Lazarev, V.N.Ushatskii, G.N.Kovalev, R.V.Venediktova, Z.A.Zhuravleva, and M.I.Kuznetsov, USSR P.448879 (1973); Byull.Isobretenii, **41**, 12 (1974).
124. F.A.Belinskaya, E.A.Materova, E.A.Militsina, B.G.Novikov, L.A.Karmanova, and V.P.Stepanova, Symposium "Neorganicheskie Ionoobmennye Materialy" (Inorganic Ion Exchangers), Izd.Leningrad.Univ., No.1, 1974, p.67.
125. E.A.Militsina, F.A.Belinskaya, and E.A.Materova, Symposium "Ionnyi Obmen i Ionometriya" (Ion Exchange and Ionometry), Izd.Leningrad.Univ., No.1, 1976, p.43.
126. V.F.Tikavyi and A.N.Bratennikova, Izv.Akad.Nauk BelorussSSR, Ser.Khim.Nauk, **2**, 127 (1976).
127. F.A.Belinskaya, E.A.Militsina, N.S.Grigorova, T.N.Runeva, V.P.Borisov, and L.I.Seletskaya, Symposium "Ionnyi Obmen i Ionometriya" (Ion Exchange and Ionometry), Izd.Leningrad.Univ., No.2, 1979, p.47.
128. M.Abe, J.Chromatogr., **134**, 507 (1977).
129. F.A.Belinskaya, T.N.Runeva, N.E.Ablesimov, and E.A.Militsina, Symposium "Ionnyi Obmen i Ionometriya" (Ion Exchange and Ionometry), Izd.Leningrad.Univ., No.1, 1976, p.51.
130. E.A.Militsina, F.A.Belinskaya, and E.A.Materova, Izv.Akad.Nauk SSSR, Neorg.Materialy, 7, 806 (1971).
131. B.G.Novikov, F.A.Belinskaya, and E.A.Materova, USSR P.324213 (1970); Byull.Izobretenii, 1972, No.2.
132. B.G.Novikov, F.A.Belinskaya, and E.A.Materova, USSR P.307063 (1970); Byull.Izobretenii, 1971, No.20.
133. B.G.Novikov, F.A.Belinskaya, and E.A.Materova, Symposium "Ionnyi Obmen i Ionometriya" (Ion Exchange and Ionometry), Izd.Leningrad.Univ., No.1, 1976, p.66.
134. B.G.Novikov, F.A.Belinskaya, and E.A.Materova, Vestnik Leningrad.Univ., **4**, 94 (1976).
135. B.G.Novikov, F.A.Belinskaya, and E.A.Materova, Symposium "Ionnyi Obmen i Ionometriya" (Ion Exchange and Ionometry), Izd.Leningrad.Univ., No.2, 1979, p.21.
136. B.G.Novikov, F.A.Belinskaya, and E.A.Materova, Symposium "Ionnyi Obmen i Ionometriya" (Ion Exchange and Ionometry), Izd.Leningrad.Univ., No.2, 1979, p.32.
137. V.V.Strelko, L.I.Bondarenko, and T.S.Kul'bich, Symposium "Adsorbtsiya i Adsorbenty" (Adsorption and Adsorbents), No.5, 1977, p.79.
138. V.I.Denisov, V.V.Strelko, L.I.Bondarenko, M.V.Kireev, R.A.Penzin, V.D.Shamarov, and Yu.I.Kandykin, Symposium "Khimiya i Tekhnologiya Neorganicheskikh Sorbentov" (Chemistry and Technology of Inorganic Sorbents), Izd.Perm'.Politekh. Inst., 1979, p.98.
139. F.A.Belinskaya, E.A.Militsina, and N.S.Grigorova, USSR P.415035 (1972); Byull.Izobretenii, 1974, No.6, p.19.
140. F.A.Belinskaya, E.A.Militsina, and N.S.Grigorova, USSR P.415034 (1972); Byull.Izobretenii, 1974, No.6, p.19.
141. F.A.Belinskaya, E.A.Militsina, and N.S.Grigorova, USSR P.415033 (1972); Byull.Izobretenii, 1974, No.6, p.19.
142. F.A.Belinskaya, E.A.Militsina, and N.S.Grigorova, USSR P.509287 (1974); Byull.Izobretenii, 1976, No.13.
143. F.A.Belinskaya, N.S.Grigorova, and E.A.Militsina, Symposium "Ionnyi Obmen i Ionometriya" (Ion Exchange and Ionometry), Izd.Leningrad.Univ., No.1, 1976, p.77.

144. N.S.Grigorova, F.A.Belinskaya, and E.A.Militsina, Symposium "Ionnyi Obmen i Ionometriya" (Ion Exchange and Ionometry), Izd.Leningrad.Univ., No.1, 1976, p.81.
145. B.P.Nikol'skii, N.S.Grigorova, F.A.Belinskaya, and E.A.Militsina, Symposium "Neorganicheskie Ionoobmennye Materialy" (Inorganic Ion Exchangers), Izd.Leningrad.Univ., 1980, No.2, p.88.
146. N.S.Grigorova, B.P.Nikol'skii, F.A.Belinskaya, E.A.Militsina, and I.N.Maslenitskaya, "Tezisy Dokladov Vsesoyuznoi Konferentsii po Ionnomu Obmenu" (Abstracts of Papers Presented to the All-Union Conference on Ion Exchange), Moscow, 1979, p.98.
147. L.I.Bondarenko, T.S.Kul'bich, and V.V.Strelko, Ukrain.Khim.Zhur., **43**, 471 (1977).
148. B.N.Laskorin, L.I.Bondarenko, T.S.Kul'bich, V.V.Strelko, and V.I.Denisov, Dokl.Akad.Nauk SSSR, **239**, 654 (1978).
149. F.A.Belinskaya, E.A.Militsina, and T.N.Runeva, USSR P.517316 (1975); Byull.Izobretenii, 1976, No.22, p.11.
150. E.A.Militsina, F.A.Belinskaya, T.N.Runeva, O.V.Nadezhdina, and I.I.Kozhina, "Tezisy Dokladov Vsesoyuznogo Seminara Khimiya i Tekhnologiya Neorganicheskikh Sorbentov" (Abstracts of Papers Presented to the All-Union Seminar on the Chemistry and Technology of Inorganic Sorbents), Perm', 1976, p.27.
151. T.N.Runeva, E.A.Militsina, and F.A.Belinskaya, Symposium "Ionnyi Obmen i Ionometriya" (Ion Exchange and Ionometry), Izd.Leningrad.Univ., 1979, No.2, p.13.
152. H.O.Phillips and K.A.Kraus, J.Amer.Chem.Soc., **84**, 2267 (1962).
153. J.R.Feuga and T.Kikindai, Compt.rend., **C264**, 8 (1967).
154. A.N.Lapitskii and V.F.Tikavyi, Vestnik Beloruss. Univ., Ser.2, **3**, 19 (1969).
155. A.N.Lapitskii, Thesis, Minsk, 1975.
156. M.Abe, T.Kenjo, and T.Ito, J.Chem.Soc.Japan, Industr.Chem.Sec., **70**, 291 (1967).
157. J.Mathew, S.N.Tandon, and J.S.Gill, J.Radioanalyt. Chem., **49**, 55 (1979).
158. V.F.Tikavyi and A.N.Lapitskii, Vestnik Beloruss. Univ., Ser.2, 1, 39 (1970).
159. A.N.Lapitskii and V.F.Tikavyi, Izv.Akad.Nauk BelorussSSR, Ser.Khim.Nauk, 5, 57 (1971).
160. A.N.Lapitskii and V.F.Tikavyi, Zhur.Neorg.Khim., **19**, 1500 (1974) [Russ.J.Inorg.Chem., No.6 (1974)].
161. V.F.Tikavyi and A.N.Lapitskii, Izv.Vys.Ucheb. Zaved., Khim.i Khim.Tekhnol., **17**, 492 (1974).
162. J.Mathew and S.N.Tandon, Canad.J.Chem., **55**, 3857 (1977).
163. J.Mathew and S.N.Tandon, J.Radioanalyt.Chem., **49**, 55 (1979).
164. M.Abe and T.Ito, J.Chem.Soc.Japan, Industr. Chem.Sec., **70**, 440 (1967).
165. M.Qureshi, V.Kumar, and N.Zehra, J.Chromatogr. **67**, 351 (1972).
166. J.Mathew and S.N.Tandon, Acta Chim.Acad.Sci. Hung., 92, 1 (1977).
167. J.Mathew, N.Singh, C.B.Gupta, and S.N.Tandon, Indian J.Chem., **A16**, 524 (1978).
168. M.Qureshi and V.Kumar, J.Chem.Soc., 1488 (1970).
169. M.Qureshi and J.P.Gupta, J.Chromatogr., **62**, 431 (1971).
170. F.A.Belinskaya and L.A.Karmanova, Symposium "Ionnyi Obmen i Ionometriya" (Ion Exchange and Ionometry), Izd.Leningrad.Univ., **1976**, No.1, p.58.
171. J.S.Gill and S.N.Tandon, J.Radioanalyt.Chem., **20**, 5 (1974).
172. M.Qureshi, N.Zehra, and S.A.Nabi, Talanta, **20**, 609 (1973).
173. J.S.Gill and S.N.Tandon, Internat.J.Appl.Radiation Isotopes, **25**, 31 (1974).
174. J.S.Gill and S.N.Tandon, J.Radioanalyt.Chem., **36**, 345 (1977).
175. M.Qureshi, K.G.Varshney, and N.Fatima, J.Chromatogr., **169**, 365 (1979).
176. J.P.Rawat and J.P.Singh, Chromatographia, **10**, 205 (1977).
177. J.P.Rawat and D.K.Singh, Anal.Chim.Acta, **87**, 157 (1976).
178. J.P.Rawat and D.K.Singh, J.Inorg.Nuclear Chem., **40**, 897 (1978).
179. M.Qureshi, R.Kumar, and H.S.Rathore, Talanta, **19**, 1377 (1972).
180. J.Mathew and S.N.Tandon, Chromatographia, **9**, 235 (1976).
181. J.S.Gill and S.N.Tandon, Talanta, **19**, 1355 (1972).
182. A.K.De and S.K.Das, J.Indian Chem.Soc., **53**, 1063 (1976).
183. A.K.De and S.K.Das, Chromatographia, **11**, 350 (1978).
184. M.Qureshi, J.P.Gupta, and V.Sharma, Analyt.Chem., **45**, 1901 (1973).
185. M.Qureshi, A.P.Gupta, T.Khan, and J.P.Gupta, J.Chromatogr., **144**, 231 (1977).
186. J.P.Gupta, D.V.Nowell, M.Qureshi, and A.P.Gupta, J.Inorg.Nuclear Chem., **40**, 545 (1978).
187. K.F.Lazarev, G.N.Kovalev, and V.N.Ushatskii, USSR P.490493 (1974); Byull.Izobretenii, 1976, No.41, p.21.
188. J.Lemerle and J.Lefebvre, Bull.Soc.chim.France, 409 (1976).
189. R.Caletka and C.Konečný, Radiochem.Radioanalyt. Letters, **9**, 285 (1972).
190. I.A.Kuzin, V.P.Taushkanov, and Yu.A.Pokhitonov, Zhur.Prikl.Khim., **48**, 2778 (1975).
191. V.P.Taushkanov, Yu.A.Pokhitonov, I.A.Kuzin, and R.D.Allabergenov,Zhur.Prikl.Khim., **49**, 63 (1976).
192. V.P.Taushkanov, Yu.A.Pokhitonov, I.A.Kuzin, and R.D.Allabergenov, Zhur.Prikl.Khim., **49**, 470 (1976).
193. L.N.Moskvich, V.A.Mel'nikov, and V.N.Epimakhov, "Tezisy Dokladov Vtoroi Vsesoyuznoi Konferentsii po Metodam Kontsentrirovaniya v Analiticheskoi Khimii" (Abstracts of Papers Presented to the Second All-Union Conference on Methods of Concentration in Analytical Chemistry), Izd.Nauka, Moscow, 1977, p.122
194. L.N.Moskvich, V.A.Mel'nikov, and V.N.Epimakhov, "Tezisy Dokladov Vsesoyuznoi Konferentsii po Ionnomu Obmenu" (Abstracts of Papers Presented to the All-Union Ion Exchange Conference), Izd. Nauka, Moscow, 1979, p.98.
195. F.A.Belinskaya, N.N.Kochergina, and L.A.Karmanova, Symposium "Khimiya i Tekhnologiya Neorganicheskikh Sorbentov" (Chemistry and Technology of Inorganic Sorbents), Perm', 1979, p.103.
196. M.Abe and T.Ito, Bull.Chem.Soc.Japan, **40**, 1013 (1967).
197. M.Abe and K.Uno, Separation Sci.Technol., **14**, 355 (1979).

198. M.Abe, Separation Sci.Technol., **13**, 347 (1978).
199. R.A.Nadkarni and W.D.Ehman, Radiochem.Radioanalyt. Letters, **2**, 161 (1969).
200. W.A.Haller and R.H.Filby, Nuclear Appl., **6**, 365 (1969).
201. S.Meloni, A.Brandone, and V.Maxia, Internat.J. Appl.Radiation Isotopes, **20**, 757 (1969).
202. A.D.Howes, W.A.Haller, and J.A.Dyer, Life Sciences, **8**, 583 (1969).
203. I.Toshio, M.Yatsuka, and M.Tetsuo, Ann.Report Radiation Centre Osaka Prefecture, **10**, 24 (1969).
204. A.Lykourghiotis, J.Hadzistelios, and N.A.Katsanos, J.Chromatogr., **110**, 287 (1975).
205. V.P.Borisov, V.F.Zhuravlev, V.A.Ivanov, and S.F.Severin, Symposium "Neotlozhnaya Pomoshch' Pri Ostrykh Radiatsionnykh Vozdeistviyakh" (Immediate Treatment of Serious Radiation Contaminations), Atomizdat, Moscow, 1976.
206. L.A.Il'in, "Osnovy Zashchity Organizma ot Vozdeistviya Radioaktivnykh Veshchestv" (Protection of the Organism from Radiation Effects), Atomizdat, Moscow, 1977.
207. L.G.Neverov and D.V.Yakovlev, "Rukovodstvo Dlya Srednego Meditsinskogo Rabotnika Radioizotopnoi Diagnosticheskoi Laboratorii" (Manual for Medical Workers in Radio-isotope Diagnostic Laboratories), Izd.Meditsina, Leningrad, 1977.
208. R.F.Brigevich and R.A.Kuznetsov, Radiokhimiya, **9**, 693 (1967).
209. T.V.Grudyno, V.A.Nikashina, and F.A.Belinskaya, Symposium "Neorganicheskie Ionoobmennye Materialy" (Inorganic Ion Exchangers), Izd.Leningrad.Univ., 1980, No.2, p.103.
210. I.B.Obukhova and B.S.Krasikov, Zhur.Prikl.Khim., **44**, 1025 (1971).
211. F.A.Belinskaya and N.N.Kochergina, Symposium "Ionnyi Obmen i Ionometriya" (Ion Exchange and Ionometry), Izd.Leningrad.Univ., 1979, No.2, p.53.
212. F.A.Belinskaya, L.A.Karmanova, and N.N.Kochergina, Symposium "Ionnyi Obmen i Ionometriya" (Ion Exchange and Ionometry), Izd.Leningrad.Univ., 1979, No.2, p.64.

Leningrad State University

Translated from *Uspekhi Khimii*, **49**, 1937-1944 (1980) U.D.C. 577.153.4:541.13

Ion-selective Electrodes in the Study of Cholinesterases

E.A.Materova and E.B.Nikol'skaya

This review is devoted to the application of various types of ion-selective electrodes in the study of the activities and catalytic properties of cholinesterases and also in chemical analysis with participation of these enzymes. Studies using a membrane "substrate" electrode, a glass pH electrode, an oxidation-reduction platinum electrode, and a polycrystalline electrode based on silver sulphide are considered. Investigations using enzyme electrodes based on immobilised cholinesterases are also described. The advantages and disadvantages of individual methods employing different types of ion-selective electrodes are discussed.
The bibliography includes 66 references.

CONTENTS

I. Introduction 953
II. The "substrate" electrode 953
III. The use of the glass pH electrode 954
IV. Other ion-selective electrodes 954
V. Enzyme electrodes using cholinesterases 955
VI. Conclusion 955

I. INTRODUCTION

The special attention devoted to the study of cholinesterases (CE) can be explained not only by the physiological importance of this enzyme, which plays a significant role in the transmission of the nerve pulse, but also by its considerable practical importance in medicine, toxicology, pharmacology, specific syntheses of certain pesticides, and analytical chemistry. Certain diseases are diagnosed on the basis of the level of activity of this enzyme and the degrees of poisoning by certain organophosphorus compounds and carbamates are determined. Cholinesterase is the target of the action of certain insectoacaricides and specific synthesis of the latter therefore requires the knowledge of the specific features of the properties of cholinesterases of different animals. In analytical chemistry enzymatic analysis of organophosphorus compounds and carbamates based on cholinesterase activity is unique in its sensitivity and selectivity.

Cholinesterase is a highly specific catalyst of the hydrolysis of choline esters and their thio-derivatives and of the hydrolysis of certain aromatic and aliphatic carboxylate esters[1]. Cholinesterases which hydrolyse acetylcholine at the highest rate have been called true cholinesterases or acetylcholinesterases (ACE) (E.C.3.1.1.7), while cholinesterases which hydrolyse other choline esters (butyrylcholine, propionylcholine, benzoylcholine, etc.) at the highest rate are called pseudocholinesterases or cholinesterases (E.C.3.1.1.8). The natural substrate of cholinesterases is acetylcholine, in the enzymatic hydrolysis of which the products are an alcohol (choline) and acetic acid:

$$[CH_3CO{-}O{-}CH_2{-}CH_2{-}N(CH_3)_3]^+ + H_2O \overset{CE}{\rightleftarrows} CH_3COOH + [HO{-}CH_2{-}CH_2{-}N(CH_3)_3]^+.$$

All studies on cholinesterases associated with their catalytic properties are bound to include the determination of the enzyme activity or of the rate of enzymatic hydrolysis. Ion-selective electrodes have found extensive applications, among other metals, in the solution of these problems[2,3]. The high selectivity and fairly high sensitivity of the method and the possibility of automation combined with a comparative simplicity of the analysis and of the relevant apparatus have made ionometry an extremely attractive and sometimes irreplaceable procedure for the investigation of the properties and activities of cholinesterases as well as the analysis of their substrates, inhibitors, and activators[4,5].

Ion-selective electrodes sensitive either to the substrate, for example, to choline esters, or to the hydrolysis products (the alcohol or acid) can be used in studies on cholinesterases.

II. THE "SUBSTRATE" ELECTRODE

Only one ion-selective membrane electrode sensitive to choline esters, which has come to be called the substrate electrode, is used nowadays[6]. The electrode is based on a liquid membrane [5% solution of acetylcholine tetra-(*p*-chlorophenyl)borate in *o*-nitroxylene] and is the first ion-selective electrode sensitive to organic cations. This electrode was first proposed by Baum for the investigation of choline esters and was subsequently used by the same worker to determine the cholinesterase activities[7] and kinetic characteristics of ACE and CE [8,9] as well as their substrate specificities[9].

The study of the selectivity of this electrode with respect to different choline esters[9] showed that it increases from choline to benzoylcholine by a factor of 10^5 in the following sequence: choline < acetylcholine < propionylcholine and acetylmethylcholine < butyrylcholine < valerylcholine < benzoylcholine. The sensitivity of the electrode to alkali metal ions[7] proved to be very low compared with acetylcholine: thus the sensitivity to potassium and ammonium ions is smaller by a factor of 10^3 and that with respect to sodium ions by a factor as large as 10^4. The kinetic characteristics of the enzymatic hydrolysis (the Michaelis constant and maximum velocity) determined with the aid of the substrate electrode for the ACE of the electric organ of the eel and the CE of horse blood serum agree satisfactorily with the available literature values of these quantities[10]. Baum and Ward[9] also used the electrode successfully for the analysis of biological media—for the determination of the cholinesterase activity in blood.

A disadvantage of the "substrate electrode" method in kinetic research is the decrease of its sensitivity with increase of the concentration of choline esters, which virtually restricts the region of its applicability to a substrate concentration limit of a little more than 10^{-3} M, because the optimum version of the enzymatic hydrolysis and the determination of its rate from the change in the substrate concentration involves conditions in which 5% hydrolysis takes place during a time interval suitable for the experiment;

this cannot be expected for a substrate concentration greater than 10^{-3} M. The substrate electrode apparently cannot be used in the study of the action of irreversible inhibitors in inhibitor analysis either, because a large substrate concentration (approximately 10^{-2} M) is required to suppress the effect of the inhibitor[11-13]. Furthermore, one should note that a large group of reversible and some irreversible inhibitors of cholinesterases contain in their structure a quaternary nitrogen group[1] and can therefore have an appreciable influence on the readings of the substrate electrode.

III. THE USE OF THE GLASS pH ELECTRODE

Historically the first ion-selective electrode used to determine the activity of cholinesterases was the glass pH electrode[14,15]. A method based on measurements of the rate of the change of pH of the reaction medium owing to the accumulation of acetic acid in the latter during the enzymatic hydrolysis of acetylcholine in an unbuffered or weakly buffered medium has been proposed[16]. The author[16] used this method to investigate the cholinesterase activity of erythrocytes and plasma. It has been called the "ΔpH" method.

The exceptional simplicity of the "ΔpH" method and its high sensitivity attracted the attention of many investigators, who modified it by introducing a number of improvements[4,17-35]. The "ΔpH" method has been applied in clinical studies on cholinesterases[16,20-22,24,25,28], in toxicology[18,19,23,26], in pharmacology[26], in the study of inhibitors and insecticides[17,18,23], and in analytical chemistry for rapid mass analyses[5,36] (up to 50 analyses per hour). It is noteworthy that the cholinesterase enzyme electrodes available at present[5,37-40], which have been described above, are also based on the "ΔpH" method.

However, together with many useful qualities, the "ΔpH" method also suffers from a series of disadvantages. Firstly, the method requires additional calibration in order to obtain the absolute activities of cholinesterases[31-34]. Secondly, the sensitivity of the method depends markedly on the buffer capacity of the system, so that it can be used only for unbuffered and weakly buffered media. Thirdly, considerable errors are associated with the influence of atmospheric CO_2, which necessitates an effective protection from CO_2.

Some of these disadvantages can be avoided in the method of potentiometric titration at constant pH, where the acid accumulated during hydrolysis is titrated with alkali[14,15,41-49]. The titration can be carried out automatically[50-52].

In Yakovlev's modification[49] involving the use of a capillary burette the potentiometric titration method proved to be very convenient for kinetic research; it is difficult to point to a field of study of cholinesterases where it has not been used. Grigor'eva[53] proposed yet another improvement to the method—additional titration with the substrate simultaneously with the titration of the liberated acid with alkali, which made it possible to carry out studies at very low constant substrate concentrations (1×10^{-5} M). Such low substrate concentration can be used only in the substrate electrode method.

The potentiometric titration method has become a kind of standard for tests on other new methods for the investigation of the activity of cholinesterases. However, one should note the limitations of this method: its application is interfered with by atmospheric CO_2 and a high buffer capacity of the medium; comparatively large volumes of solutions of the reactants are required, since a decrease in the volume of the reaction medium entails an appreciable decrease in the accuracy of the method.

IV. OTHER ION-SELECTIVE ELECTRODES

As already mentioned, the hydrogen ion is the first product of cholinesterase hydrolysis which became the object of ionometric measurements. At the present time ionometry has advanced so much both qualitatively and quantitatively that it has become possible to use also other ions produced by the enzymatic hydrolysis in the study of cholinesterases. Ion-selective electrodes based on perfluoroacyl groups, sensitive to acetate, propionate, and butyrate ions, have been developed in the Ionometric Laboratory of Leningrad State University[54] and have been used to determine the activities of cholinesterases in the Laboratory of the Chemistry of Biologically Active Substances of the Institute of Evolutionary Physiology and Biochemistry. Experiments showed that the activity of cholinesterases can be determined in this way; however, the electrodes investigated proved to be insufficiently selective with respect to carboxylate anions in the presence of chloride and bromide anions in 100–1000-fold excess compared with the pyranil determined. The interfering ions cannot be eliminated or their elimination is fairly difficult. The successful application of this method therefore requires other anion-sensitive ion-selective electrodes with a high selectivity with respect to the test anion in the presence of Br^- and Cl^-.

The activity of cholinesterases can be studied in relation to another hydrolysis product—the alcohol, for example, choline, which contains a quaternary nitrogen cationic group. The choline electrode exists, but so far there has been no information about its applications in the analysis of cholinesterase hydrolysis.

Thiocholine has been more convenient for the application of ionometry. The point is that, owing to its SH group, thiocholine is a comparatively powerful reductant, being oxidised by many oxidants, including atmospheric oxygen, to the disulphide (the oxidation-reduction potential of this system is approximately 300 mV), which permits the use of oxidation-reduction electrodes for the determination of thiocholine. Apart from potentiometric methods amperometric and polarographic methods have been used for the determination of thiocholine[3,56]. This review deals only with potentiometric methods.

In 1962 Guilbault et al.[57] used platinum electrodes to determine the activity of cholinesterases with respect to thiol ethers on the basis of the amount of thiocholine. Two platinum electrodes and a reference electrode (a silver|silver chloride electrode) were placed in a buffer solution of the enzyme to which a solution of potassium iodide was added. A small constant current (5–25 μA) was passed through the solution; free iodine was then evolved at the anode in a small and constant amount. The platinum anode and the reference electrode were connected to a potentiometer. When a current was passed, a constant potential difference (approximately 400 mV) arose at the anode. After the addition of the thiocholine ether as the substrate to the reaction mixture, enzymatic hydrolysis began, which resulted in the appearance in the system of thiocholine, a more active reductant than I^-, which caused the depolarisation of the electrode and reduced the potential difference. The rate of decrease of potential in the same range, for example, between 300 and 100 mV, then proved to be directly proportional to the activity of cholinesterase and the final potential depended on the concentration of the thiocholine ether[4,58]. The method is satisfactorily sensitive and highly accurate (to within approximately 1.5%); it is possible to automate the analysis[59]. The inventors of the method have used it successfully to analyse organophosphorus compounds and carbamates[60]. It is noteworthy that the involvement of

platinum electrodes made it necessary to use the method with caution in the study of media with a large amount of protein, since platinum can be "poisoned" under these conditions.

In order to determine the amount of thiol obtained in the hydrolysis of thiocholine esters, an HS-sensitive ion-selective electrode with a polycrystalline membrane based on Ag_2S has also been used[5,61,62]. The method exhibits a high sensitivity combined with an adequate accuracy. However, the readings of the HS^- electrode are unstable in time, probably owing to the erosion of the surface, which appreciably restricts its use for the determination of the activity of cholinesterases[5]. More reliable results are obtained by potentiometric titration with a silver electrode[63].

V. ENZYME ELECTRODES USING CHOLINESTERASES

In the application of cholinesterases for analytical purposes, the device developed in Ref.64, which combines the immobilised enzyme with the corresponding ion-selective electrode, is convenient; it has been called the enzyme electrode. Enzyme electrodes exhibit a high selectivity and permit the analysis not only of ions, but also of non-ionic organic substances[65].

In Guilbault's review[5], devoted to the use of enzyme electrodes in analytical chemistry, a cholinesterase enzyme electrode is described, where cholinesterase solutions are immobilised on the surface of a glass pH electrode with a thin membrane†. Apart from the CE solution, Crochet and Montalvo[37] immobilised in this way a substrate solution, which enabled them not only to determine the concentration of inhibitors in the reaction medium, but also to estimate the activity of CE in biological samples. However, the method has not been used widely in practical applications owing to the technical difficulty of the preparation of the electrode and its short lifetime, which is largely due to the method of immobilisation of the enzyme.

The method of covalent binding of the enzyme to an inert protein has a considerable advantage in this respect. This method of immobilisation has been developed for acetylcholinesterase by a group of French investigators[66], which enabled them to prepare an acetylcholinesterase electrode[38,39] for the determination of the concentrations of acetylcholine and cholinesterase inhibitors—proserine and eserine. After 2 months, the activity of the immobilised enzyme decreased by 90%, while the sensitivity of the electrode to acetylcholine was 1×10^{-4} M. The dependence of the electrode potential on the logarithm of the acetylcholine (AC) concentration in the range 10^{-4}–10^{-2} M at pH 8.5 remained linear ($\Delta E/\lg [AX] \cong 35$ mV). With increase of acetylcholine concentration above 10^{-2} M, the electrode potential remained almost unchanged. Thus the acetylcholinesterase enzyme electrode for the measurement of the acetylcholine concentration is very inferior to the substrate electrode described above. However, in the measurement of the concentrations of certain ACE inhibitors, for example nicotine and particularly proserine (neostigmine) and eserine (physostigmine), the enzyme electrode proved to be extremely sensitive. Thus a linear dependence of this potential on the logarithm of the inhibitor concentration was observed up to 5×10^{-8} M in eserine solutions and up to 5×10^{-7} M in proserine solutions, which makes it possible to regard the enzyme electrode method as extremely promising for analysis.

VI. CONCLUSION

Comparison of the possibilities of a wide variety of methods—"ΔpH", potentiometric titration with a pH electrode, the substrate electrode, and Guilbault's oxidation-reduction method for thiocholine esters (see Table)—shows that, despite the large number of methods (including their modifications), none is universal. In each specific study it is

Brief characteristics of the principal potentiometric methods for the determination of the activity of cholinesterases (under optimum conditions).

Method	Ion-selective electrode	Ion being determined	Sensitivity of method			Accuracy of method	Limitations of method
			w.r.t. enzyme activity, mg^{-1}	w.r.t. substrate concn., M	w.r.t. concn. of hydrolysis product		
"ΔpH"	pH electrode (glass)	hydrogen ion	0.02	$(1-2) \times 10^{-4}$	1×10^{-5}	~10%	unbuffered and weakly buffered media; the presence of CO_2 interferes; special calibration is required
Potentiometric titration with alkali at constant pH	pH electrode (glass)	hydrogen ion	0.01–0.02	1×10^{-5}	1×10^{-5}	~4%	weakly buffered medium; the presence of CO_2 interferes; a large volume of reaction mixture (~10 ml) is required
Substrate electrode method	membrane ion-selective electrode sensitive to choline esters	organic cations: AC, PrC, BuC, and other choline esters	0.01–0.02	1×10^{-5}	—	~8%	high substrate concentrations ($> 10^{-3}$ M) cannot be used; the presence of other quaternary hydrogen compounds interferes
Oxidation-reduction potentiometry	oxidation-reduction electrodes	thiocholine ion	0.005	1×10^{-4}	1×10^{-5}	~1.5%	a protein medium interferes; additional apparatus for electrolysis is needed; the method requires calibration; only thiocholine esters can be used

†This electrode was made by Crochet and Montalvo in 1973.[37]

necessary to select carefully a suitable method which nevertheless introduces errors into the results, frequently exceeding the random errors of the measurements.

All this makes it necessary to seek and design new ion-selective electrodes whose application would improve the method for the investigation of cholinesterases. From our point of view, such research should be carried out by designing new, more sensitive "substrate" electrodes, anion-sensitive electrodes with a response to carboxylate ions and a high selectivity in the presence of halide ions, and a choline electrode with a high selectivity in the presence of choline esters.

A second approach involves the creation of new enzyme electrodes based on cholinesterase preparations. For its successful development, it is necessary to manufacture industrially highly active and stabilised cholinesterase preparations and to develop new methods for their immobilisation.

REFERENCES

1. G.Coelle, "Handbuch der Experimentallen Pharmacologie, Cholinesterases and Anticholinesterase Agents", Springer Verlag, Berlin–New York, 1963.
2. N.U.Bergmeyer (Editor), "Methods of Enzymatic Analysis", Acad.Press, New York–London, 1965.
3. G.G.Guilbault, "Enzymatic Methods of Analysis", Pergamon Press, New York, 1970.
4. C.D.Christian, Advances in Biomedical Engineering and Medical Physics, **4**, 95 (1970).
5. G.G.Guilbault, Comprehensive Analytical Chemistry, **8**, 1 (1977).
6. G.Baum, Anal.Letters, **3**, 105 (1970).
7. G.Baum, Anal.Biochem., **42**, 65 (1971).
8. G.Baum, F.B.Ward, and S.Yaverbaum, Clin.Chim. Acta, **36**, 405 (1972).
9. G.Baum and F.B.Ward, Anal.Biochem., **42**, 487 (1971).
10. A.P.Brestkin, Yu.G.Zhukovskii, and T.M.Sipenkova, Biokhimiya, **39**, 13 (1974).
11. A.P.Brestkin, R.I.Volkova, and E.V.Rozengart, Dokl.Akad.Nauk SSSR, **157**, 1459 (1964).
12. R.I.Volkova, Biokhimiya, **30**, 292 (1965).
13. A.P.Brestkin and E.V.Rozengart, Reakts.Sposob. Org.Soed., **3**, 231 (1966).
14. D.Glick, Biochem.J., **31**, 521 (1937).
15. G.Scos and C.Cattameo, Enzymologia(Italian), **4**, 157 (1937).
16. H.O.Michel, J.Lab.Clin.Med., **34**, 1564 (1949).
17. P.A.Giang and S.A.Nall, Anal.Chem., **23**, Suppl.156, 1 (1959).
18. D.O.Namblin and J.F.Marchand, "Cholinesterase Tests and Their Applicability in the Field", American Cyanamid Co., New York, 1951.
19. J.F.Marchand, J.Amer.Med.Ass., **149**, 738 (1952).
20. W.N.Aldridge and D.R.Davies, Brit.Med.J., 1, 945 (1952).
21. J.H.Wolfsie, Arch.Indust.Health, 16, 403 (1957).
22. J.H.Wolfsie and C.D.Winter, Arch.Indust.Hyg., **6**, 43 (1952).
23. J.H.Tryer, R.G.D.Steel, and H.H.Williams, Arch. Indust.Health, 12, 406 (1955).
24. J.M.O.Alcalde, J.Lab.Clin.Med., **36**, 391 (1950).
25. W.E.MacDonald, C.B.Pollard, and A.H.Gropp, Arch. Indust.Hyg., **6**, 241 (1952).
26. J.P.Frawley, H.N.Fuyat, E.C.Hagan, and O.G.Fitzhugh, J.Pharmacol.Exp.Ther., **105**, 156 (1952).
27. S.Shibata and H.Takahashi, Bull.Yamagushi Med. School, 1, 188 (1953).
28. D.N.Molander, M.M.Friedman, and J.S.La Due, Ann.Intern.Med., **41**, 1139 (1954).
29. J.Grégoire, M.Cotte, J.Grégoire, and N.Limozin, Bull.Soc.Chim.Biol.Paris, **37**, 65 (1955).
30. S.Greenberg and C.Calvert, Med.Techn.Bull., 8, 59 (1957).
31. L.-E.Tammelin, Scand.J.Clin.Lab.Invest., 5, 267 (1953).
32. L.-E.Tammelin and H.Low, Acta Chem.Scand., 5, 322 (1951).
33. L.-E.Tammelin and B.Strindberg, Acta Chem.Scand., 6, 1021 (1952).
34. D.W.Evsel, H.J.Frurnit, S.D.Silver, and E.C.Steiner, Anal.Chem., **28**, 408 (1956).
35. D.A.Courville and W.Ledington, J.Biol.Chem., **190**, 575 (1951).
36. G.G.Guilbault and K.Gibson, Anal.Chim.Acta, 76, 245 (1975).
37. K.L.Crochet and J.G.Montalvo, Anal.Chim.Acta, **66**, 259 (1973).
38. C.T.Minh, R.Guyonnet, and J.Beax, Compt.rend., **286C**, 115 (1978).
39. C.T.Minh and R.Guyonnet, Compt.rend., **286C**, 357 (1978).
40. P.Duraket, Biochim.Biophys.Acta, **527**, 277 (1978).
41. G.A.Alles and R.C.Hawes, J.Biol.Chem., **133**, 375 (1940).
42. M.C.Sanz, Helv.Physiol.Pharmacol.Acta, 2, 29 (1944).
43. N.Schümmelfeder, Arch.exp.Path.Pharmak., **204**, 454 (1947).
44. A.L.Delannois and H.Casier, Arch.int.Pharmacodyn., **75**, 371 (1948).
45. W.S.H.M.Mommaerts, P.A.Khairallah, and M.F.Dickens, Circulat.Res., 1, 460 (1953).
46. B.N.Smallman and L.S.Wolfe, Enzymologia, **17**, 133 (1955).
47. A.B.Hargreaves, An.Acad.Bras.cienc., 25, 291 (1953).
48. A.B.Hargreaves and da Silva, Hospital (Rio de J.), 55, 99 (1959).
49. V.A.Yakovlev, "Kinetika Fermentativnogo Kataliza" (The Kinetics of Enzyme Catalysis), Izd.Nauka, Moscow, 1965.
50. J.B.Neilands and M.D.Cannon, Anal.Chem., 27, 29 (1955).
51. L.Larsson and B.Hansen, Svensk.kem.tidskr., **68**, 521 (1956).
52. J.Jensen-Holin, H.H.Lansen, K.Miethers, and K.O.Moller, Acta Pharmac., **15**, 304 (1959).
53. G.M.Grigor'eva, Biokhimiya, **29**, 716 (1964).
54. E.A.Materova, S.A.Ovchinnikova, and V.S.Karavan, Elektrokhimiya, 25, 1185 (1979).
55. N.Lakshminarayanaiah, "Membrane Electrodes" (Translated into Russian), Izd.Khimiya, Leningrad, 1979.
56. G.G.Guilbault, Comprehensive Anal.Chem., **8**, 71 (1977).
57. G.G.Guilbault, D.N.Kramer, and P.L.Cannon, Anal.Chem., **34**, 842 (1962).
58. G.G.Guilbault, D.N.Kramer, and P.I.Goldberg, Anal.Biochem., **5**, 208 (1963).
59. E.K.Bauman, L.H.Goodson, G.G.Guilbault, and D.N.Kramer, Anal.Chem., **37**, 1378 (1965).

60. G.G.Guilbault, D.N.Kramer, and P.L.Cannon, Anal.Chem., **34**, 1437 (1962).
61. W.R.Hussein, L.N.von Storp, and G.G.Guilbault, Anal.Chim.Acta, **61**, 89 (1972).
62. G.G.Guilbault and L.N.von Storp, Anal.Chim.Acta, **62**, 425 (1972).
63. L.H.Gruen and B.S.Harrap, Anal.Biochem., **42**, 377 (1971).
64. Recommendations for Nomenclature of Ion-Selective Electrodes, Pure Appl.Chem., **48**, 127 (1976).
65. E.A.Materova and T.Ya.Bart, Symposium, "Ionnyi Obmen i Ionometriya" (Ion Exchange and Ionometry), 1979, No.2, p.73.
66. C.T.Minh, E.Selegny, and C.Brown, Compt.rend., **275C**, 309 (1972).

Leningrad State University

Sechenov Institute of Evolutionary Physiology and Biochemistry, USSR Academy of Sciences, Leningrad

Translated from *Uspekhi Khimii*, 49, 1945-1962 (1980) U.D.C. 546,719'161

Rhenium Fluorides

E.G.Rakov, A.S.Dudin, and A.A.Opalovskii

The properties of simple and complex fluorides of rhenium have been reviewed, and the most important directions of study in the field of rhenium fluorides have been formulated.
The bibliography contains 152 references.

CONTENTS

I. Introduction 958
II. Simple rhenium fluorides 958
III. Rhenium oxide fluorides 960
IV. Complex fluorides and oxide fluorides of rhenium 962
V. Conclusion 963

I. INTRODUCTION

The electronic configuration of the rhenium atom (d^5s^2) and its position in the periodic system make it unusual among transition metals. It can form compounds in which it has oxidation numbers from −1 to +7 (including zero in the carbonyls), many of which are thermally stable. Rhenium compounds have coordination numbers from 4 to 9. Rhenium is the only metal forming a stable heptafluoride. The relative similarity in the affinities of rhenium for oxygen and fluorine leads to the formation of a large number of oxide fluorides and oxofluoro-anions.

The melting point of rhenium (3190°) [1] is exceeded only by those of tungsten (3420°) [1] and carbon, and this opens up extensive possibilities for its practical application. Because of the extremely low concentration of rhenium in ores and concentrates[2,3], a special place in the technology of this metal is occupied by processes for obtaining alloys and coatings; one of the most progressive methods for producing the latter is considered to be the reduction of gaseous fluorides by hydrogen[4-7]. Dozens of papers have been devoted to the development of this method, and their examination represents an independent problem.

Thus rhenium fluorides are of interest from the viewpoints of both chemistry and technology. However, the only review summarising the properties of rhenium fluorides[8] requires supplementing and correcting.

The aim of the present review is to systematise the methods of preparation and properties of rhenium fluorides, and to outline the principal directions of study in this field.

II. SIMPLE RHENIUM FLUORIDES

Rhenium hepta-, hexa-, penta-, and tetrafluorides are known. The highest fluoride, ReF_7, was first obtained from the elements[9,10]. To isolate pure rhenium heptafluoride, the mixture of ReF_6 and ReF_7 formed by fluorinating the metal was heated at 400 °C and a fluorine pressure of ~3 atm. For this purpose, Slivnik and coworkers[11] recommended more rigorous conditions—a fluorine pressure of ~50–60 atm and a temperature of 150–500°. ReF_7 has been successfully synthesised using a solution of KrF_2 in anhydrous HF.[12] Small quantities of the heptafluoride having a low concentration of ReF_6 (~1%) can be obtained by exploding rhenium wire in an atmosphere of fluorinating reagents[13].

The physical properties of the heptafluoride are similar to those of ReF_6 and other metal hexafluorides (Table 1).[14] The high-temperature modification of ReF_7 is cubic, with lattice parameters 6.26 Å at 25° and 6.14 Å at −90°.[14,17] There is no published information on the low-temperature modification. The vapour pressure of ReF_7 is given by the equations[10,14]:

$$\lg p, [\text{atm}] = 10.1624 - 1.4703 \lg T - 2205.8/T \quad (258.68 \leqslant T \leqslant 321.45\ \text{K})$$
$$\lg p, [\text{atm}] = -24.4643 + 9.90825 \lg T - 244.28/T \quad (321.45 \leqslant T \leqslant 347.76\ \text{K}).$$

Table 1. Physical properties of ReF_7 and ReF_6.[10,14]

Parameter	Value	
	ReF_7	ReF_6
Melting point, °C	48.3±0.1	18.5±0.1
Boiling point, °C	73.7±0.2	33.7±0.1
Temperature of phase transformation, °C	−110	−3.45±0.10
Heat of formation in the gaseous state at 298.2 K, kcal mole^{-1}	−337±3[16]	−324±3[16]
Heat of the phase transformation, kcal mole^{-1}	—	2.02±0.01
Heat of fusion, kcal mole^{-1}	1.3±0.2	1.09±0.01
Heat of volatilisation, kcal mole^{-1}	7.6±0.2	6.76±0.05
Heat capacity of the gas at 298.2 K, cal mole^{-1} K^{-1}	31.6±0.3	28.6±0.3
Entropy of the gas at 298.2 K, cal mole^{-1} K^{-1}	84.7*	86.9±0.5
Density of the crystal, g cm^{-3}	4.32 (cubic)	4.06 (cubic) 4.68 (orthorh.)
Density of the liquid, g cm^{-3}	3.65 (52° C)	3.58±0.02 (22° C)

*This value is apparently too low.

The vibrational spectra of ReF_7 (Table 2) have been interpreted with the assumption that the molecule has the pentagonal bipyramidal configuration[18]; this has been confirmed by the ^{19}F NMR spectra[19].

Vapour-phase electron diffraction has confirmed that the ReF_7 molecule belongs to the symmetry point group D_{5h},[24] and the average internuclear distance Re–F has been calculated (1.835 Å). It was also shown that this model is not completely adequate, and that the axial distances are greater than the equatorial distances, by 0.062 Å. The ReF_7 molecule has a non-zero dipole moment[25,26], which is not compatible with simple D_{5h} symmetry. Nevertheless, it is usually assumed that the distortions are small, and this

symmetry has been assumed in calculations of the force constants[22,23,27] and thermodynamic properties[14,22,23].

The photoelectron spectra of ReF_7 have been characterised[28,29], and the ionisation potentials determined. The range 14.1–17.0 eV contains bands assumed to be due to a contribution from molecular orbitals of the p_π-type; the most intense band lies at 14.6 eV.

Table 2. Vibrational wavenumbers in the spectra of ReF_7 (cm^{-1}).

Raman (gas) (Ref.20)	Infrared (gas) (Ref.20)	Raman (liquid) (Ref.21)	Raman (solution in HF) (Ref.21)	Assignment
736	—	736 v.s.*	741 v.s.	$\nu_1=\nu_2$
—	703	—	—	ν_5
645	—	650 w.	650 w.	
597	—	590 med.	594 med.	ν_8
489	—	—	488 s.	ν_{10}
—	—	385 s.	—	
352	353	351 med.	360	$\nu_4=\nu_9$
—	299	—	—	ν_7
—	217	—	—	ν_6

*Symbols: v.s. = very strong, s. = strong, med. = medium, w. = weak.
The wavenumbers ν_3 and ν_{11} were estimated as 800 cm^{-1} and 241 cm^{-1}.[23]

The chemical properties of ReF_7 have been little studied. It is hydrolysed rapidly by water to HF and $HReO_4$. ReF_7 does not react with oxygen up to 500°.[10] In the opinion of some authors[30], the reactivity of ReF_7 in redox reactions is similar to that of ReF_6. Thermodynamic calculations[31] show, however, that ReF_7 is a much stronger oxidising agent than ReF_6. This is confirmed, for example, by the fact that, at the same temperatures, ReF_7 reacts with metallic rhenium, and ReF_6 does not[10].

Attempts to obtain Re^{VII} complexes by bringing ReF_7 into contact with alkali metal fluorides under pressure were unsuccessful[10], but ReF_7 reacts with nitryl and nitrosyl fluorides to form $NOReF_8$ and NO_2ReF_8.[32] The compounds $[ReF_6]^+[SbF_6]^-$ and $[ReF_6]^+[Sb_2F_{11}]^-$ have been isolated by heating ReF_7 with antimony pentafluoride[33]. The force constants of the bond in the $[ReF_6]^+$ cation were found to be much greater than those for ReF_6 and WF_6, indicating the high electronegativity of Re^{VII}.

The solubility of ReF_7 in anhydrous HF at 25° is 0.26 mole in 1000 g HF.[21] The solutions are weakly ionised.

Rhenium hexafluoride has been much more fully characterised. It was first obtained from the elements at 120 to 125°.[34–36] It is usually formed in a mixture with ReF_7,[9] and can be purified by reducing the latter by metallic rhenium at 400°,[10] or by distilling in a stream of dry hydrogen.[37] ReF_6 can also be obtained by treating the metal with ClF_3 [38] or O_2F_2.[39]

The kinetics of the reaction of rhenium and a W–Re alloy with fluorine have been studied[40,41]. An interesting feature is that the fluorination of the metal has a much lower activation energy than the fluorination of transition metal oxides, the activation energy of which is close to 25 kcal $mole^{-1}$.[42] The thermodynamic parameters of the fluorination (from out-of-date original data) have been published[43].

The chief physical properties of ReF_6 are given in Table 1. The low-temperature orthorhombic modification of ReF_6 (VF_3 structure, space group *Pnma*) at −22° has the following lattice parameters: $a = 9.61$; $b = 8.76$; $c = 5.06$ Å; $Z = 4$. The low-temperature modification is isostructural with the cubic phase MoF_6 ($Z = 2$), and at 10 °C has lattice parameters 6.26 ± 0.02 Å.[17] The cubic crystals are glassy. The magnetic moment of ReF_6 is only 0.25 B.M. [8]

The vapour pressure of ReF_6 is given by the equations[10,14]:

$$\lg p, \text{ [atm]} = 9.8264 - 2303.6/T - 0.8327 \lg T \ (262.68 \leqslant T \leqslant 269.70 \text{ K})$$

$$\lg p, \text{ [atm]} = 6.2421 - 1765.4/T - 0.1790 \lg T \ (269.7 \leqslant T \leqslant 291.65 \text{ K})$$

$$\lg p, \text{ [atm]} = 16.3273 - 1956.7/T - 3.599 \lg T \ (291.65 \leqslant T \leqslant 321.21 \text{ K}).$$

These results[10,14] agree with earlier measurements[44]. The wavenumbers in the vibrational spectrum of ReF_6 are given in Table 3. All authors agree that ReF_6 has a regular octahedral configuration. The anomalies in the wavenumbers are attributed to the Jahn–Teller effect[50–52]. Electron diffraction measurements[53] show that the interatomic distances in the octahedron are 1.832 ± 0.004 Å. The force constants of ReF_6 have been published[54].

Table 3. Vibrational frequencies in the spectra of ReF_6 (cm^{-1}).

Infrared (gas) (Refs. 45–48)	Raman (gas) (Refs. 46–48)	Raman (soln. in HF) (Ref. 49)	Assignment	Infrared (gas) (Refs. 45–48)	Raman (gas) (Refs. 46–48)	Raman (soln. in HF) (Ref. 49)	Assignment
755	755	756	ν_1	257	257	—	ν_4
715	715	—	ν_3	246	246	249	ν_5
596	596	578	ν_2	193	193	—	ν_6

The electronic structure of ReF_6 has been described[28,29,55–59]. The photoelectron spectra have been recorded[28,29], and the ionisation potentials of WF_6 and ReF_6 correlated; the bands in the range 15.1–17.2 eV correspond to p_π-orbitals, those in the range 18.0–20.1 eV to p_σ-orbitals, and the band having a maximum at 11.43 eV is due to the additional electron of ReF_6, situated in a $2t_{2g}$-orbital.

The chemical properties of ReF_6 resemble those of other metal hexafluorides[60,61]. It is hydrolysed extremely readily, and on contact with atmospheric moisture it disproportionates to give flocculent black rhenium dioxide[62]. Traces of moisture convert ReF_6 into $ReOF_4$.[63] Hydrolysis by water is sometimes accompanied by the formation of an unstable green solution, which rapidly becomes dark and non-transparent. The green colour of the solution has been attributed to the formation of the unstable anion $ReOF_5^-$.[64]

ReF_6 is coordinatively unsaturated, and forms complexes with alkali metal fluorides[65]; it gives ionic compounds with NOF and NO_2F.[66] In the hexafluoride series, ReF_6 is intermediate between the most reactive PtF_6 and the kinetically most stable SF_6; its properties are similar to those of MoF_6.[30,61]. Like MoF_6 [67,68] and WF_6,[4,69] ReF_6 is reduced to the metal by hydrogen[4,7]. At 200°, the reaction stops when ReF_4 is formed[70,71], but at 250° in a large excess of hydrogen it gives up to 75% yield of the metal[7].

The Gibbs free energies for the reduction of ReF_6 by hydrogen and for the simultaneous reduction of ReF_6 and the higher fluorides of a series of elements of groups III–VI have been calculated[31]. The simultaneous reduction of ReF_6 with

BF_3, NbF_5, MoF_6, and WF_6 by hydrogen is probable at room temperature, and that with SiF_4, TiF_4, and TaF_5 at a temperature above 500–650 K. SO_2 reduces ReF_6; at 400° it converts ReF_6 into ReF_4.[71] Thermodynamic calculations show that many elements can reduce ReF_6 to the metal; the strongest reducing agents include Zr, Ti, and Si.[31]

ReF_6 reacts with the carbonyls of rhenium, tungsten, and molybdenum to give $ReOF_4$, and also ReF_5 in an excess of tungsten carbonyl[72]. A detailed study of the reaction of ReF_6 with $Re_2(CO)_{10}$ in liquid HF made it possible to identify two compounds, for which X-ray diffraction indicated the formulae $Re(CO)_5F.ReF_5$ and $[Re(CO)_6]^+[Re_2F_{11}]^-$.[73] The fluorination of a solution of $Re_2(CO)_{10}$ in 1,1,2-trichlorofluoroethane by xenon difluoride also gives the first of these salts[74].

In HF solution, rhenium hexafluoride is reduced by $N_2H_6F_2$ to $N_2H_6ReF_6$ and $N_2H_6(ReF_6)_2$,[75] and in solution in SO_2 and IF_5 it is reduced by alkali metal iodides to M_2ReF_6 and $MReF_6$ respectively (M = Na, K, Rb, Cs).[76,77] ReF_6 is also reduced by NO ($NOReF_6$ is formed),[66] BCl_3 ($ReCl_5$ is formed),[16] etc.[30] In IF_5 solution, elemental iodine is oxidised to I_2^+ by rhenium hexafluoride.

ReF_6 is readily soluble in anhydrous HF (1.75 mole in 1000 g HF).[49] The molar conductance of this solution is 0.70 Ω·cm·mole, and the degree of ionisation of ReF_6 in solution is ~0.2%.

Rhenium pentafluoride can be obtained together with ReF_4 and $ReOF_4$ by the reaction of tungsten carbonyl with an excess of ReF_6.[72] ReF_5 is also obtained by reducing ReF_6 by hydrogen, silicon[78], metallic tungsten or rhenium[79,80], and PF_3.[30]

Various physical properties of ReF_5 are given in Table 4. ReF_5 crystallises in the orthohombic system, with lattice parameters: $a = 5.70$; $b = 17.23$; $c = 7.67$ Å.[81]

Table 4. Physical properties of ReF_5.[14,72]

Parameter	Value
Melting point, °C	48.0
Boiling point, °C	221.3*
Heat of volatilisation, kcal mole^{-1}	12.0 (221.3 °C)
Heat capacity of the gas at 298.2 K, cal mole^{-1} K^{-1}	25
Entropy of the gas at 298.2 K, cal mole^{-1} K^{-1}	80.7
Entropy of volatilisation, cal mole^{-1} K^{-1}	24.2 (221.3 °C)
Curie–Weiss temperature, K	580

*The boiling point was determined by extrapolation, since above 180 °C ReF_5 disproportionates irreversibly to ReF_4 and ReF_6.[72]

The vapour pressure of ReF_5 is given by the equation[44]:

$$\lg p, [\text{atm}] = 9.024 - 3037/T \quad (321.15 \leqslant T \leqslant 413.15\ \text{K}) .$$

The vibrational wavenumbers of the two possible structural forms of ReF_5, and the thermodynamic properties in the temperature range 298–3200 K, have been calculated[82]. Reference works[14,83] give estimated values of S^0_{298} and C^0_p (298.2) for gaseous ReF_5 (cal mole^{-1} K^{-1}): 81 and 25, and 84.1 and 28.55 [83] respectively.

The mass spectrum of ReF_5 [84–86] has shown that it is associated in the gaseous phase, and exists as dimers and trimers at temperatures close to room temperature.

The chemical properties of ReF_5 have been little studied. It reacts with CCl_4 [72] and is hydrolysed instantly by water to give $ReO_2.2H_2O$ and the ions F^-, ReO_4^-, and ReF_6^{2-}.[8] Like ReF_6, ReF_5 is coordinatively unsaturated, but only a few fluoro-complexes of Re^V are known[8].

Rhenium tetrafluoride is obtained by reducing ReF_6 by metallic rhenium, hydrogen, or SO_2, or by the disproportionation of ReF_5.[72,79] Crystalline ReF_4 sublimes above 300°.[72]

The X-ray diffraction pattern of ReF_4 has been indexed[8] on the basis of a tetragonal cell having the parameters $a = 10.12$ Å and $c = 15.95$ Å.

Estimated values of the thermodynamic functions of gaseous ReF_4 have been published[14,82].

Rhenium tetrafluoride is readily hydrolysed by water according to the equation[8]:

$$ReF_4 + 4\,H_2O \rightarrow ReO_2 \cdot 2H_2O + 4H^+ + 4F^- .$$

The existence of fluorides of rhenium having an oxidation number less than +4 has been doubted by many workers, but Malm and Selig[10] have reported the preparation of the fluoride $ReF_{3.5}$. Other authors[13] considered that they isolated $ReF_{2.99 \pm 0.17}$ and $ReF_{2.05 \pm 0.16}$ by exploding rhenium wire in at atmosphere of SF_6 and PF_5. There are apparently no grounds for regarding these products as individual compounds.

III. RHENIUM OXIDE FLUORIDES

Possible simple oxide fluorides of rhenium(V–VII) are given in Table 5. ReO_3F, ReO_2F_3, $ReOF_5$, and $ReOF_4$ have been most reliably characterised[8]. $ReOF_3$ has also been isolated and described[72].

Table 5. Rhenium oxide fluorides.

Oxidation state of rhenium		
V	VI	VII
$ReOF_3$ (ReO_2F)	$ReOF_4$ (ReO_2F_2)	$ReOF_5$ ReO_2F_3 ReO_3F

Rhenium trioxide fluoride was first obtained by the reaction of ReO_3Cl with anhydrous HF.[87] It can also be synthesised by the reaction of $KReO_4$ with IF_5,[88] of Re_2O_7 with ReF_7,[89] and of Re_2O_7 or $KReO_4$ with an excess of anhydrous HF.[90] ReO_3F melts at 147° and boils at 164° with slight decomposition[87]. At the same time, it has been reported[89] that ReO_3F has the highest thermal stability among rhenium oxide fluorides.

The microwave spectrum of gaseous ReO_3F showed that the bond lengths are Re–O 1.692 Å and Re–F 1.859 Å, and the angle F–Re–O is 109.5°.[91] The calculated dipole moment is 0.85.

The infrared and electronic spectra of gaseous ReO_3F [92] and the Raman and NMR spectra of its solutions in anhydrous HF [90] show that the ReO_3F molecule belongs to the symmetry group C_{3v}. Thus the infrared and Raman spectra show all six vibrational wavenumbers expected for this structure[93,94]; the force constants of the ReO_3F molecule isolated in an argon matrix have been calculated. The photoelectron spectra of

gaseous ReO_3F have been recorded[28,29], and the ionisation potentials determined; the first ionisation potential is 12.37 eV. The calculated thermodynamic functions of gaseous rhenium trioxide fluoride have been published[14,95].

All that is known of the chemical properties of ReO_3F is that it is readily hydrolysed in a moist atmosphere to give HF and $HReO_4$.

Rhenium dioxide trifluoride ReO_2F_3 has been obtained (with small quantities of $ReOF_5$) by fluorinating rhenium oxides or $KReO_4$ in flow[96] and static[89] systems. It is also obtained by the action of a mixture of O_2 and F_2 on metallic rhenium[44]. Pure ReO_2F_3 can be isolated by the reaction of a mixture of Re_2O_7 and KBr (1:1) with bromine trifluoride[94]. Various physical properties of ReO_2F_3 are given in Table 6.

Table 6. Physical properties of ReO_2F_3.[8]

Parameter	Value
Melting point, °C	90
Boiling point, °C	185.4
Heat of volatilisation, kcal mole^{-1}	15.7
Entropy of volatilisation, cal mole^{-1} K^{-1}	34.3

The vapour pressure of ReO_2F_3 is given by the equation[14,44]

$$\lg p,[\text{atm}]=7.48-3437/T \quad (363\leqslant T\leqslant 443\ \text{K}) .$$

Falconer and coworkers[97] found that the ReO_2F_3 molecule is non-polar and apparently belongs to the symmetry point group D_{3h}, with the oxygen atoms in the *trans*-position. Later studies[94] showed that in the gaseous phase, ReO_2F_3 is chiefly monomeric and has a trigonal bipyramidal structure, but with the oxygen atoms in the *cis*-position (symmetry C_{2v}). A study of the dimer $(ReO_2F_3)_2$ in the gaseous phase[26] established the relatively high stability of the system, formed by two oxygen bridges. The high viscosity of ReO_2F_3 indicates association in the liquid phase[8].

The chemical properties of rhenium dioxide trifluoride have been little studied. It is stable in the glass up to the boiling point. Like other Re^{VII} oxide fluorides, it is rapidly hydrolysed to HF and $HReO_4$.

Rhenium oxide pentafluoride $ReOF_5$ is formed by the same reactions as ReO_2F_3, but is obtained in smaller yields[96]. The difference in the volatilities of ReO_2F_3 and $ReOF_5$ makes it possible to separate these substances easily by sublimation. The physical properties of $ReOF_5$ resemble those of ReF_6 and ReF_7 (Table 7).[8,14,44]

The vapour pressure is given by the equations[14,44]:

$$\lg p,[\text{atm}]=6.700-2250/T \quad (273\leqslant T\leqslant 303\ \text{K})$$
$$\lg p,[\text{atm}]=5.739-1958.9/T \quad (303\leqslant T\leqslant 314\ \text{K})$$
$$\lg p,[\text{atm}]=4.846-1678.6/T \quad (314\leqslant T\leqslant 346\ \text{K}) .$$

Analysis of the NMR,[19] infrared, and Raman spectra[98,99] indicates that the $ReOF_5$ molecule belongs to the symmetry group C_{4v}. Thus for gaseous $ReOF_5$, all eleven wavenumbers required for this configuration were detected: 989.8, 738.6, 643, 309, 652, 234, 334, 713, 260, 365, and 125 cm^{-1}.

The calculated thermodynamic functions of gaseous $ReOF_5$ have been published[14]; these have been used[31] to calculate the parameters of the reduction of $ReOF_5$ by hydrogen, and it was shown that it is possible to obtain the metal at room temperature. The first ionisation potential of gaseous $ReOF_5$, determined from the photoelectronic spectrum, is 13.53 eV.[28,29]

Table 7. Physical properties of $ReOF_5$ and $ReOF_4$.[8,14]

Parameter	Value	
	$ReOF_5$	$ReOF_4$
Melting point, °C	40.8	108
Boiling point, °C	73.0	171
Temperature of phase transformation, °C	30	—
Heat of formation in the crystalline state at 298.2 K, kcal mole^{-1}	−294*	—
Heat of the phase transformation, kcal mole^{-1}	1.339	—
Heat of fusion, kcal mole^{-1}	1.220	—
Heat of volatilisation, kcal mole^{-1}	7.720	14.59
Heat of sublimation, kcal mole^{-1}	10.280**	17.82
Heat capacity of the gas at 298.2 K, cal mole^{-1} K^{-1}	28.0	21.7
Entropy of the gas at 298.2 K, cal mole^{-1} K^{-1}	85.6	78.7
Entropy of the phase transformation, cal mole^{-1} K^{-1}	3.868	—
Entropy of fusion, cal mole^{-1} K^{-1}	3.886	—
Entropy of volatilisation, cal mole^{-1} K^{-1}	22.3	32.7
Curie–Weiss temperature, K	—	307

*From published data[100].
**Value at temperatures below 30 °C; above 30 °C, the heat of sublimation is 8.940 kcal mole^{-1}.

The chemical properties of $ReOF_5$ resemble those of ReF_6;[101] at the same time, it is more readily reduced to rhenium(VI) by organic compounds, compared with ReO_2F_3, and on hydrolysis it gives HF and $HReO_4$. The reaction of $ReOF_5$ with NOF and NO_2F gives the ionic salts $NOReOF_6$ and NO_2ReOF_6.[32]

Rhenium oxide tetrafluoride can be obtained by the reactions of $W(CO)_6$ with ReF_6,[72] of ReF_6 with SiO_2,[102] of ReF_6 with ReO_3,[29] of ReF_6 with aqueous HF solution[89,102], and also by fluorinating metallic rhenium or ReO_3 at fluorine : oxygen ratios of 4:1 and 2:1 respectively[89]. Various physical properties of $ReOF_4$ are given in Table 7.

$ReOF_4$ crystals have a monoclinic lattice, space group $C2/c$.[103,104] The values of a, b, and c are 19.01, 5.57, and 14.72 Å; $\beta = 114°$, $Z = 16$; the bond lengths are Re–O 1.65 Å, Re–F(terminal) 1.86 Å, and Re–F(bridging) 1.99 Å and 2.30 Å. The calculated density is 5.28 g cm^{-3}. The magnetic moment of $ReOF_4$ agrees with that expected for Re^{VI}.[8]

The vapour pressure of $ReOF_4$ is given by the equations[44]:

$$\lg p_i[\text{atm}]=8.92-3888/T \quad (323\leqslant T\leqslant 380\ \text{K})$$
$$\lg p_i[\text{atm}]=7.21-3206/T \quad (381\leqslant T\leqslant 445\ \text{K}) .$$

The structural and spectroscopic characteristics of gaseous $ReOF_4$ have been estimated[105]; it has been assigned to the symmetry group C_{2v}, and the thermodynamic functions at 298–2000 K have been calculated on this basis[106]. Later studies[107,108] of the infrared spectra of $ReOF_4$ isolated in an argon matrix indicate that the rhenium oxide tetrafluoride molecule has C_{4v} symmetry. The corrected thermodynamic functions of $ReOF_4$ have been published[95].

Mass-spectrometric studies[89,102] showed that $ReOF_4$ is monomeric in the gaseous phase. The ionisation potentials of gaseous $ReOF_4$ have been published[29]; the first ionisation potential is 10.98 eV. Like $ReOF_5$, $ReOF_4$ can be reduced by hydrogen to the metal[31].

The chemical properties of $ReOF_4$ have been little studied. It reacts vigorously with water to give HF, $ReO_2.2H_2O$, and $HReO_4$; it reacts with CCl_4 to give $ReCl_5$.[72] In HF solution, rhenium oxide tetrafluoride is weakly ionised according to the scheme[102]:

$$ReOF_4 + 2HF \rightleftarrows H_2F^+ + ReOF_5^- .$$

At 250°, $ReOF_4$ vapour reacts slowly with Pyrex, forming black non-volatile $ReOF_3$.[72]

Rhenium oxide trifluoride is extremely hygroscopic; it crystallises in the tetragonal system with unit cell parameters $a = 8.54$ Å and $b = 8.21$ Å.[72] $ReOF_3$ dissolves in water to give a pale-blue solution. The mechanism of the process has not been established.

No reports of the existence of other oxide fluorides have been published, particularly containing rhenium having an oxidation number below +5. This is probably due to the fact that this class of compound has been little studied. At the same time it has been reported[89] that the non-volatile residues formed by the reactions of ReO_2F_3 with Si and of $ReOF_4$ with Si consist of mixtures of lower oxide fluorides of rhenium, which when heated to 500° disproportionate to give ReO_3F, which is more stable at this temperature.

IV. COMPLEX FLUORIDES AND OXIDE FLUORIDES OF RHENIUM

Fluoro-complexes of rhenium are known only for rhenium having oxidation numbers from +4 to +7. The properties of the Re^{IV} salts have been most fully studied, firstly because of their stability and relative ease of handling, and secondly because of the interest in the electronic configuration of the rhenium ion in a d^3-octahedral environment. Complex oxide fluorides are known only for rhenium(V–VII).

Hexafluororhenates(IV) can be obtained either by reducing ReF_6 by alkali metal iodides in liquid SO_2 [109] or by ion exchange from K_2ReF_6, which is formed by the hydrofluorination of hexachloro-, hexabromo-, or hexa-iodorhenates(V),[63,110] and also by treating molten KHF_2 with a $KReO_4 + KI$ mixture or K_2ReBr_6.[79]

The fluororhenates of Na^+, NH_4^+, K^+, Rb^+, and Cs^+ have the K_2GeF_6 structure; the Re–F distance in the almost regular octahedron is ~2 Å.[111,112] The magnetic moment of the crystalline salts (3.3 B.M. at 300 K) and the aqueous solutions (3.47 B.M.) is lower than the spin-only value for a regular d^3-octahedron[113].

The vibrational spectra of a number of salts show that the ReF_6^{2-} ion has D_{4h} symmetry (the force constants and mean amplitudes of the vibrations of the Re–F bond have been published[114,117]). The electronic, infrared, and Raman spectra of a single crystal of Cs_2ReF_6 [118,119] confirmed these conclusions. The ionic character and energy of the Re–X bond in ReX_6^{2-} anions (X = F, Cl, Br, I) decrease from fluorine to iodine[120,121].

Hexafluororhenates(IV) are stable to hydrolysis, and can be recrystallised from aqueous solutions. The solubility decreases from the Na^+ to the Cs^+ salts. The enthalpy of solutions of crystalline K_2ReF_6 in water, determined calorimetrically, is 15.05 kcal mole^{-1}; the calculated enthalpy of hydration of the gaseous ReF_6^{2-} anion is 239 kcal mole^{-1}.[122] Alkalies slowly decompose the ion ReF_6^{2-}, giving ReO_2; decomposition is complete in molten alkali[63]. The thermal decomposition of $(NH_4)_2ReF_6$ in air is accompanied by hydrolysis and oxidation. One of the decomposition products is NH_4ReO_4,[123] taken as ReNF by other workers[79].

Hexafluororhenates(V) are formed by reducing ReF_6 by alkali metal iodides in SO_2 or IF_5 solution[76,109]; $NOReF_6$ is obtained by bringing ReF_6 into contact with nitric oxide[66]. The reaction of Cd, Cu, and Tl with a solution of ReF_6 in acetonitrile gives the solvates $Cd(ReF_6)_2.5CH_3CN$, $CuReF_6.4CH_3CN$, and $TlReF_6.2CH_3CN$.[124] The structure of salts of the ReF_6^- anion is similar to that of the compounds MoF_6^- and WF_6^-.[125]

The anomalies in the temperature dependence of the magnetic properties of the number of hexafluororhenates(V) were attributed to antiferromagnetic interaction[76]. The infrared, Raman, and electronic spectra of the salts $M^+ReF_6^-$ indicate that the ReF_6^- anion belongs to the symmetry group O_h; the force constants of the Re–F bond have been calculated[109,126,127].

Salts of the type $M^+ReF_6^-$ react vigorously with water to give hydrated rhenium dioxide, F^-, ReO_4^-, and ReF_8^{2-};[76] like salts of the type $M_2^+ReF_8^{2-}$, however, decomposition is complete only when fused with alkali.

Fluororhenates(VI) are obtained by the reaction of ReF_6 with alkali metal fluorides. Depending on the conditions, the reactions give salts of the type $M^+ReF_7^-$ or $M_2^+ReF_8^{2-}$,[65] which differ sharply in colour, crystal form, and other properties. The salt K_2ReF_8 crystallises in the orthorhombic system, space group *Pnma*, lattice parameters $a = 8.70 \pm 0.02$ Å, $b = 5.91 \pm 0.02$ Å, $c = 12.53 \pm 0.03$ Å, pyknometric density 4.33 ± 0.03 g cm^{-3}.[128] The basic structural unit of K_2ReF_8 is the $[ReF_8]^{2-}$ anion, having the form of a twisted cube with angle of rotation 45°.[129] The Re–F distance is 1.90 ± 0.03 Å. The magnetic moment of the K^+, Rb^+, and Cl^+ salts lies in the range 1.6–1.7 B.M., and differs considerably from the low moment of ReF_6.[65] The alkali metal octafluororhenates are thermally stable[130].

The action of ReF_6 on M_2ReF_8 gives yellow salts having the composition $MReF_7$ ($M = K^+$, Rb^+, Cs^+).[65] The thermal stability of the hexafluororhenates decreases in the order $Cs^+ > Rb^+ > K^+$. Magnetic measurements[65] showed that these salts are weakly paramagnetic (0.6–0.7 B.M.).

The vibrational spectra of hepta- and octafluoro-complexes of rhenium(VI) [131] show that the MF_8^{n-} ion is a square antiprism, whereas the spectra of $RbReF_7$ and $CsReF_7$ are similar to the spectra of ReF_7 and IF_7, and the ReF_7^- anion can be assigned D_{5h} symmetry.

Hepta- and octafluororhenates(VI) are hydrolysed, with the intermediate formation of $MReOF_5$.[132] The stability to hydrolysis decreases in the order $Na^+ > K^+ > Rb^+ > Cs^+$. K_2ReF_8 dissolves in anhydrous HF with decomposition according to the equation[133]:

$$K_2ReF_8 + n\,HF \rightarrow ReF_6 + 2KF \cdot n\,HF .$$

When this solution is evaporated in a stream of dry nitrogen, ReF_6 volatilises, with the partial entrainment of HF.

As already noted, ReF_7 reacts with nitrosyl and nitryl fluorides to give the adducts $NOReF_8$ and NO_2ReF_8. The Raman spectra of the solid salts and the ^{19}F NMR spectra of their solutions in anhydrous HF show that these complexes are ionic, and that the ReF_8^- anion has D_{4d} symmetry[32].

The complex oxide fluoride of Re^V, $NH_4ReO_{1.5}F_3.H_2O$, has been obtained by the reaction of NH_4ReO_4, NH_4HF_2, and Re at 400 °C and high pressure[134]. The product crystallises in the cubic system (space group *Fm*3*m*) with parameter $a = 16.563$ Å. The calculated density (for $Z = 32$) is 3.55 g cm^{-3}, and the measured density 3.57 g cm^{-3}. The magnetic properties showed the presence of unpaired electrons, possibly due to the existence of isolated $Re_8O_{12}F_{24}$ molecules, joined by NH_4^+ bridges.

Complex oxide fluorides of Re^{VI} can be isolated by the careful hydrolysis of complex fluorides of Re^{VI}.[109,130] The hydrolysis products—salts of the type $M^+ReOF_5^-$—are soluble in methyl ethyl ketone. The oxidation number of rhenium in the caesium salt is +6, and the magnetic moment 1.40 B.M. [132] The vibrational spectra of a series of salts containing the $ReOF_5^-$ anion showed that it has C_{4v} symmetry; the force constants were also calculated[109].

Complex oxide fluorides of Re^{VII}, which can be regarded as derivatives of ReO_3F, ReO_2F_3, and $ReOF_5$, are also known. The first of these ($M_2ReO_3F_3$ and $MReO_2F_4$) are obtained by the action of IF_5 and BrF_3 [135,136] on alkali and alkaline earth metal perrhenates. In addition, ReO_3F complexes of the type $ReO_3F.2DMF$ and $[(CH_3)_4N]ReO_3F_3$ [137] have been isolated, and their infrared spectra studied. The vibrational spectra of $K_2ReO_3F_3$ and $KReO_2F_4$ have been studied[109], and the force constants of both anions have been calculated assuming C_{2v} symmetry.

The only known derivatives of $ReOF_5$ are the ionic complexes $NOReOF_6$ and NO_2ReOF_6, formed by the reaction of $ReOF_5$ with NOF and NO_2F. The $ReOF_6^-$ anion has C_{5v} symmetry[32].

Conductometric titration of $KReO_4$ solutions in hydrofluoric acid[138] showed the formation of the ionic complex $[ReO_4F]^{2-}$. Attempts to isolate the fluoro-complexes of K^+, $Co(NH_3)_6^{3+}$, and $[Co(en)_3]^{3+}$ were unsuccessful. A later study of the ReO_4^-–HF–H_2O system[139] showed the formation of the anionic complexes $[ReO_3(OH)F_2]^{2-}$ at an F^- ion concentration of 0.05–0.26 M, and $[ReO_2(OH)(HF_2^-)_3]^-$ at 0.5–5.3 M, with stability constants $\lg\beta_2 = 4.8 \pm 0.4$ and $\lg\beta_3 = 2.8 \pm 0.4$ respectively.

The synthesis of $H_2[ReOF_5]$ in HF solution has been reported[140]. The electronic spectra of the systems $ReOF_5^{2-}$–H_2SO_4–HF and Re^{VII}–H_2SO_4–HF showed that $[ReOF_5]^-$ ions are formed in solution in the first case, and rhenium(VII) complexes in the second.

V. CONCLUSION

As expected, the physicochemical properties of rhenium fluorides to a large extent resemble those of molybdenum fluorides. The hexafluorides of the two elements show extremely similar chemical and thermodynamic properties[30]. The oxide tetrafluorides have similar melting points and boiling points (108° and 171° for $ReOF_4$, and 97.2° and 186° for $MoOF_4$).[14] The oxide tetrafluorides are polymerised in the crystalline state[104,141] and partly in the vapour. The properties of rhenium dioxide difluoride, which has not yet been obtained, are probably similar to those of molybdenum dioxide difluoride. The pentafluorides also have similar melting points and boiling points (48.0° and 221° for ReF_5, and 67° and 214° for MoF_5),[14] and also tend to polymerise in the liquid and even in the vapour[93].

The extremely limited amount of experimental data for rhenium tetrafluoride and more particularly rhenium trifluoride makes a reliable comparison difficult, but there are grounds for assuming that in this case, analogies with the corresponding molybdenum fluorides will be observed.

Definite similarities are observed in the methods of synthesis and chemical and physicochemical properties of the fluoro- and oxofluoro-complexes of rhenium and molybdenum[61], although in this case also it is difficult to make an exhaustive comparison, because of the limited amount of data for fluoroderivatives of rhenium.

The main difference between rhenium fluorides and oxide fluorides and the analogous molybdenum compounds is the higher reactivity of the rhenium derivatives. Rhenium fluorides are much more sensitive to hydrolysis, and are more readily reduced by hydrogen, organic compounds, and many metals.

Moreover, rhenium, unlike molybdenum, forms compounds in which it has an oxidation number of +7, and this extends considerably the range of fluorides and oxide fluorides formed.

An important problem in the chemistry of rhenium fluorides is the development of reliable methods of synthesis giving sufficiently pure products.

Table 8. Methods of preparing higher fluorides and oxide fluorides of rhenium.

Rhenium fluoride	Starting material	Reagent	Conditions of reaction	Side products	Refs.
ReF_7	Re	F_2	400 °C, 2–3 atm	—	9, 10
ReF_7	Re	F_2	150–500 °C, 50–60 atm	—	11
ReF_7	Re	SF_6	exploding Re wire	~1% ReF_6, SF_4	13
ReF_7	Re	soln. of KrF_2 in HF	20 °C, 1 atm	Kr	12
ReF_6	Re	F_2	120–125 °C, 1 atm	ReF_7	9, 10, 34–36
ReF_6	Re	F_2	150 °C, 1 atm	ReF_7	40, 41
ReF_6	Re	ClF_3	300 °C, 1 atm	—	38
ReF_6	Re	O_2F_2	< 100 °C	—	39
ReO_3F	ReO_3Cl	HF	80 °C, 1 atm	HCl	87
ReO_3F	$KReO_4$	IF_5	100 °C, 1 atm	IO_2F, KF	88
ReO_3F	Re_2O_7	ReF_7	$Re_2O_7:ReF_7 = 4.6:1$*; 150 °C, > 1 atm, 20 h	ReO_2F_3, lower oxide fluorides	89
ReO_3F	Re_2O_7	ReF_7	$Re_2O_7:ReF_7 = 3.6:1$; 150 °C, > 1 atm, 20 h	—	89
ReO_2F_3	Re_2O_7	BrF_3	$Re_2O_7:KBr = 1:1$ excess of BrF_3, 20 → 140 °C, vacuum**	Br_2O_2	94
ReO_2F_3	ReO_2	F_2	100–300 °C, 1 atm	$ReOF_5$, O_2	96
ReO_2F_3	ReO_2	F_2	$ReO_2:Fe_2 = 1:2$; 400 °C > 1 atm	$ReOF_5$, O_2	89
ReO_2F_3	ReO_3	F_2	$ReO_3:Fe_2 = 1:1$; 200 °C, > 1 atm	$ReOF_5$, O_2	89
ReO_2F_3	Re_2O_7	F_2	$ReO_7:F_2 = 1:4$; 200 °C, > 1 atm, 65 h	O_2	89
ReO_2F_3	$KReO_4$	F_2	300 °C, > 1 atm	$ReOF_5$, O_2, KF	96
ReO_2F_3	$KReO_4$	F_2	traces of SiO_2, 350 °C, 1 atm	$ReOF_5$, O_2, KF	89
ReO_2F_3	Re	F_2+O_2	> 25% O_2, 100 °C, 1 atm	$ReOF_5$, ReF_6	96
$ReOF_5$	ReO_2	F_2	100–300 °C, 1 atm	ReO_2F_3, O_2	96
$ReOF_5$	$KReO_4$	F_2	300 °C, 1 atm	ReO_2F_3, O_2, KF	96
$ReOF_5$	Re	F_2+O_2	25% O_2, 100 °C, 1 atm	ReO_2F_3, ReF_6	96
$ReOF_5$	$ReOF_4$	F_2	50% excess of F_2, 300 °C, > 1 atm	—	89
$ReOF_5$	ReO_2	F_2	10% excess of F_2, 250 °C, 12 h, > 1 atm	12 и ReF_6, O_2	89, 99
$ReOF_5$	ReO_3	F_2	200 °C, > 1 atm, 17 h	ReO_2F_3, O_2	89
$ReOF_4$	ReF_6	$Re_2(CO)_{10}$	excess of ReF_6, 20 °C, 1 atm	lower fluorides, CO	72
$ReOF_4$	ReF_6	$W(CO)_6$	large excess of ReF_6, 20 °C, 1 atm	CO, WF_6, ReF_4	72
$ReOF_4$	ReF_6	$W(CO)_6$	small excess of ReF_6, 20 °C, 1 atm	CO, WF_6, ReF_4, ReF_5	72
$ReOF_4$	ReF_6	$M(CO)_6$	20 °C, 1 atm	lower fluorides	72
$ReOF_4$	ReF_6	SiO_2	$ReF_6:SiO_2 = 2:1$; 20 °C, 1 atm	CO, ReF_5, MoF_5 SiF_4	102
$ReOF_4$	ReF_6	H_2O	traces of H_2O in HF, $ReF_6:H_2O = 1:1$	—	89
$ReOF_4$	Re	Fe_2+O_2	$F_2:O_2 = 4:1$; 300 °C, > 1 atm, 17 h	—	89
$ReOF_4$	ReO_3	F_2	$F_2:ReO_3 = 2:1$; 200 °C, > 1 atm	—	89
$ReOF_4$	ReF_6	B_2O_3	$ReF_6:B_2O_3:3:1$, 1 atm	BF_3	152

*Here and subsequently, the molar ratio is given.
**Heating from 20 °C to 140 °C.

An analysis of methods for obtaining higher fluorides and oxide fluorides of rhenium (Table 8) shows that these methods require improvement. Thus the preparation of ReF_7 requires the use of fluorine under pressure, and the only reagent which makes it possible to carry out the synthesis at low temperature and atmospheric pressure is KrF_2. Available published data indicate that even more effective methods of obtaining rhenium heptafluoride may be developed by fluorination using atomic fluorine and by using catalysts[142,143].

Existing methods for synthesising ReF_6 from the elements are simple and satisfactory. Here, however, the main problem of the purification of the starting materials and products is still unsolved; even traces of oxygen in the metal or fluorine lead to the contamination of ReF_6 by oxide fluorides.

Of the methods for synthesising ReO_3F, the best yield with a low concentration of impurities is given by the reaction between ReF_7 and Re_2O_7 (1:3.6).[89]

ReO_2F_3 and $ReOF_5$ are most simply obtained in a mixture by the reactions of oxides of rhenium[89,96] or the metal[96] with a mixture of fluorine and oxygen. The improvement of the synthesis of these individual oxide fluorides will involve the development of effective methods of separation.

The synthesis of $ReOF_4$ using metal carbonyls[72] is complicated, and gives a low yield of the main product, which is difficult to purify. Methods for preparing $ReOF_4$ by fluorinating the metal and ReO_3 are simpler[89], but in this case the product contains impurities which are difficult to remove. The purest oxide tetrafluoride can be obtained by the careful hydrolysis of ReF_6.[89,102] Here, the complexity of the method is associated with the need to observe carefully the reagent ratio and the reaction conditions. The optimum method may be the reaction of B_2O_3 with a slight excess of ReF_6.[152]

The synthesis of lower fluorides and oxide fluorides of rhenium (Table 9) involves the reduction of the higher fluorides by carbonyls, metals, and hydrogen, and also by sulphur dioxide and phosphorus trifluoride. Many transition metals (for example Zr, Ti, etc.) can also be used as reducing agents. Thermodynamic calculations[31] show, however, that many of these reagents can reduce the higher fluorides and oxide fluorides of rhenium to the metal, and this may give mixtures difficult to separate.

Table 9. Methods of preparing lower fluorides and oxide fluorides of rhenium.

Rhenium fluoride	Starting material	Reagent	Conditions of reaction	Side products	Refs.
ReF_5	ReF_6	$W(CO)_6$	small excess of ReF_6, 20 °C, 1 atm	$ReOF_4$, WF_6, ReF_4	72
ReF_5	ReF_6 in WF_6	$W(CO)_6$	small excess of ReF_6, large excess of WF_6, 20 °C, 1 atm	ReF_4, lower fluorides	72
ReF_5	ReF_6	$Mo(CO)_6$	20 °C, 1 atm	$ReOF_4$, MoF_5	72
ReF_5	ReF_6 in HF	Si	20 °C, 1 atm	SiF_4	77
ReF_5	ReF_6 in HF	H_2	20 °C, 3.5 atm	—	77
ReF_5	ReF_6	W	600 °C, < 1 atm	—	80
ReF_5	ReF_6	Re	600 °C, 1 atm	—	80
ReF_5	ReF_6	PF_3	<20 °C, 1 atm	PF_5	30
ReF_4	ReF_6	$W(CO)_6$	large excess of ReF_6, 20 °C, 1 atm	$ReOF_4$, WF_6	72
ReF_4	ReF_6	$W(CO)_6$	small excess of ReF_6, 20 °C, 1 atm	$ReOF_4$, WF_6, ReF_5	72
ReF_4	ReF_6 in WF_6	$W(CO)_6$	small excess of ReF_6, large excess of WF_6, 20 °C, 1 atm	ReF_5	72
ReF_4	ReF_6	Re	400 °C, 1 atm	—	79
ReF_4	ReF_6	SO_2	400 °C, 1 atm	SF_6, O_2	71
ReF_4	ReF_5 in HF	Si	20 °C, 1 atm	SiF_4	77
ReF_4	ReF_6 in HF	Si	20 °C, 1 atm	SiF_4	77
ReF_4	ReF_6	H_2	200 °C, 1 atm	HF	70, 71
ReF_4	ReF_5 in HF	H_2	20 °C, 3.5 atm	HF	77
ReF_4	ReF_6 in HF	H_2	20 °C, 3.5 atm	ReF_5	77
ReF_4	ReF_5	—	240 °C, 1 atm	ReF_6	72
$ReOF_3$	$ReOF_4$	SiO_2	250 °C, 1 atm	SiF_4, O_2	72

In general, the lower fluorides of rhenium have been much less extensively studied than the analogous compounds of molybdenum and tungsten. Thus molybdenum fluorides have been studied by Opalovskii and Khaldoyanidi[61], and the lower fluorides of molybdenum and tungsten by Pervov[144–150], whereas rhenium fluorides have not been studied.

The data in Table 10 indicate that methods for the synthesis of fluoro-complexes of rhenium are insufficiently developed. The synthesis of rhenium complexes is based on reactions of three types—the combination of a rhenium fluoride with the fluoride ion, oxidation–reduction, and partial replacement of oxygen by fluorine in the starting material. There is only one example of the partial hydrolysis of a fluoro-complex to give an oxofluoro-complex (Table 10). Even this group of methods, however, does not exhaust all possible ways of obtaining fluoro- and oxofluoro-derivatives of rhenium. For example, the possible hydrolysis of oxofluoro-complexes has not been carried out, although new methods of synthesis and the preparation of new substances can be expected here; the reactions of $ReOF_5$, ReO_2F_3, and ReO_3F with alkali metal fluorides in the absence of solvent and in non-aqueous solutions have not been studied.

Table 10. Methods of preparing complex fluorides and oxide fluorides of rhenium.

Complex fluoride of rhenium	Starting material	Reagent	Conditions of reaction	Side products	Refs.
$NOReF_8$	ReF_7	NOF	20° C, 1 atm	—	32
NO_2ReF_8	ReF_7	NO_2F	20° C, 1 atm	—	32
M_2ReF_8	ReF_6	MF	200° C, 1 atm	—	65
$MReF_7$	ReF_6	M_2ReF_3	20° C, 1 atm	—	65
$MReF_8$	ReF_6	MI in SO_2 or in IF_5	—60° C, 1 atm	M_2ReF_6, I_2	76
			20° C, 1 atm		109
$MReF_6 \cdot n CH_3CN$	ReF_6 in CH_3CN	M *	20° C, 1 atm	—	125
M_2ReF_6	ReF_6	MI in SO_2	—60° C, 1 atm	—	109
M_2ReF_6	M_2ReX_6 **	HF	450° C, 1 atm	HX	63, 110
$KReF_6$	K_2ReBr_6	KHF_2	700° C, 1 atm	HBr	79
K_2ReF_6	$KReO_4$	KHF_2+KI	800° C, 1 atm	H_2O, I_2	79
$NOReOF_6$	$ReOF_5$	NOF	20° C 1 atm	—	32
NO_2ReOF_6	$ReOF_5$	NO_2F	20° C, 1 atm	—	32
$MReO_2F_4$	$MReO_4$	BrF_3	25° C, 1 atm	Br_2, O_2	136
$M_2ReO_3F_3$	$MReO_4$	IF_5+MF	100° C, 1 atm	IO_2F, MIO_3	135
$ReO_3F.2DMF$	R_2O_7	HF + DMF	25° C, 1 atm	H_2O	137
$[(CH_3)_4N]_2 \times ReO_3F_3$	$ReO_3F.2DMF$	$[(CH_3)_4N]F$	25° C, 1 atm	—	137
$MReOF_5$	$MReF_8$	H_2O	25° C, 1 atm	HF, MF	132
$MReOF_5$	$MReF_7$	H_2O	25° C, 1 atm	HF	109
$NH_4ReO_{1.5}F_3 \cdot H_2O$	NH_4ReO_4+Re	NH_4HF_2	400° C, 1360 atm	—	134

* M=Cd, Cu, Tl.
** X=Cl, Br, I.

Rhenium should form a larger number of fluoro-complexes than are known at present. The known crystalline compounds containing the anions ReF_8^-, $ReOF_6^-$, $ReO_2F_4^-$, $ReO_3F_3^{2-}$, ReF_8^{2-}, ReF_7^-, $ReOF_5^-$, ReF_6^-, $ReO_{1.5}F_3.H_2O^-$, and ReF_6^{2-} [32,65,76,109,132,134,135,136] apparently do not exhaust the possible complex compounds of rhenium. Their theoretical and practical importance is potentially very high, since complex fluorides might be used to separate rhenium fluorides and oxide fluorides, and to purify them and remove them from gas streams.

The detailed study of fluoro-complexes of rhenium containing organic ligands would reveal the regular features of the change in the structure of transition metal compounds.

The thermochemistry and thermodynamics of rhenium fluorides are among the unsolved problems in this field. Their solution would make possible a deeper understanding of the regular features of the change in the strength of the bonds formed by metals with fluorine with change in the position of the metals in the periodic system. The first studies in the thermochemistry of rhenium fluorides were carried out only recently[15,16,100], however, and unfortunately do not extend to complex fluorides.

Simple rhenium fluorides deserve more extensive study. Thus ReF_6 is still the only rhenium fluoride whose electronic structure has been described.

Preliminary calculations by the present authors have shown that ReF_7 can decompose with the liberation of fluorine at 500 °C. The liberation of fluorine or oxygen may be expected when rhenium(VII) oxide fluorides are heated. This is of interest, since at present, PuF_6 is the only known volatile metal fluoride decomposing with the liberation of fluorine[151].

The problems in the field of the chemistry and technology of rhenium fluorides are wider than those listed, but the latter appear to be the most important.

REFERENCES

1. V.P.Glushko (Editor), "Termicheskie Konstanty Veshchestv" (The Thermal Constants of Substances), No.VII, Part 1, VINITI, Moscow, 1974.
2. K.B.Lebedev, "Renii" (Rhenium), Metallurgizdat, Moscow, 1963.
3. V.A.Bardin, V.L.Pokrovskaya, O.V.Popov, and V.S.Matveev, in collected papers "Renii.Khimiya, Tekhnologiya, Analiz" (Collected Papers on the Chemistry, Technology, and Analysis of Rhenium), Izd.Nauka, Moscow, 1976. p.5.
4. V.E.Ivanov, E.P.Nechiporenko, V.M.Krivoruchko, and V.V.Sagalovich, "Kristallizatsiya Tugoplavkikh Metallov iz Gazovoi Fazy" (The Crystallisation of Refractory Metals from the Gaseous Phase), Atomizdat, Moscow, 1974, pp.107, 234.
5. J.I.Federer and C.F.Leitten, Trans.Amer.Nucl. Soc., **7**, 425 (1964).
6. Yu.V.Lakhotkin and A.I.Krasovskii, "Tezisy Dokladov V Vsesoyuznogo Simpoziuma po Khimii Neorganicheskikh Ftoridov" (Summaries of Papers Presented at the Fifth All Union Symposium on the Chemistry of Inorganic Fluorides), Izd.Nauka, Moscow, 1978, pp.158, 159.
7. F.W.Hoertel and J.G.Donaldson, Electrodeposition and Surface Treatment, **2**, 343 (1973/74).
8. R.D.Peacock, in "Comprehensive Inorganic Chemistry", Vol.3, Pergamon Press, Oxford, 1973.
9. J.G.Malm, H.Selig, and S.Fried, J.Amer.Chem.Soc., **82**, 1510 (1960).
10. J.G.Malm and H.Selig, J.Inorg.Nucl.Chem., 20, 189 (1961).
11. J.Slivnik, A.Smalc, and A.Zemljic, Nucl.Inst. Josef Stefan, NIJS Rep. No.R-472, 1965.
12. Yu.V.Drobyshevskii, A.V.Ryzhkov, and V.B.Sokolov, "Tezisy Dokladov V Vsesoyuznogo Simpoziuma po Khimii Neorganicheskikh Ftoridov" (Summaries of Papers Presented at the Fifth All Union Symposium on the Chemistry of Inorganic Fluorides), Izd.Nauka, Moscow, 1978, p.100.
13. R.L.Johnson and B.Siegel, J.Inorg.Nucl.Chem., 31, 2391 (1969).
14. "Osnovnye Svoistva Neorganicheskikh Ftoridov" (Basic Properties of Inorganic Fluorides), Atomizdat, Moscow, 1975.
15. J.Burgess, J.Fawcett, R.D.Peacock, and D.Pickering, J.Chem.Soc., Dalton Trans., 1363 (1976).
16. J.Burgess, C.J.W.Fraser, I.Haigh, and R.D.Peacock, J.Chem.Soc., Dalton Trans., 501 (1973).
17. S.Siegel and D.A.Northrop, Inorg.Chem., **5**, 2187 (1966).
18. H.H.Claassen and H.Selig, J.Chem.Phys., **43**, 103 (1965).
19. N.Bartlett, S.Beaton, L.W.Reeves, and E.J.Wells, Canad.J.Chem., **42**, 2531 (1964).
20. H.H.Claassen, E.L.Gasner, and H.Selig, J.Chem. Phys., **49**, 1803 (1968).
21. H.Selig and E.L.Gasner, J.Inorg.Nucl.Chem., **30**, 658 (1968).
22. G.P.Bhavsar and K.Sathianandan, Current Sci. (India), **41**, 173 (1972).
23. E.Wendling and S.Mahmoudi, Rev.Chim.miner., **9**, 291 (1972).
24. E.J.Jacob and L.S.Bartell, J.Chem.Phys., **53**, 2235 (1970).
25. E.W.Kaiser and J.S.Muenter, J.Chem.Phys., **53**, 53 (1970).
26. W.E.Falconer, Isr.J.Chem., **17**, 31 (1978).
27. S.Mahan, Acta Cienc.Indica, **4**, 31 (1978).
28. V.I.Vovna, A.S.Dudin, L.M.Avkhutskii, E.G.Rakov, F.I.Vilesov, and E.G.Ippolitov, "Tezisy Dokladov V Vsesoyuznogo Simpoziuma po Khimii Neorganicheskikh Ftoridov" (Summaries of Papers Presented at the Fifth All Union Symposium on the Chemistry of Inorganic Fluorides), Izd.Nauka, Moscow, 1978, p.70.
29. A.S.Dudin, V.I.Vovna, E.G.Rakov, and S.N.Lopatin, Izv.Vys.Ucheb.Zaved.SSSR, Khim.i Khim.Tekhnol., **21**, 1564 (1978).
30. J.H.Canterford, T.A.O'Donnell, and A.B.Waugh, Austral.J.Chem., **24**, 243 (1971).
31. A.S.Dudin, V.P.Zagorets, A.P.Darienko, G.A.Yagodin, and E.G.Rakov, "Tezisy Dokladov V Vsesoyuznogo Simpoziuma po Khimii Neorganicheskikh Ftoridov" (Summaries of Papers Presented at the Fifth All Union Symposium on the Chemistry of Inorganic Fluorides), Izd.Nauka, Moscow, 1978, p.102.
32. H.Selig and Z.Karpas, Isr.J.Chem., **9**, 53 (1971).
33. E.Jacob and M.Fähnle, Angew.Chem., **88**, 190 (1976).
34. O.Ruff and W.Kwasnik, Z.anorg.allgem.Chem., **209**, 113 (1932).
35. O.Ruff and W.Kwasnik, Z.anorg.allgem.Chem., **219**, 65 (1934).
36. O.Ruff and W.Kwasnik, Z.anorg.allgem.Chem., **220**, 96 (1934).
37. E.G.Ippolitov, Candidate's Thesis, Institute of General and Inorganic Chemistry, Academy of Sciences of the USSR, Moscow, 1962.
38. N.S.Nikolaev and E.G.Ippolitov, Dokl.Akad.Nauk SSSR, **134**, 358 (1961).
39. A.A.Artyukhov, V.N.Bezmel'nitsyn, Yu.V.Drobyshevskii, V.A.Legasov, V.B.Sokolov, and B.B.Chaivanov, "Tezisy Dokladov V Vsesoyuznogo Simpoziuma po Khimii Neorganicheskikh Ftoridov" (Summaries of Papers Presented at the Fifth All Union Symposium on the Chemistry of Inorganic Fluorides), Izd.Nauka, Moscow, 1978, p.36.
40. E.G.Rakov, S.V.Khaustov, B.V.Gromov, and M.N.Tul'skii, "Tezisy Dokladov IV Vsesoyuznogo Simpoziuma po Khimii Neorganicheskikh Ftoridov" (Summaries of Papers Presented at the Fourth All Union Symposium on the Chemsitry of Inorganic Fluorides), Izd.Nauka, Moscow, 1975, p.35.
41. N.P.Galkin, M.F.Sviderskii, N.P.Petranin, and V.A.Bardin, Zhur.Neorg.Khim., **16**, 1345 (1971) [Russ.J.Inorg.Chem., No.5 (1971)].
42. B.V.Gromov, E.G.Rakov, and G.A.Yagodin, "Tezisy Dokladov XI Mendeleevskogo S'ezda po Obshchei i Prikladnoi Khimii, Vyp.1, Neorganicheskaya Khimiya i Teknologiya Neorganicheskikh Veshchestv" (Summaries of Papers Presented at the Eleventh Mendeleev Congress on Pure and Applied Chemistry,

No.1, Inorganic Chemistry and the Technology of Inorganic Substances), Izd.Nauka, Moscow, 1975, p.46.
43. N.P.Galkin, M.F.Sviderskii, V.A.Bardin, and N.P.Petranin, in collected papers "Metallurgiya Reniya" (Collected Papers on the Metallurgy of Rhenium), Izd.Nauka, Moscow, 1970, p.120.
44. G.H.Cady and G.B.Hargreaves, J.Chem.Soc., 1568 (1961).
45. H.H.Claassen, J.G.Malm, and H.Selig, J.Chem. Phys., **36**, 2890 (1962).
46. H.H.Claassen and H.Selig, Isr.J.Chem., 7, 499 (1969).
47. H.H.Claassen, G.L.Goodman, J.H.Holloway, and H.Selig, J.Chem.Phys., **53**, 341 (1970).
48. R.McDiarmid, J.Mol.Spectrosc., **38**, 495 (1971).
49. B.Frlec and H.H.Hyman, Inorg.Chem., 6, 1596 (1971).
50. I.W.Levin, S.Abramowitz, and A.Mueller, J.Mol. Spectrosc., **42**, 415 (1972).
51. R.S.McDowell and L.B.Asprey, J.Mol.Spectrosc., **45**, 491 (1973).
52. G.R.Meredith, J.D.Webb, and E.R.Bernstein, Mol.Phys., **34**, 995 (1977).
53. E.J.Jacob and L.S.Bartell, J.Chem.Phys., **53**, 2231 (1970).
54. A.K.Dublish, B.B.Strivastava, and A.N.Pandey, Indian J.Pure Appl.Phys., **14**, 413 (1976).
55. R.McDiarmid, J.Mol.Spectrosc., **39**, 332 (1971).
56. D.E.Ellis and A.Rosen, Z.Phys., A, 283, 3 (1977).
57. H.J.T.Preston and J.J.Kaufman, Int.J.Quantum Chem., **12**, 471 (1977).
58. E.R.Bernstein, U.S.NTIS, AD.Rep.1977, AD-AO 43340; Chem.Abs., **88**, 30045 (1978).
59. J.D.Webb and E.R.Bernstein, J.Amer.Chem.Soc., **100**, 483 (1978).
60. B.Weinstock, Chem.Eng.News, **42**, 86 (1964).
61. A.A.Opalovskii, I.I.Tychinskaya, Z.M.Kuznetsova, and P.P.Samoilov, "Galogenidy Molibdena" (Molybdenum Halides), Izd.Nauka, Novosibirsk, 1972.
62. F.A.Cotton and G.Wilkinson, "Advanced Inorganic Chemistry" (Translated into Russian), Vol.3, Izd. Mir, Moscow, 1969, p.395.
63. R.D.Peacock, "The Chemistry of Technetium and Rhenium", Elsevier, Amsterdam, 1966, p.47.
64. J.H.Holloway and J.B.Raynor, J.Chem.Soc., Dalton Trans., 737 (1975).
65. N.S.Nikolaev and E.G.Ippolitov, Dokl.Akad.Nauk SSSR, **140**, 129 (1961).
66. N.Bartlett, S.P.Beaton, and N.K.Jha, Chem. Communs., 168 (1966).
67. D.S.Kopchikhin, A.V.Rychagov, Yu.M.Korolev, and E.G.Rakov, Trudy Moskov.Khim.-Tekhnol.Inst.im. D.I.Mendeleeva, No.62, 60 (1969).
68. M.N.Huberman and R.A.Holzl, J.Appl.Phys., **35**, 1357 (1964).
69. E.G.Rakov and N.A.Veleshko, Atomnaya Tekhnika za Rubezhom, No.1, 18 (1974).
70. J.Gaunt, Trans.Faraday Soc., **50**, 209 (1954).
71. A.G.Sharpe, "Advances in Fluorine Chemistry" (Translated into Russian; Russian translation edited by A.P.Sergeev), Vols.1 and 2, Izd.Khimiya, Moscow–Leningrad, 1964, p.108.
72. G.B.Hargreaves and R.D.Peacock. J.Chem.Soc., 1099 (1960).
73. D.M.Bruce, J.H.Holloway, and D.R.Russell, Chem. Communs., 321 (1973).
74. D.M.Bruce, J.H.Holloway, R.D.Peacock, and E.B.Wilson, "V European Sympos. on Fluorine Chemistry, Abstracts", Aviemore, Scotland, 1974, p.31.
75. B.Frlec, H.Selig, and H.H.Hyman, Inorg.Chem., 6, 1775 (1967).
76. R.D.Peacock, J.Chem.Soc., 467 (1957).
77. G.B.Hargreaves and R.D.Peacock, J.Chem.Soc., 3776 (1958).
78. R.T.Paine and L.B.Asprey, Inorg.Chem., 14, 1111 (1975).
79. D.E.LaValle, R.M.Steele, and W.T.Smith, J.Inorg. Nucl.Chem., **28**, 260 (1966).
80. W.E.Falconer, G.R.Jones, W.A.Sunder, I.Haigh, and R.D.Peacock, J.Inorg.Nucl.Chem., **35**, 751 (1973).
81. A.J.Edwards and G.R.Jones, J.Chem.Soc., A, 1651 (1969).
82. N.P.Galkin, Yu.N.Tumanov, and Yu.P.Butylkin, "Termodinamicheskie Svoistva Neorganicheskikh Ftoridov, Spravochnik" (Reference Book on the Thermodynamic Properties of Inorganic Fluorides), Atomizdat, Moscow, 1972.
83. K.K.Kelley and E.G.King, Contribution to the Data on Theoretical Metallurgy, XIV, Entropies of the Elements and Inorganic Compounds, Bur.Min., Bull. 592, Washington, 1961.
84. M.J.Vasile, G.R.Jones, and W.E.Falconer, Int. J.Mass Spectrom. and Ion Phys., **10**, 457 (1973).
85. M.J.Vasile, G.R.Jones, and W.E.Falconer, Adv.Mass Spectrom., **6**, 557 (1974).
86. W.E.Falconer, G.R.Jones, W.A.Sunder, M.J.Vasile, A.A.Muenter, T.R.Dyke, and W.Klemperer, J.Fluor. Chem., **4**, 213 (1974).
87. A.Engelbrecht and A.V.Grosse, J.Amer.Chem.Soc., **76**, 2042 (1954).
88. E.E.Aynsley and M.L.Hair, J.Chem.Soc., 3747 (1958).
89. W.A.Sunder and F.A.Stevie, J.Fluor.Chem., **6**, 449 (1975).
90. H.Selig and U.El-Gad, J.Inorg.Nucl.Chem., **35**, 3517 (1973).
91. J.F.Lotspeich, A.Javan, and A.Engelbrecht, J.Chem. Phys., **31**, 633 (1959).
92. P.J.Aymonino, H.Schulze, and A.Mueller, Z. Naturforsch., **24b**, 1508 (1969).
93. J.Binenboym, U.El-Gad, and H.Selig. Inorg.Chem., **13**, 319 (1974).
94. I.R.Beattie, R.A.Crocombe, and J.S.Ogden, J.Chem. Soc., Dalton Trans., 1481 (1977).
95. N.I.Zavalishin and A.A.Mal'tsev, Vestnik Moskov. Gos.Univ., Ser.Khim., 17, 123 (1976).
96. E.E.Aynsley, R.D.Peacock, and P.L.Robinson, J.Chem.Soc., 1622 (1950).
97. W.E.Falconer, A.J.Edwards, R.D.Peacock, W.A.Sunder, and M.J.Vasile, V European Sympos. on Fluorine Chemistry, Abstracts, Aviemore, Scotland, 1974, p.72.
98. V.C.Deshpande and R.S.Joshi, Curr.Sci.(India), **44**, 302 (1975).
99. J.H.Holloway, H.Selig, and H.H.Claassen, J.Chem. Phys., **54**, 4305 (1970).
100. J.Burgess, J.Fawcett, N.Morton, and R.D.Peacock, J.Chem.Soc., Dalton Trans., 2149 (1977).
101. N.Bartlett, Angew.Chem., **80**, 453 (1968).
102. R.T.Paine, Inorg.Chem., **12**, 1457 (1973).
103. A.J.Edwards and G.R.Jones, Chem.Communs., 462 (1967).

104. A.J.Edwards and G.R.Jones, J.Chem.Soc., A, 2511 (1968).
105. E.G.Rakov, B.N.Sudarikov, and L.K.Marinina, Trudy Moskov.Khim.-Tekhnol.Inst.im.D.I.Mendeleeva, No.71, 21 (1972).
106. E.G.Rakov, L.G.Koshechko, B.N.Sudarikov, and V.V.Mikulenok, Trudy Moskov.Khim.-Tekhnol.Inst. im.D.I.Mendeleeva, No.71, 28 (1972).
107. R.T.Paine, K.L.Treuil, and F.E.Stafford, Spectrochim.Acta, **A29**, 1891 (1973).
108. R.T.Paine and R.S.McDowell, Inorg.Chem., **13**, 2366 (1974).
109. W.D.Kuhlmann and W.Sawodny, J.Fluor.Chem., 9, 341 (1977).
110. J.H.Canterford and R.Colton, "Halides of the Second and Third Row Transition Metals", Wiley, London, 1968, p.302.
111. E.Weise, Z.anorg.Chem., **283**, 377 (1956).
112. G.R.Clark and D.R.Russell, Acta Crystallogr., **B34**, 894 (1978).
113. K.Schwochau, A.Knappwost, E.Burkard, and T.S.B.N.Raju, Z.Naturforsch., **19a**, 1128 (1964).
114. W.Krasser, Kernforschungsanlage Juelich, JUEL-628-CA, 1969, S.157.
115. W.Krasser and K.Schwochau, Z.Naturforsch., **25a**, 206 (1970).
116. N.K.Sanyal and L.Dixit, Indian J.Pure Appl.Phys., 11, 452 (1974).
117. A.K.Mithal, D.K.Sharma, and A.N.Pandey, Indian J.Phys., 57, 853 (1974).
118. J.A.LoMenzo, S.Strobridge, H.H.Patterson, and H.Engstrom, J.Mol.Spectrosc., 66, 150 (1977).
119. A.M.Black and C.D.Flint, J.Mol.Spectrosc., **70**, 481 (1978).
120. B.N.Figgis, J.Lewis, and F.E.Mabbs, J.Chem. Soc., 3138 (1961).
121. R.Bell, K.Roessler, G.Stoecklin, and S.R.Upadhyay, J.Inorg.Nucl.Chem., **34**, 461 (1972).
122. J.Burgess, N.Morton, and R.D.Peacock, J.Fluor. Chem., **11**, 197 (1978).
123. M.Cowie, C.J.L.Lock, and J.Ozog, Canad.J.Chem., **48**, 3760 (1970).
124. J.A.Berry, A.Prescott, D.W.A.Sharp, and J.M.Winfield, J.Fluor.Chem., **10**, 247 (1977).
125. R.D.W.Kemmitt, D.R.Russell, and D.W.A.Sharp, J.Chem.Soc., 4418 (1962).
126. R.D.Peacock and D.W.A.Sharp, J.Chem.Soc., 2762 (1959).
127. J.A.M.El-Sharkawy and K.D.Warren, Inorg.Nucl. Chem.Letters, **12**, 643 (1976).
128. E.G.Ippolitov and P.A.Koz'min, Dokl.Akad.Nauk SSSR, **142**, 1081 (1962).
129. P.A.Koz'min, Zhur.Strukt.Khim., 5, 70 (1964).
130. E.G.Ippolitov and N.S.Nikolaev, Izv.Akad.Nauk SSSR, Ser.Khim., 748 (1962).
131. A.Beuter, W.D.Kuhlmann, and W.Sawodny, J.Fluor.Chem., **6**, 367 (1975).
132. E.G.Ippolitov, Zhur.Neorg.Khim., **7**, 940 (1962) [Russ.J.Inorg.Chem., No.4 (1962)].
133. N.S.Nikolaev and E.G.Ippolitov, Dokl.Akad.Nauk SSSR, **136**, 111 (1961).
134. F.Pintchovsky, S.Soled, R.G.Lawler, and A.Wold, Inorg.Chem., **14**, 1390 (1975).
135. W.D.Kuhlmann and W.Sawodny, J.Fluor.Chem., **9**, 337 (1977).
136. R.D.Peacock, J.Chem.Soc., 602 (1955).
137. U.Gerlach and C.Ringel, Z.Chem., 17, 306 (1977).
138. M.C.Chakravorti and M.K.Chaudhuri. Z.anorg. allgem.Chem., **398**, 221 (1973).
139. N.D.Ivanova, K.B.Kladnitskaya, N.A.Kostromina, and N.I.Taranenko, Zhur.Neorg.Khim., **22**, 399 (1977)[Russ.J.Inorg.Chem., No.2 (1977)].
140. L.B.Borisova, E.I.Plastinina, and A.N.Ermakov, Dokl.Akad.Nauk SSSR, **223**, 609 (1975).
141. A.J.Edwards and G.R.Jones, J.Chem.Soc., A, 2074 (1968).
142. G.A.Yagodin and E.G.Rakov, "Tezisy Dokladov V Vsesoyuznogo Simpoziuma po Khimii Neorganicheskikh Ftoridov" (Summaries of Papers Presented at the Fifth All Union Symposium on the Chemistry of Inorganic Fluorides), Izd.Nauka, Moscow, 1978, p.7.
143. V.A.Legasov, "Tezisy Dokladov V Vsesoyuznogo Simpoziuma po Khimii Neorganicheskikh Ftoridov" (Summaries of Papers Presented at the Fifth All Union Symposium on the Chemistry of Inorganic Fluorides), Izd.Nauka, Moscow, 1978, p.9.
144. A.V.Gusarov, V.S.Pervov, I.S.Gotkis, L.I.Klyuev, and V.D.Butskii, Dokl.Akad.Nauk SSSR, **216**, 1296 (1974).
145. V.S.Pervov and A.V.Gusarov, Izv.Akad.Nauk SSSR, Neorg.Materialy, 12, 133 (1976).
146. V.D.Butskii and V.S.Pervov, Zhur.Neorg.Khim., **22**, 14 (1977)[Russ.J.Inorg.Chem., No.1 (1977)].
147. V.D.Butskii, V.S.Pervov, and V.G.Sevost'yanov, Zhur.Neorg.Khim., **22**, 1416 (1977)[Russ.J.Inorg. Chem., No.5 (1977)].
148. A.S.Alikhanyan, A.V.Steblevskii, I.P.Malkerova, V.S.Pervov, V.D.Butskii, and V.I.Gorgoraki, "Tezisy Dokladov V Vsesoyuznogo Simpoziuma po Khimii Neorganicheskikh Ftoridov" (Summaries of Papers Presented at the Fifth All Union Symposium on the Chemistry of Inorganic Fluorides), Izd.Nauka, Moscow, 1978, p.29.
149. I.S.Gotkis, A.V.Gusarov, V.S.Pervov, and V.D.Butskii, "Tezisy Dokladov V Vsesoyuznogo Simpoziuma po Khimii Neorganicheskikh Ftoridov" (Summaries of Papers Presented at the Fifth All Union Symposium on the Chemistry of Inorganic Fluorides), Izd.Nauka, Moscow, 1978, p.92.
150. V.S.Pervov, V.D.Butskii, and V.M.Novotortsev, "Tezisy Dokladov V Vsesotuznogo Simposiuma po Khimii Neorganicheskikh Ftoridov" (Summaries of Papers Presented at the Fifth All Union Symposium on the Chemistry of Inorganic Fluorides), Izd.Nauka, Moscow, 1978, p.226.
151. V.A.Zuev and V.I.Lomov, "Geksaftorid Plutoniya" (Plutonium Hexafluoride), Atomizdat, Moscow, 1975.
152. R.C.Burns, T.A.O'Donnell, and A.B.Waugh, J.Fluor.Chem., **12**, 505 (1978).

Mendeleev Moscow Institute of Chemical Technology

Institute of the Mineralogy, Geochemistry, and Crystal Chemistry of the Rare Elements

Translated from *Uspekhi Khimii*, 49, 1963-1989 (1980) U.D.C. 532.61:621.039.3

The Isotope Effect for Diffusion in Solids

A.N.Murin, I.V.Murin, and V.I.Portnyagin

The theory of the isotope effect and its application to studies of migration in metals, ionic crystals, oxides, and other solids are discussed. Methods of measuring the isotope effect are briefly described. 96 references.

CONTENTS

I.	Introduction	968
II.	Theory of the isotope effect	970
III.	Self-diffusion in pure metals	972
IV.	Isotope effects in hetero-diffusion in metals	973
V.	Diffusion in alkali metal halide crystals and in silver halides	974
VI.	Diffusion in transition metal oxides	976
VII.	Other applications of the diffusion isotope effect	978
VIII.	Methods of measuring the diffusion isotope effect	978

I. INTRODUCTION

The study of diffusion processes in solids began several decades ago, and the results obtained have been presented in thousands of original papers and discussed in excellent textbooks and reviews[1-4]. We must nevertheless agree with the reviewer[1] who stated, when discussing diffusion in crystals of alkali metal halides, that "in spite of a large volume of careful work we still lack a detailed understanding of diffusion processes, even in materials as familiar as NaCl". Further developments in our theoretical models and in our experimental techniques are needed to provide a deeper understanding of the nature of migration processes in solids.

The migration of structural units in transport processes (diffusion, ionic conduction, thermo-diffusion, etc.) occurs by a series of jumps from one equilibrium position to the next. Many different models have been proposed to describe these elementary diffusion acts, but most of these models rely on the motion of two types of defect: vacancies (unoccupied crystal lattice sites) and interstitial atoms or ions, or combinations of these defects (divacancies, interstitial configurations, etc.).

We shall confine our discussion (except in the case of electrical conduction) to the direct methods of determining diffusion coefficients by monitoring the redistribution of the diffusing "impurity" atoms in the solid. In this context the term impurity includes labelled atoms, i.e. isotopic indicators (such as ^{22}Na or ^{24}Na) which are chemically almost indistinguishable from the atoms of the matrix (^{23}Na). In some cases (e.g. when nuclear isomers are used) the indicator atoms and the matrix atom have the same weight as well as being chemically identical. The macroscopic significance of the diffusion coefficient D follows directly from Fick's familiar laws, and its microscopic significance (in the simplest case of an isotropic medium) from the Einstein relationship $D = \langle R^2\rangle/6t$, where $\langle R^2\rangle$ is the mean square displacement in time t. For the displacement of a diffusing atom in a simple cubic lattice we can write

$$\langle \mathbf{R}^2\rangle = \omega a^2 t + \left\langle 2 \sum_{j,k} (\mathbf{a}_j \mathbf{a}_k) \right\rangle, \qquad (1)$$

where $\mathbf{a}_i$ is the elementary jump, $(\mathbf{a}_j\mathbf{a}_k)$ is the scalar product of vectors, $a = |\mathbf{a}_i|$, and ω is the jump "frequency" of the diffusing atom in unit time.

In the diffusion of a labelled atom each jump is correlated with the previous jump, and only a fraction of the jumps contributes to random diffusion. It is easy to see that in the vacancy mechanism the probability of a diffusion jump in any direction depends on the direction of the previous jump, since each jump of a diffusing labelled atom leaves behind a vacancy and thus increases the probability of a jump in the reverse direction. Clearly, if an atom carries out a "forward" jump followed by its correlated "backward" jump (to the initial position) the two jumps are mutually compensating. Thus the term $2 \sum_{j,k} (\mathbf{a}_j\mathbf{a}_k)$ in the right-hand side of Eqn.(1), which vanishes in the case of random motion, is not zero in the general case.

We shall introduce the concept of the correlation coefficient f, equal to the fractional number of jumps which make an effective contribution to the random diffusion: $\omega_{\text{eff}} = f\omega$. Hence Eqn.(1) can be re-written

$$D_T = \omega_{\text{eff}} a^2 t = f\omega a^2 t. \qquad (2)$$

The correlation factor f also appears in the expression [equivalent to Eqn.(2)]

$$D_T = D_{\text{real}} = f D_{\text{rand}},$$

where D_{rand} is the diffusion coefficient of the atom for fully random (spatially independent) successive diffusion jumps. Throughout this review we shall use the term self-diffusion coefficient to refer to the "real" diffusion coefficient of isotopically labelled atoms or ions (D_T). In most cases this quantity is independent (to a first approximation) of the difference in mass between the indicator atoms (for example, ^{22}Na or ^{24}Na) and the matrix atoms (^{23}Na), though of course diffusion isotope effects are the subject of this review.

In the case of self-diffusion in cubic crystals the correlation factor (to this approximation) is a purely geometric coefficient, depending only on the diffusion mechanism and on the crystal structure. As an example, the calculated correlation factors for self-diffusion in a face-centred cubic lattice (f.c.c.) are listed in Table 1.

Experimental measurement of the correlation factor should at least help to identify the elementary mechanism of the diffusion process. For the isotropic self-diffusion of particles having a single jump frequency ω the diffusion coefficient can be written $D = A\omega f$, where A includes geometric and other factors independent of the jump frequency.

Table 1. Calculated correlation factors for self-diffusion by different mechanisms in a b.c.c. lattice.

Diffusion mechanism	f_0
Vacancy	0.781
Divacancy	0.475
Interstitial	1.000
Relay:	
collinear jumps	0.667
non-collinear jumps	0.969

We shall now compare the diffusion coefficients for the atoms of two isotopes of mass m_α and m_β. We shall express their ratio as

$$D_\alpha/D_\beta = f_\alpha\omega_\alpha/f_\beta\omega_\beta. \quad (3)$$

The difference in mass between the isotopes leads to differences in the jump frequencies ω_α and ω_β, and hence in the correlation factors f_α and f_β (which depend on ω_α and ω_β). This statement is true both for self-diffusion and for the diffusion of impurities, since in self-diffusion the labelled atom (having a different mass) acts as an impurity atom with respect to the atoms of the host lattice. Hence f_α and f_β are true correlation coefficients for the impurity atoms. The correlation factor for "true" self-diffusion ($f = f_0$, see Table 1) is, strictly speaking, meaningful only in the ideal case when the diffusing atom and the matrix atom have identical jump frequencies. The approximate equality $f_\alpha \cong f_\beta \cong f_0$ is obeyed satisfactorily in most cases.

For the systems considered the correlation factor of the impurity can be expressed as $f = (u/\omega + u)$, where u is the jump frequency of the matrix atoms only. Assuming that this expression is valid for any labelled atom, i.e. that u is independent of the mass of the labelled atom, we can express f_α and f_β as

$$f_\alpha = u/(\omega_\alpha + u);\ f_\beta = u/(\omega_\beta + u). \quad (4)$$

Eliminating u and one of the correlation factors from (3) and (4) we obtain the following expression for the fractional difference between D_α and D_β:

$$\Delta D/D_\beta = f_\alpha\ \Delta\omega/\omega_\beta, \quad (5)$$

where $\Delta D = D_\alpha - D_\beta$, and $\Delta\omega = \omega_\alpha - \omega_\beta$.

Since the absolute value of the jump frequency cannot be determined in a diffusion experiment, for practical purposes the ratio $\Delta\omega/\omega$ in expressions such as (5) must be written as a function of the isotopic masses m_α and m_β. Treating the diffusional jump as the motion of an atom through a potential barrier, we write

$$\omega = \nu \exp(-Q/kT),$$

where Q is the energy (enthalpy) of activation of the jump, and ν is the mean vibrational frequency of the migrating atom.

Since Q denotes the height of the potential barrier, its value should be the same for chemically identical isotopes. Atomic vibration frequencies vary with the mass of the atom as $\nu \propto m^{-1/2}$. Hence

$$\Delta\omega/\omega_\beta = [(m_\alpha/m_\beta)^{-1/2} - 1]. \quad (6)$$

Combining (5) and (6) gives the following expression for the diffusion isotope effect:

$$E_\beta^\alpha = \frac{\Delta D/D_\beta}{(m_\beta/m_\alpha)^{1/2} - 1} = f_\alpha \simeq f_0. \quad (7)$$

Expressions like (6) and (7) were derived for conditions in which only the migrating atom is able to jump, and no allowance was made for changes in the state of the lattice. Obviously, allowing for the part played by the neighbours of the diffusing atom in the migration act must modify Eqn.(6) in the sense of decreasing the magnitude of the isotope effect. Introducing the correction coefficient

$$\Delta K = \Delta\omega/\omega_\beta \left[\left(\frac{m_\beta}{m_\alpha}\right)^{1/2} - 1\right]^{-1},$$

we convert Eqn.(7) into

$$E_\beta^\alpha = \frac{\Delta D/D_\beta}{(m_\beta/m_\alpha)^{1/2} - 1} \simeq f_0\Delta K. \quad (8)$$

An expression for the diffusion isotope effect in the form of Eqn.(8) was first proposed by Mullen[4]. Using the classical theory of reaction rates ΔK can be interpreted as the fraction of the kinetic energy of the diffusing atom at the saddle point associated with motion in the direction of the jump. Thus, ΔK can vary between zero and unity. It follows from Eqn.(8) that by measuring the isotope effect E_β^α it should be possible to evaluate the product $f\Delta K$: hence, in order to obtain the coefficient f (and thus to identify the diffusion mechanism) we must introduce additional information. We shall examine first of all the possibility of measuring (and interpreting) quantities such as the electrical conductivity σ (in the case of ionic conductors) and the activation volumes of diffusion or ionic conduction processes.

The well known Einstein–Nernst expression related the mobility μ and the diffusion coefficient D of a charged particle:

$$\mu/D = q/kT \quad (9)$$

where q is the charge of the particle, k is Boltzmann's constant, and T is the absolute temperature.

The electrical conductivity (resulting from the migration of charged particles in an electric field) is $\sigma = \mu qN$, where N is the number of current-carrying particles per unit volume. To simplify the discussion we shall consider the case of unipolar ionic conduction, for which we can write

$$D/\sigma = kT/q^2N. \quad (10)$$

In Eqns.(9) and (10) the quantity D is the "random" or "chaotic" diffusion coefficient, wheras the real diffusion coefficient D_T (measured experimentally with radioactive indicators) is related to σ by the generalised expression $D_T/\sigma = (kT/q^2N)f$.

Comparative measurements of the real self-diffusion coefficient D_T and of the ionic conductivity coefficient σ allow (in some cases) the coefficient f to be determined. Measurements of the quantity called the "activation volume" can also help to identify diffusion mechanisms. The diffusion coefficient D_T can be described with adequate generality by the expression[2]

$$D_T = \gamma a^2 f\nu \exp(-\Delta g/kT) = \gamma a^2 f\nu \exp\left(\frac{\Delta S}{k}\right)\exp\left(-\frac{\Delta H}{kT}\right),$$

where γ depends on the geometry of the crystal lattice, ν is

the frequency, and Δg, ΔS, and ΔH are the changes in thermodynamic potential, entropy, and enthalpy which accompany each diffusional jump. Using the standard thermodynamic relation $(\partial g/\partial p)_T = V$ (where p is pressure and V is volume) we can write to a good approximation

$$\left(\frac{\partial \ln D}{\partial p}\right)_T \simeq \left(\frac{\partial \Delta g}{\partial p}\right)_T = \Delta V,$$

where ΔV is called the activation volume. Using the Einstein–Nernst relation, the activation volume for ionic salts can be determined also from electrical conductivity data. The quantities Δg, ΔH, and ΔS can be expressed as sums of the free energy (enthalpy, entropy) of formation of the lattice defect responsible for the diffusion (i.e. Δg_f, ΔH_f, ΔS_f) and of the corresponding quantities for the migration process itself (Δg_m, ΔH_m, ΔS_m). In exactly the same way ΔV can be separated into its components ΔV_f (the activation volume of formation) and ΔV_m (the activation volume of migration).

Theoretical models of the effect of high pressures on migration processes in solids allow some of these quantities to be calculated. For example, in the case of self-diffusion in metals the quantity $\Delta V^1\nu$ for diffusion by single vacancies is approximately $^1/_2$–$^3/_4$ of the atomic volume, and $\Delta V^2\nu$ for the divacancy mechanism is slightly less than $2\Delta V^1\nu$; the corresponding quantities for interstitial diffusion are very much smaller[2].

There are many other physical parameters whose measurement can help to establish the nature of the point in solids and hence to identify the diffusion mechanism. For example, useful measurements include anomalous thermal expansion, specific heat anomalies, high-precision density and lattice parameter measurements, relaxation studies, measurements of optical properties, etc. We shall refer to the results of these (and other) methods in our discussion of isotopic experiments.

II. THEORY OF THE ISOTOPE EFFECT

The general theory of diffusion in solids (and, in particular, the basic elements of the theory of isotope effects in diffusion) are discussed in many theoretical publications both by Eyring's theory of absolute reaction rates and by the dynamic variants of the theory, in both the harmonic and the anharmonic approximation. Eyring and Bigeleisen's general theory of the kinetic isotope effect predicts that the effect will be most marked when the isotopic atoms are loosely bound in the activated complex.

Zener[5] and others developed Eyring's theory of rate processes by treating the diffusion process as the motion of an atom through a potential barrier. They showed that the average jump frequency of the atom is related to its mass by the expression $\omega \propto m^{-1/2}$. In this model the elementary diffusion act is carried out by a single particle: the contribution from the crystal lattice is not considered. Other assumptions made in the model include: 1) an activated state can exist at the top of the potential barrier, and its life time is long enough to determine it thermodynamic properties; 2) irreversibility of the diffusion is produced by an unexplained mechanism which causes the migrating atom to lose so much energy that it is unable to re-cross the barrier in the backward direction.

Prigogine and Bak[6] proposed a theory in which irreversibility of the diffusion follows from the anharmonicity of the interactions between the normal modes of the matrix and those of the moving particle. Their model ignores the participation of the lattice atoms in the formation of the activated complex in the saddle-point configuration; a consequence of this model is that the diffusion coefficient is inversely proportional to the square of the mass of the migrating atom.

The contribution to the formation of the activated complex by the nearest neighbours of the diffusing atom can be allowed for by making the frequency of the jumps into a vacancy proportional to $(m^*)^{-1/2}$, where m^* is an effective mass whose value is determined by the highest and the lowest mass of the whole configuration. Rice and Frisch[7] allowed for the participation of the lattice in the saddle configuration and used a dynamic model free from the assumptions of the classical theory. According to their model the jump of a diffusing atom is the result of the fluctuations in its energy and momentum (quantity of motion) produced by the thermal vibrations. In order to calculate the amplitude of these fluctuations they introduce a definition of the reaction co-ordinate which allows for the displacement of both the migrating atom and the barrier atoms. This quantity can be treated as a measure of the extent to which the thermal motion has been able to overcome the resistance of the neighbouring atoms to the passage of the migrating particle. A jump is assumed to take place each time the reaction co-ordinate exceeds some critical distance. Thus, the basic feature of the dynamic theory is the assumption that a jump can occur only as a result of a specified type of fluctuation of the reacton co-ordinate, determined by the lattice geometry. However, the energy of this fluctuation cannot be calculated in the present state of the theory. The dynamic theory of diffusion has been developed also by other workers[8–12].

Discussion of the diffusion isotope effect from the standpoint of the dynamic theory produces results similar to those of the classical model. Hence, both theories can be used for practical purposes. The classical model has the advantage of being simpler, as well as offering the possibility of calculating the thermodynamic characteristics of the diffusion jump. Our discussion of the isotope effect will therefore be confined to this variant of the theory.

A problem still not fully solved is the mechanism by which the energy of the activated atom is dissipated when this atom has gone beyond the saddle point. Unless the energy is dissipated very rapidly the atom may retain enough energy to undergo the backward jump. Clearly, the diffusion problem is closely bound up with our interpretation of the isotope effect, i.e. with the physical significance of the term ΔK which appears in Eqn.(8).

The jump frequency of an atom in the saddle configuration (at the top of the potential barrier) should be given by an expression including the frequencies of the normal lattice modes for the initial configuration (ν_j) and for the activated complex (ν_j'). Le Claire[13] showed that one of the normal modes corresponding to the saddle configuration (of frequency ν_1') is unstable, and leads to the breakdown of that configuration and to completion of the jump. Changes in the mass of the migrating atom affect the frequency of this unstable mode only. By treating the jump as the motion of an atom at the saddle point through the potential barrier we demonstrate (in accordance with the above discussion) that ΔK is the fraction of the total kinetic energy of the system (at the saddle point) which is assigned to the migrating atom only. Thus the quantity ΔK provides information on the energetics of an individual act of diffusion, which is not obtainable by any other method.

Eqns.(7) and (8) apply only if the mechanism of the migration act involves only one particle (vacancy mechanism, direct interstitial mechanism, etc.). If the elementary displacement

requires the simultaneous motion of n atoms (as in the indirect interstitial or in the ring mechanism) Eqns.(7) and (8) become

$$E_{\beta}^{\alpha}=\frac{\Delta D}{D_{\beta}}\left[\left(\frac{m_{\beta}+(n-1)m_0}{m_{\alpha}+(n-1)m_0}\right)^{1/2}-1\right]^{-1}=f_{\alpha}\Delta K, \qquad (11)$$

where m_0 is the average mass of the matrix atoms.

Since ΔK allows for the contribution of the lattice atoms to the elementary diffusion act we can establish the relationship between this quantity and the relaxation of the atoms adjacent to the defect. This correlation was first investigated by Barr and Mundy[14], who expressed the activation volume for diffusion ΔV in units of the atomic volume and found that ΔK was numerically very similar to $\Delta V/V$. Le Claire[13] looked for a correlation between the kinetic energy of an atom at the saddle point and vibrating with the frequency ν_1', on the one hand, and the jump distance of this atom, on the other hand, and he obtained the following expression for ΔK:

$$\Delta K=\left[1+\frac{n}{3}\left|1-\Delta V_f\right|\right]^{-1}, \qquad (12)$$

where n is the number of relaxed atoms taking part in the saddle configuration. For the self-diffusion of Na atoms in metallic sodium we have $\Delta K = 0.50$ [15] and $\Delta V_f = 0.52$.[16] This gives, from Eqn.(12), $n = 6$, which is the same as the number of neighbours of a migrating atom in a body-centred cubic (b.c.c.) crystal. However, this agreement must be treated with some caution: very probably the number of relaxing atoms is greater than six, but their contribution to ΔK is not uniform. In the case of self-diffusion in metallic silver $\Delta K = 0.86$ [17] and $\Delta V_f = 0.70$. These values lead to $n = 1.6$, which is not surprising, since the number of relaxing atoms in the more closely packed f.c.c. structure must be smaller than in the b.c.c. lattice.

It is interesting to establish whether n is a constant, characteristic of a given type of crystal structure. If so, Eqn. (12) can be used to calculate ΔK values appropriate to the isotope effect in impurity diffusion. Most workers assume that ΔK_S for self-diffusion is equal to ΔK_{imp} for impurity diffusion: this assumption is consistent with the experimental fact that the activation volumes for impurtiy diffusion and for self-diffusion do not differ very markedly (for example, $\Delta V_{In/Ag}$ and $\Delta V_{Ag/Ag}$ differ by 5%; $\Delta V_{Sb/Ag}$ and $\Delta V_{Ag/Ag}$ differ by 10%).[2] Theoretical calculations for structures in which ΔK_S is not very different from 1 lead to the same conclusion: in the case of an f.c.c. lattice, for which $\Delta K_S = 0.9$,[17] substitutional impurities should have ΔK values differing from ΔK_S by not more than 8%.[9-11] However, the same is not true of crystals in which $\Delta K_S \ll 1$.

Theoretical calculations of ΔK have been reported for various crystal structures. Brown and coworkers[18] obtained $\Delta K = 0.998$ for NaCl, in excellent agreement (within experimental error) with the experimental value[19] $\Delta K = 0.93 \pm 0.09$. They also calculated ΔK for copper[20]. A comparison of ΔV and ΔK values is shown in Table 2.

Achar[12] used the dynamic theory of diffusion to calculate ΔK for several f.c.c. and b.c.c. metals. The results are consistent with experiment.

Eqn.(8) was obtained by classical statistical mechanics, without allowance for quantum effects. Experiment shows that this expression adequately describes the diffusion isotope effect in most systems. The only exception is the diffusion of the hydrogen isotopes, for which Eqn.(8) gives unacceptably low values of E. It has been clearly shown[13,21,22] that quantum effects cannot be ignored in the diffusion of such light isotopes. The contribution of quantum corrections to the hydrogen diffusion isotope effect has been discussed for Pt [23] and Nb [24] matrices. A study[25] of the diffusion of hydrogen, deuterium, and tritium in Ni and Cu has shown the need to allow for the anharmonicity of the lattice vibrations in addition to the quantum corrections.

Table 2. Calculated and experimental values[2] of ΔK and $\Delta V/V$.

Matrix	Isotope pair	ΔK_{calc}	ΔK_{exper}	$\Delta V/V$
Ag	^{105,111}Ag	0.80[12]	0.86±0.05[17]	0.90[34]
γ-Fe	^{55,59}Fe	—	0.74±0.08[29]	0.77[35]
Cu	^{64,67}Cu	0.82[12]	0.87±0.02[30]	0.90[36]
			0.92[20]	
Na *	^{22,24}Na	0.54[12]	0.50±0.05[15]	0.52[16]
α-Fe *	^{52,59}Fe	0.51[12]	0.56±0.05[31]	—
Zn **	^{65,69}Zn	—	0.93±0.08[32]	0.43[37]
NaCl	^{22,24}Na	0.99[18]	0.93±0.09[19]	1.20[38]
AgBr	^{105,111}Ag	—	0.66±0.02[33]	0.69[33]

*b.c.c. structure; ** close-packed hexagonal structure; in every other case f.c.c. structure.

The experimental value of E has been found to be temperature-dependent in several studies of the isotope effect in self-diffusion (for example, in the self-diffusion of ^{105,110}Ag in metallic silver[17] and in the self-diffusion of ^{22,24}Na in NaCl).[26] Since $E = f\Delta K$, the temperature dependence of the isotope effect may be due to a variation with temperature of either f, or ΔK, or both. The correlation factor in self-diffusion is a purely geometrical parameter, depending only on the type of lattice and on the diffusion mechanism; on the other hand, as was shown theoretically for Ag and Al,[12] the quantity ΔK should also be independent of temperature. Thus, in order to explain the temperature dependence of the isotope effect we must postulate the simultaneous operation of several diffusion mechanisms. Changes in the contribution of each mechanism to the overall diffusion process may account for the observed dependence of E on temperature.

Bakker[27] derived an expression for the isotope effect in the case of two simultaneous mechanisms (vacancy and divacancy diffusion) in an f.c.c. lattice:

$$E=\frac{D_1}{D_1+D_2}f_1\Delta K_1+\frac{D_2}{D_1+D_2}f_2\Delta K_2; \qquad (13)$$

where D_i, f_i, and ΔK_i are the diffusion coefficients and the isotope effects for each mechanism. The most general expression for the diffusion isotope effect in the case of diffusion by several simultaneous mechanisms is

$$\frac{\Delta D}{D_{\beta}}=\sum p_i\Delta K_i f_i \delta_{m_i}, \qquad (14)$$

where p_i is the fractional amount of diffusion by the stated mechanism, and δ_{m_i} is the mass term (for the vacancy and the direct interstitial mechanism $\delta_{m_i} = [(m_{\beta}/m_{\alpha})^{1/2}-1]$).[27] Eqns.(13) and (14) can be used to calculate the contribution of each mechanism to the overall diffusion process.

We shall now consider the limits of the validity of expressions of the type of (8), (11), and (14). Both the derivation and the practical use of these and similar expressions involve the following assumptions:

a) $\Delta f/f_{\beta}$ is small compared with unity, i.e. $f_{\alpha} = f_{\beta} = f_0$;

b) changes in mass affect only ω in Eqn.(2), and they have no effect on u;

c) the number of labelled atoms introduced into the crystal by diffusion is much smaller than the number of matrix atoms, and therefore the probability of finding an impurity atom among the nearest neighbours of a diffusing atom is negligibly small.

LeClaire has shown[13] that the measured diffusion isotope effect is only slightly affected by these assumptions, since the necessary corrections are less than 2% and therefore beyond the precision of the experiment (5–10%).

III. SELF-DIFFUSION IN PURE METALS

1. Face-centred Cubic Metals

Diffusion isotope effects have been studied in a large number of metals with a face-centred cubic lattice. In most cases the conclusion is that self-diffusion in f.c.c. metals is mainly by the single vacancy mechanism. A contribution from the divacancy mechanism is observed near the melting point.

Self-diffusion in copper has been studied in several laboratories[30,36]. We shall dwell mainly on Rothman and Peterson's results[30], obtained in an investigation of the effect of temperature on diffusion isotope effects. At relatively high temperatures (698–1061 °C) the diffusion is described by the following parameters: $D_0 = 0.78$ cm^2 s^{-1}, $Q = 2.18$ eV. From the diffusion of ^{64}Cu and ^{67}Cu in copper single crystals the ratio $D_{64}/D_{67} = 0.0155 \pm 0.0003$ was obtained, and found to be independent of temperature. These results led to the value $\Delta K = 0.87 \pm 0.02$, and to the conclusion that self-diffusion by the single vacancy mechanism is predominant in copper. The variation of E_{67}^{64} with temperature is negligibly small, showing that the contribution of divacancies to the diffusion process is slight.

The pressure dependence of the diffusion coefficient for self-diffusion in Cu [36,39] gives an activation volume of 0.9 of the atomic volume, corresponding to diffusion by the single vacancy mechanism or by a combination of the single vacancy and the divacancy mechanism. Mehrer and Seeger[40] arrived at the following series of optimum parameters for the defects in Cu by combining data on the temperature dependence of D and on the isotope effect with data[41] on high-temperature defect equilibria: $H_f^{1V} = 1.03$ eV, $\Delta S_f^{1V} = 0.3\ k$, $H_m^{1V} = 1.06$ eV, $\nu^{1V}\exp(\Delta S_m^{1V}/k) = 1.4 \times 10^{14}$ s^{-1}, $H_m^{2V} - H_b^{2V} = 0.54$ eV, $\Delta S_f^{2V} = 2k$, $\nu^{2V}\exp(\Delta S_f^{2V}/k) = 1.6 \times 10^{14}$ s^{-1}. Electron-microscopic studies by Bowden[42] have confirmed Mehrer and Seeger's interpretation (which allows for divacancy migration).

Self-diffusion in Ag has been studied by several workers. Rothman's results[17] show a small, systematic deviation from an Arrhenius dependence of ln D on $1/T$, which he ascribes to the presence of a second diffusion mechanism. The temperature dependence of the isotope effect for self-diffusion in Ag (Fig. 1) gives additional evidence for the presence of two diffusion mechanisms[17]. At low temperatures the E value corresponds to diffusion by the single vacancy mechanism ($\Delta K^{1V} = 0.92$), decreasing at higher temperatures to a level which suggests an increasing contribution from divacancies. Reimers and Bartdorff[43] also measured the temperature dependence of E: their results are less accurate than Rothman's but consistent with them.

Two extreme cases of the contribution of divacancies to self-diffusion in silver can be defined. On the one hand, the difference between E and f^{1V} can be ascribed wholly to the contribution from divacancies (i.e. $\Delta K^{1V} = 1$). Assuming $\Delta K^{1V} - \Delta K^{2V} = 1$, and $f^{2V} = 0.475$, we find that the divacancy contribution is a maximum ($D^{2V}/D^{1V} = 0.872$) at high temperatures ($E = 0.639$), falling to 0.263 at low temperatures ($E_{111}^{105} = 0.718$). Since only the single vacancy mechanism operates at low temperatures, i.e. $\Delta K^{1V} = 0.918$, and divacancy effects on E appear only at high temperatures, we can obtain $D^{2V}/D^{1V} = 0.12$ by assuming that ΔK is independent of temperature and that the contribution of divacancies at the melting point is a minimum for $\Delta K^{2V} = 0$. A critical analysis of all the experiment data[44] leads to the following set of thermodynamic parameters for the defects and for their mobility in metallic silver: $H_f^{1V} = 0.99$ eV, $H_m^{1V} = 0.86$ eV, $\Delta S_f^{1V} = 0.5\ k$, $H_m^{2V} - H_b^{2V} = 0.34$ eV, $H_m^{2V} = 0.58$ eV, $\Delta S_f^{2V} = 2.6\ k$.

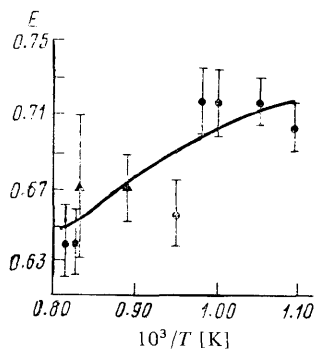


Figure 1. Isotope effect for self-diffusion in Ag:[17,33] the curve is taken from Mehrer's analysis[44] of these results.

Isotope effects for self-diffusion in Pd and γ-Fe have been measured accurately enough to identify the diffusion mechanism, but the temperature dependence of E was not measured to an accuracy sufficient to justify the calculation of the thermodynamic properties of the defects. Peterson[45] investigated the isotope effect for self-diffusion in Pd, and found $E = 0.79 \pm 0.04$ in a narrow region of temperature near the melting point. Since ΔK cannot be greater than unity, self-diffusion in Pd must take place by the single vacancy mechanism, with $(1 - \Delta K) \leq 0.02$. The experimental temperature range was too narrow to allow the contribution of divacancies to be detected, but the numerical value of the isotope effect suggests that this contribution is very small.

Published studies[29,46] of the isotope effect for self-diffusion in γ-Fe are consistent ($E_{59}^{55} = 0.53$–0.57), and suggest that the single vacancy diffusion mechanism predominates. The observed temperature dependence of E allows for some contribution from divacancies to the transport processes in γ-Fe.[29]

2. Body-centred Cubic Metals

Studies of self-diffusion in b.c.c. metals have yielded inconsistent results, and the diffusion parameters in these systems cannot yet be interpreted unambiguously. For most b.c.c. metals the diffusion coefficient near the melting point is ~10^{-7} cm^2 s^{-1}, as compared with ~10^{-8} cm^2 s^{-1} for f.c.c. metals. Interesting results were obtained for the self-diffusion effects in sodium. The model of self-diffusion in Na is more complicated than the model for f.c.c. metals, and is probably typical of the majority of metals which crystallise in a body-centred cubic lattice. The anomalously low value

of the ratio $\Delta D/D_{24} = 0.016$ was pointed out early on[14]: such a value of the mass effect may be due to an indirect interstitial mechanism, diffusion occurring along split interstitials. However, since the predominant defect in Na has been shown independently[16] to be a lattice vacancy, a diffusion model involving relaxed vacancies is proposed: this gives a lower value of f and explains the low value of E.

Later work in the same laboratory showed a decrease in the magnitude of the isotope effect near the melting point of sodium[15]: $\Delta D/D_{24} = 0.016$ at 40–84 °C, and $\Delta D/D_{24} = 0.013$ at $t > 84$ °C. Evidently, diffusion occurs by more than one mechanism at temperatures near the melting point, but the nature of these mechanisms has not been established. On the other hand, two models of the relaxed vacancy have been proposed for the region of constant E: $f_1 = 0.5$ and $\Delta K_1 = 0.72$, or $f_2 = 1$ and $\Delta K_2 = 0.36$. However, the authors are unable to choose between these models.

The isotope effect in Na has been calculated theoretically[18] for different types of defect. Agreement with experiment is best for the interstitial diffusion mechanism.

Mundy[28] attempted to explain unambiguously the mechanism of self-diffusion in sodium by carrying out a complex investigation over a range of hydrostatic pressures. His results, and in particular the irregularities in the plot of $\ln D = f(1/T)$, suggest that at least two diffusion mechanisms are operative: a high-temperature and a low-temperature mechanism. Within the high-temperature region two separate mechanisms can be distinguished. Thus, the total number of mechanisms involved is three. The dependence of self-diffusion on pressure at 14.8 and 91.4 °C indicates that at 14.8 °C approximately 2/3 of the diffusion takes place by the low-temperature mechanism, whereas at 91.4 °C this mechanism accounts for only 40% of the diffusion. When several mechanisms are possible an increase in pressure causes an increased contribution from the low-temperature processes. Therefore the decrease in the isotope effect at 91.4 °C becomes less marked when the pressure is raised to 7 kbar, though this effect may be due to the increase in the melting point of sodium at high pressures (145 °C at 7 kbar).

Thus the experimental results show that self-diffusion in sodium involves at least two mechanisms. The following pairs of mechanisms have been proposed for the two-process model: 1) a vacancy and an interstitial, and 2) a vacancy and a divacancy. By associating (in the first variant) the interstitial mechanism with the low-temperature region and the vacancy mechanism with the high-temperature region we can explain many experimental results. However, this model does not allow us to explain the variation of E with temperature. On the other hand, the temperature dependence of the isotope effect is easily explained by postulating two types of divacancy whose relative contribution to the transport of matter varies with temperature. Evidence for this model is provided by the similarity of the activation volumes for the two high-temperature processes ($\Delta V_2/V = 0.68 \pm 0.21$, and $\Delta V_3/V = 0.68 \pm 0.25$ at 91.3 °C).[28]

For the model which includes three self-diffusion mechanisms Mundy[28] suggests the following processes: a low-temperature (interstitial) process with $\Delta D/D = 0.018$ and two high-temperature processes with $\Delta D/D = 0.014$ and 0.003 respectively. The latter value is surprisingly small, and we have to use Eqn. (11) to calculate the number of atoms taking part in the elementary act: the result is $n = 20$. This is not too surprising, since neutron diffusion experiments in liquid sodium have shown that at temperatures slightly above the melting point ~30 atoms are involved in each diffusion jump. We may assume that the concentration of vacancies increases steeply near the melting point, and therefore the relaxation around one vacancy may affect other vacancies. This type of interaction may lead the formation of regions within the crystal in which diffusion is a polyatomic process.

Studies of isotope effects in self-diffusion in α-Fe [31,46] and δ-Fe [47] have been reported. The results are mutually consistent, the E values in α-Fe and δ-Fe being similar to those in Na at the same reduced temperatures (i.e. at temperatures referred to the melting point of the appropriate metal, T/T_f). The complex temperature dependence of the isotope effect in α-Fe, δ-Fe, and Na suggests that the migration of atoms in these b.c.c. metals occurs by the same mechanism. In order to test this hypothesis with a higher-melting b.c.c. metal, Mundy and coworkers[48] studied the isotope effect of chromium, and they again observed a decrease in the E_{51}^{48} value for the effect with increase of temperature (0.52–0.31 at 1440–1810 °C). The high values of the Arrhenius parameters (as in the case of self-diffusion on vanadium) are consistent with a predominantly divacancy migration mechanism in chromium, with a negligibly small contribution from single vacancies. The temperature dependence of the isotope effect is explained (as in the case of sodium) by the participation of two types of divacancy in the transport process.

Evidently, further work on diffusion isotope effects in other b.c.c. metals is needed to solve the problem of anomalous diffusion in these materials, which are industrially important.

3. Close-packed Hexagonal Metals

Isotope effects in the self-diffusion in zinc, which has an anisotropic lattice, have been reported[32,49]. At 289–418 °C the self-diffusion coefficients parallel (∥) and perpendicular (⊥) to the sixth-order symmetry axis are different, but the isotope effects are identical (within experimental error) in the two directions, and do not depend on temperature. The numerical values of the diffusion isotope effect suggest transport by a single vacancy mechanism in both directions, without a significant contribution from divacancies, i.e. $f_\parallel = f_\perp$ and $\Delta K_\parallel = \Delta K_\perp$. Different configurations of barrier atoms for these two cases can be proposed from geometrical considerations. However, the experimental values of ΔV are identical for both directions[37].

Stein and coworkers[50] proposed a method of calculating the correlation factor for self-diffusion in close-packed hexagonal metals by the single vacancy and divacancy mechanism. The results have been compared with experimental data[49] on the isotope effect for self-diffusion in zinc. The calculated correlation factor was shown to be the upper limit of the diffusion isotope effect.

IV. ISOTOPE EFFECTS IN HETERO-DIFFUSION IN METALS

Mundy and McFall[51] studied the diffusion of copper in metallic lithium, and observed deviations from linearity in the $\ln D = f(1/T)$ plots, which they ascribed to the presence of two diffusion mechanisms. The numerical value of the diffusion isotope effect ($E_{Cu/Li} = 0.11 \pm 0.03$) is incompatible with both the vacancy and the direct interstitial mechanism. For the vacancy mechanism the E value should be ≅0 (i.e. $f_{Cu/Li} \to 0$), whereas for interstitial diffusion E should be close to unity. Assuming a dissociative mechanism for the dissolution of Cu in Li, involving an equilibrium between the numbers of copper atoms in normal lattice sites and in interstitials respectively, the authors[51] conclude that diffusion takes place by a direct interstitial and a vacancy mechanism simultaneously. The two mechanisms are thought to contribute to a similar extent

to the transport process, since they involve comparable activation energies for diffusion. These considerations led the authors to the values $E = 0.17$ and $E = 0.05$ for the two mechanisms respectively. By measuring the diffusion isotope effects of $^{105,110}Ag$ and $^{22,24}Na$ in lithium Mundy and McFall[52] were able to compare experimental results with conclusions from the dynamic theory of diffusion.

An interesting example of the use of the isotope effect in identifying the diffusion mechanism of an impurity is provided by the fast diffusion of $^{105,110}Ag$ in lead[53]. An interstitial diffusion mechanism is almost invariably assumed to account for the abnormally fast diffusion of an impurity. The vacancy mechanism is excluded by the very small effect of the added impurity on the rate of self-diffusion. However, the effect cannot be explained on the assumption that the diffusion occurs wholly by an interstitial mechanism. To resolve this problem, the diffusion isotope effect of Ag in Pb was measured. The result[53] was $E_{Ag/Pb} = 0.25 \pm 0.05$, and the effect of the Ag impurity of $E_{Ag/Pb}$ was undetectable (addition of 0.08 at.% of Ag giving $E = 0.26 \pm 0.02$). The effect of temperature on $E_{Ag/Pb}$ was also negligibly small. These experimental observations were explained by postulating that the diffusion of Ag in Pb involves two mechanisms, though the contribution of the interstitial mechanism is predominant (80%). The remaining 20% is ascribed to any mechanism in which the diffusion of the impurity is directly linked to the diffusion of the solvent. Typical of these mechanisms is diffusion by impurity–vacancy pairs, with the silver atoms in interstitial sites. The relatively small contribution from the pair diffusion mechanism (20%) explains the failure of Ag additions to accelerate the self-diffusion in Pb. On the other hand, this small contribution from impurity–vacancy pairs to the overall diffusion process tends to obscure the influence of this mechanism on the isotope effect and to make the isotope effect temperature-independent.

Thus it is firmly established that most of the transport of Ag in Pb occurs by the interstitial mechanism. We also know that in this case $E \cong 1$, whereas the experimental value is $E = 0.25$. Since there is no reason to assume that either ΔK or f is very different from unity in this case, we must conclude that according to Eqn.(11) $n \neq 1$, i.e. several particles are involved in the elementary migration act. The most important defect in solutions of silver in lead is the split interstitial. If this defect consists (as in the present case) of two Ag atoms the presence of the impurity should accelerate the diffusion much more substantially than is found in practice. If on the other hand the split interstitial is composed of one Ag atom and one Pb atom, the Ag atom can perform one migration act by jumping from this defect into a normal site of the lead lattice. In this case $n = 3$, and if $f = 1$ and $\Delta K = 1$ the E value calculated from Eqn.(11) is 0.20, which agrees with the experimental value[53].

The isotope effects in the diffusion of cadmium (E_{115}^{109}) [54] and copper (E_{67}^{64}) [55] in lead were studied for the same purpose, i.e. in order to identify the hetero-diffusion mechanism. In the latter case the isotope effect ($E_{67}^{64} = 0.23 \pm 0.08$) was found to be close to the corresponding value for the diffusion of $^{105,110}Ag$ in Pb,[53] suggesting a similarity between the migration mechanisms of the impurities in the two systems. We should note that because of the low solubility of copper in lead the concentration dependence of the rate of diffusion could not be studied over a significantly wide range. Thus, the measurement of the isotope effect is the only method available for identifying the hetero-diffusion mechanism.

It should be remembered that in a pure metal the correlation factor f_0 is a constant, and depends only on the type of crystal structure and on the diffusion mechanism, whereas in impurity diffusion the correlation factor depends on the jump frequencies of the impurity atoms and of the solvent atoms. Therefore the quantity f_{imp} obtained from measurements of the diffusion isotope effect can be combined with other data (such as the dependence of the self-diffusion coefficient on the impurity concentration) to give the ratio of the jump frequencies of impurity and matrix atoms. For example, data on the isotope effect for the diffusion of zinc in silver[2] and data on the effect of zinc impurities on the rate of self-diffusion in Ag have allowed this ratio to be calculated for different temperatures. Results from studies of isotope effects accompanying the diffusion of Fe in Ag and Cu,[4] of cadmium in zinc[49], etc. have been interpreted in a similar way.

V. DIFFUSION IN ALKALI METAL HALIDE CRYSTALS AND IN SILVER HALIDES

Work on diffusion isotope effects in alkali metal halide crystals and in silver halides has been confined mainly to determining the contribution of vacancy pairs to the overall diffusion, and to evaluating the parameter n in Eqn.(11) for the case of simultaneous motion of two (or more) ions, since the indirect interstitial mechanism appears to operate in silver halides. From the results, thermodynamic parameters describing the migration under hetero-diffusion conditions have been calculated. The experimental data are summarised in Table 3.

Table 3. Experimental values of the diffusion isotope effect in single crystals of alkali metal halides and silver halides.

Solvent	Δt, C°	$E_\beta^{\alpha*}$	References
	$^{22,24}Na$		
NaCl	644	0.727	13
NaCl	600—750	0.75	67
NaCl	622—797	0.695—0.485	26
NaBr	730—798	0.65	68
KCl	574—772	0.441—0.689	67
KBr	600—695	0.523—0.637	67
RbCl	380—707	0.107—0.362	65
AgCl	180—450	0.989	69
	$^{131,137}Cs$		
CsI	470—600	0.54	60
	$^{6,7}Li$		
LiF	600—750	0.42	59
AgCl	250—400	0.75	70
	$^{105,111}Ag$		
AgCl	239—253	0.0076	33
AgBr	175—337	0.0045	33

* In the case of $^{105,111}Ag$ the $\Delta D/D_\beta$ values are given

1. Contribution of the Divacancy Mechanism

As was stated above, the concentration of vacancy pairs increases steeply in many crystal structures at temperatures close to the melting point, and the contribution of vacancy pairs to the diffusion process increases correspondingly. The presence of a second diffusion mechanism will be reflected also by the magnitude of the isotope effect.

Attempts have been made in recent years to calculate the contribution of vacancy pairs to the diffusion of Na^+ ions in

sodium chloride. Nelson and Friauf[56] measured the self-diffusion coefficients of Na^+ in NaCl and also monitored (at the same time) the migration of this ion in an electric field, and concluded that the contribution from vacancy pairs was ~40%. Though the contacts to the crystal during the measurements in an electric field were far from ideal, the results obtained in this way are more accurate than those of independent measurements of D and σ.

Beniere and coworkers[57] calculated the contribution of vacancy pairs to the diffusion of the sodium ion in sodium chloride (~10%) from measurements of D_{Cl} in NaCl samples containing small amounts of bivalent cation impurities. The addition of bivalent cations is known to lower the concentration of single anion vacancies, and therefore at sufficiently high concentrations of M^{2+} the anions should migrate almost exclusively along vacancy pairs. However, these workers[57] based their calculations on the assumed equivalence[58] of cation and anion diffusion by the divacancy mechanism. By combining this (to say the least) arguable assumption with their experimental results on D_{Cl}, D_{Na}, and σ they obtained[57] $f^{1V} = 1$.

Rothman and coworkers[26] studied the isotope effect in the self-diffusion of Na in NaCl. Measurements of E_{24}^{22} in NaCl had been carried out even earlier[19], but the effect of temperature on this parameter had not been observed, and it had been concluded[57] that correlation is absent in the diffusion of Na in NaCl (i.e. $f=1$). Rothman[26] observed a change in E_{24}^{22} in NaCl: from 0.484 at 796.6 °C to 0.624 at 589.3 °C. By ascribing the lack of constancy of the isotope effect to an increasing contribution from divacancies to the diffusion process they evaluated[26] this contribution at different temperatures. This calculation is more complex for an ionic crystal than for a metal, since f becomes a function of the ratio of the jump frequencies of the anion (ω_a) and of the cation (ω_c) into the divacancy, and it can vary from zero to 0.782. The value of ΔK^{2V} for divacancy diffusion is also unknown.

Rothman and coworkers[26] define two limiting cases for the participation of divacancies in the transport process: 1) assuming that $E^{2V} = 0$ at the melting point, and noting that $E^{1V} = 0.624$, they estimate the minimum contribution from vacancy pairs at the melting point to be 22%; 2) assuming that at 796.6 °C the diffusion is wholly along divacancies they find $E^{2V} = 0.484$. Then, if $\Delta K_2 \leq 0.8$, we have $f^{2V} \leq 0.6$ and $\omega_a/\omega_c < 0.5$. Using these values they obtain[26] the maximum value of $D_2/(D_1 + D_2) = 53\%$ at 589 °C. A more critical analysis of the experimental results suggests that the most reasonable of all the possible values of E^{2V} is <0.2: in this case $f^{2V} \leq 0.25$ and $\omega_a/\omega_c \leq 0.1$. Adopting these values we find that the difference in activation energy between the two diffusion mechanisms is $\Delta Q = Q^{2V} - Q^{1V} = 0.82-0.9$ eV, and the contribution of vacancy pairs to diffusion near the melting point is 30–45%.

Using the ratio $\omega_a/\omega_c \leq 0.1$ to interpret the results of Beniere and coworkers[57] we find that the contribution of vacancy pairs at 800 °C is 50%, i.e. not very different from Rothman's value[26]. Also, with this value of $D_2/(D_1 + D_2)$ Beniere's results[57] give an f_{1V} value nearer to 0.78 than to 1, in good agreement with Nelson and Friauf's value[56].

Self-diffusion isotope effects have been studied also in single crystals of LiF [59] and CsI.[60] In both cases the migration mechanism was found to be by single vacancies.

2. Self-diffusion Istope Effect in Systems with Frenkel' Defects

In all the systems discussed so far the predominant defects are vacancies. As an example of the application of the isotope effect to structures containing Frenkel' defects we shall consider the diffusion of $^{105,111}Ag$ in AgCl.[33]

Studies[61-63] of ionic conduction in AgCl and AgBr single crystals (both pure and doped with divalent cations) have shown that most of the Ag ions migrate by the direct interstitial mechanism in pure AgCl and AgBr. The variation of the quantity $\Phi = \mu_i/\mu_V$ with temperature and pressure (where μ_i and μ_V are the mobilities of the interstitial ions and of the vacancies) has also been studied[61,62]. Self-diffusion can take place by indirect interstitial mechanisms involving collinear (frequency ν_1) or non-collinear jumps. Non-collinear jumps of two types are possible (frequencies ν_2 and ν_3). Peterson and coworkers[33] consider only the ν_1 and ν_2 jumps, pointing out that the ν_3 jump is energetically unfavourable, and they arrive at the following expression for the effect of mass on self-diffusion in silver halides:

$$\frac{D_\alpha}{D_\beta} - 1 = \frac{\Delta D_{tot}}{D_{\beta,\,tot}} = \frac{\Delta D_v}{D_v}\left(\frac{D_v}{D_{tot}}\right) + \frac{\Delta D_i}{D_i}\left(1 - \frac{D_v}{D_{tot}}\right);$$

where $\Delta D_V/D_V$ and $\Delta D_i/D_i$ are the relative differences between the self-diffusion coefficients of the two isotopes for the vacancy and the interstitial mechanism, and $\Delta D_{tot}/D_{tot}$ is the experimentally observed mass effect.

Introducing the functions $F_1(\chi)$ and $F_2(\chi)$, relating the frequencies of the collinear and the non-collinear jump ($\chi = \nu_1/\nu_2$), Peterson and coworkers obtain[33]

$$\Delta D_{tot}/D_{tot} = \alpha_1 \Delta K_1 + \alpha_2 \Delta K_2 + \alpha_v \Delta K_v, \qquad (15)$$

where

$$\alpha_1 = [1-(M_\alpha/M_\beta)^{1/2}]F_1(\chi)[1-D_v/D_{tot}],$$
$$\alpha_2 = [1(M_\alpha/M_\beta)^{1/2}]F_2(\chi)[1-D_v/D_{tot}],$$
$$\alpha_v = [1-(M_\alpha/M_\beta)^{1/2}]f_v D_v/D_{tot},$$

and $M_\alpha = [m_\alpha + (n-1)m_0]$, $M_\beta = [m_\beta + (n-1)m_0]$ for $n = 2$. The ratio D_V/D_{tot} can be obtained from the expression

$$\frac{D_v}{D_{tot}} = \frac{f_v}{(D_{tot}/D_v)(1-\Phi)},$$

where f_V is the correlation factor for the vacancy mechanism. Thus, by using Eqn.(15), the quantities α_1, α_2, and α_V can be calculated for different temperatures.

In order to determine ΔK_V Peterson and coworkers[33] measured the isotope effect for the self-diffusion of $^{105,111}Ag$ in AgBr doped with $CdBr_2$, because diffusion in this system is entirely (100%) by the vacancy mechanism. The best agreement between experiment and calculation was obtained by putting $\Delta K_1 = 1$ and $\Delta K_2 = 0.1$ (note that ΔK_V is constant in very case, $\Delta K_V = 0.66$). This result suggests that the interaction between the migrating atom and the lattice is weak during a collinear jump, whereas during a non-collinear jump the interaction is substantial. This conclusion is confirmed by other experimental results, showing that the activation energy is much lower for the collinear than for the non-collinear jump ($Q_1 = 0.058$ eV, $Q_2 = 0.274$ eV). The difference between the pre-exponential factors is even more striking ($D_{01} = 6.1$ cm^2 s^{-1}, $D_{02} = 1090$ cm^2 s^{-1}), indicating a large entropy of activation for the ν_2 jumps (due to the large number of particles taking part in this process).

3. The Isotope Effect in Hetero-diffusion

Tosi and Doyama[64] calculated the energy of formation (Hf) and the energy of migration (Hm) of cation vacancies in NaCl, KCl, and RbCl, the energy of migration of Na^+, K^+, and Rb^+ impurities in these chlorides, and the impurity–vacancy bond energy (Hb) for these impurities. They obtained[64] a very small value for the energy of migration of Na in RbCl (0.22 eV) in comparison with the Hm value for the migration of Rb^+.

The activation energy for the hetero-diffusion in the "intrinsic" (high-temperature) region is given by the expression

$$Q_{\text{intr}} = \frac{1}{2}H_f + H_m - k\left(\partial \ln f/\partial \frac{1}{T}\right)_{\text{intr}} + H_b.$$

In the "extrinsic" (low-temperature) region, in which no new defects are formed and therefore the term $\frac{1}{2}Hf$ can be ignored, we have

$$Q_{\text{extr}} = H_m - k\left(\partial \ln f/\partial \frac{1}{T}\right)_{\text{extr}} + H_b.$$

Experimental measurements of the temperature dependence of f in both regions give $\frac{1}{2}Hf$ and $(Hm + Hb)$, which can be compared with the calculated values[64]. Peterson and Rothman[65] measured the diffusion coefficients of Na in RbCl and the diffusion isotope effect of $^{22,24}Na$ at different temperatures. Plots for evaluating the ratio $[\partial \ln f/\partial (1/T)]_{\text{extr}}$ are shown in Fig. 2. The experimental results give $Q_{\text{intr}} = 2.06 \pm 0.02$ eV, $Q_{\text{extr}} = 0.59 \pm 0.01$ eV, $[\partial \ln f/\partial (1/T)]_{\text{intr}} = -0.19 \pm 0.02$ eV, $[\partial \ln f/\partial (1/T)]_{\text{extr}} = 0.05 \pm 0.03$ eV. They also obtained[65] $(H_m + H_b) = 0.65$ eV, and $\frac{1}{2}Hf = 1.22$ eV. According to Tosi and Doyama's calculations[64] the interaction energy of the Na^+ ion with a vacancy in RbCl is 0.1 eV. Taking $H_b = 0.1$ eV, we find $H_m = 0.55$ eV, in contrast to the calculated value[64] $H_m = 0.22$ eV. As expected from the theory, the energy of migration of the Na^+ ion is experimentally found to be higher than the energy of migration of the native rubidium ions. The experimental value $\frac{1}{2}Hf = 1.22$ eV also differs significantly from the calculated values (1.05 eV;[64] 1.12 eV),[66] but the migration energy calculated by the conventional ionic model is usually lower than the experimental value in all the alkali metal halide crystals. This discrepancy can be ascribed[66] to an excessive allowance for the polarisation energy of the ions surrounding the vacancy.

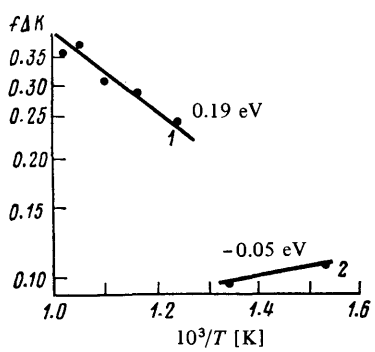


Figure 2. Isotope effect for the diffusion of Na in RbCl in (*1*) the intrinsic region and (*2*) the impurity region[65].

In order to determine $\frac{1}{2}Hf$ Peterson and coworkers[65] assumed that $(H_m + H_b)$ is the same in the intrinsic and the extrinsic state, i.e. that the energy needed to exchange a Na^+ ion with a vacancy and the bond energy are independent of whether the vacancy is free or attached to a multivalent impurity. This assumption was not tested experimentally.

The changed sign of $[\partial \ln f/\partial (1/T)]$ observed on going from the intrinsic to the extrinsic region has been explained qualitatively as follows[65]. In the intrinsic region the Na^+ ion can exchange places with a vacancy very much faster than any of the neighbouring Rb^+ ions. At 575 °C the rate of the Na^+–vacancy exchange (ω_2) is 10 times greater than the rate of the Rb^+–vacancy exchange (ω_0) if all the other jump frequencies are assumed to be equal. On raising the temperature ω_2 increases more slowly than ω_0, i.e. $Hm(Na^+) < Hm(Rb^+)$. This leads to low values of the correlation factor for the diffusion of the impurity, increasing with temperature. On the other hand, in the extrinsic region some of the vacancies may be bound to multivalent impurity ions. If these ions exchange places with vacancies more seldom than sodium ions the correlation factor should be much lower than in the intrinsic region. On the other hand, if H_m for the multivalent ion is intermediate in value between $Hm(Na^+)$ and $Hm(Rb^+)$ the correlation factor will be independent of temperature, or it may even increase as the temperature falls. This behaviour is consistent with both the temperature dependence and the low value of E observed experimentally in the extrinsic region.

VI. DIFFUSION IN TRANSITION METAL OXIDES

Unlike the majority of ionic compounds, many transition metal oxides can exist in non-stoichiometric compositions. These oxides contain non-stoichiometric defects whose concentration depends on temperature and on the oxygen partial pressure. We shall discuss only the oxides NiO, CoO, and FeO, all of which have the NaCl structure and can be described by the general formula $M_{1-x}O$ (in which cation vacancies are assumed to be the main non-stoichiometric defect). In order to preserve the electrical neutrality of the crystal an equal number of electron holes must be produced. At high temperatures the localised electron holes can migrate from one cation site to the next, giving rise to p-type semiconductivity.

In the absence of defect association the formation of cation vacancies in $M_{1-x}O$ can be described by the expression

$$\frac{1}{2}O_2 + \alpha M^{2+} \rightarrow O^{2-} + V_c^{\alpha'} + \alpha M^{3+},$$

where $V_c^{\alpha'}$ is a cation vacancy (negatively charged with respect to the lattice), M^{2+} and O^{2-} are a metal cation and an oxygen anion in their respective lattice sites, and M^{3+} is a cation bearing a localised hole. Obviously, the concentration of cation vacancies and of holes will be proportional to $p_{O_2}^{1/n}$ at a given temperature, where p_{O_2} is the equilibrium partial pressure of oxygen and $n = 2(\alpha + 1)$. Thus, if the electrical conductivity and the self-diffusion of cations are determined exclusively by electron holes and cation vacancies we expect both the cation self-diffusion coefficients and the electrical conductivity to be a function of p_{O_2}.

1. Self-diffusion in NiO and CoO

The effect of oxygen partial pressure on the self-diffusion of cations in NiO and CoO was studied by Volpe and Reddy[71], who found values of n (in the expression $D \propto p_{O_2}^{1/n}$) of 2.9, 3.3, and 3.6 for CoO at 1000, 1150, and 1350 °C respectively, and

6.25 and 5.0 for NiO at 1245 and 1380 °C respectively. The deviation of the n value from 4 (or 6) shows that the single defect model is incapable of interpreting the experimental results adequately. Non-integral values of n can be explained by postulating more than one type of ionised cation vacancy. Since electron holes are more mobile than cation vacancies, the ionised state of a cation vacancy can change many thousands of times during the life time of the vacancy. Hence, if more than one type of ionised cation vacancy is contributing to the equilibrium, a migrating vacancy can have an effective negative charge α which is not necessarily an integer. If we adopt this approach we must introduce a distinction between the mobilities of neutral, singly charged, and doubly charged vacancies in these materials.

Recent work on isotope effects in the self-diffusion of cations has helped to identify the diffusion mechanisms in CoO and NiO crystals. Measurements[72] of the diffusion of ^{55,60}Co in CoO gave $E_{60}^{55} = 0.58 \pm 0.01$ (independent of temperature between 1081 and 1411 °C). The temperature-independence of the isotope effect is evidence that the self-diffusion of Co in CoO involves only one mechanism, and the observed value of E_{60}^{55} suggests a single vacancy mechanism with $\Delta K = 0,75$. Volpe and coworkers[73] also studied the isotope effect for the self-diffusion of ^{57,66}Ni in NiO crystals, and obtained the value $E_{66}^{57} = 0.61 \pm 0.02$, independent of temperature in the range 1201–1678 °C. In an earlier paper[71] the same workers had suggested that a temperature-dependent (interstitial) mechanism may be needed, in addition to the vacancy mechanism, to account for the diffusion of cations in nickel oxide. However, their measurement of the isotope effect clearly shows that in NiO (as in CoO) cation transport occurs exclusively by the single vacancy mechanism, with $\Delta K = 0,78$.

2. Self-diffusion in $Fe_{1-x}O$

The wüstite lattice always contains an apparent excess of oxygen (at 1400 °C the range of compositions is $Fe_{0,95}O$–$Fe_{0,84}O$). The non-stoichiometric excess of oxygen is shown (by X-ray diffraction) to be due to a large number of cation vacancies[74]. At these high concentrations of defects we can no longer use the simple model of individual vacancies, and we must allow for the formation of defect associations (or clusters). Extended defects may give rise to whole regions having the spinel (Fe_3O_4) structure in wüstite. Thus, cluster formation perturbs the direct relationship between the diffusion coefficient and the departure from stoichiometry (x). Not surprisingly, early studies of this relationship gave inconsistent results. For example, a study of diffusion in $Fe_{1-x}O$ with radioactive indicators gave D values increasing with the extent of non-stoichiometry[75], whereas the D values calculated from chemical diffusion coefficients decrease as x increases.

A detailed study of the mechanism of diffusion of cations in wüstite and of the formation of clusters in this material (and its effect on diffusion) was based on measurements[76] of the diffusion coefficients and of the diffusion isotope effect of ^{52,59}Fe in $Fe_{1-x}O$. The results indicate a non-linear relationship between D and x. At high temperatures (1200 °C) and compositions in the range $0.05 \leq x \leq 0.10$ the D values increase by 20% as x increases, but at 800 °C they fall by 40%, and at 1000 °C they are almost independent of x. The measurements of the isotope effect are summarised in Fig. 3, which shows a plot of $E = f(x)$ for different temperatures.

As was pointed out above, the numerical values of E for NiO and CoO are consistent with the single-vacancy mechanism ($f = 0,78$ and $\Delta K = 0,78$ and 0,75 respectively), and are independent of temperature and composition. In wüstite of a given composition E is independent of temperature, but it decreases as the deviation from stoichiometry increases. This effect can be ascribed to changes in the correlation factor if we assume ΔK to be constant for wüstite and for NiO and CoO (a plausible assumption, since all three oxides have the same crystal structure). The fact that the E values are lower in FeO than in NiO and CoO suggests a contribution to the diffusion process from divacancies and even higher-order associations. The experimental results show that the iron cations diffuse by exchanging places with mobile vacancies, with a single mechanism operating over the whole range of composition (as shown by the constancy of the isotope effect parameters at different temperatures but constant x).[76]

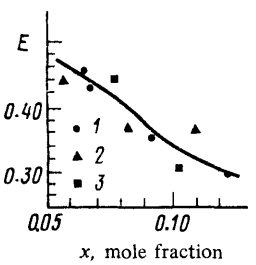


Figure 3. Isotope effect for the self-diffusion of ^{52,59}Fe in $Fe_{1-x}O$ as a function of x [76] at different temperatures: *1*) 1200, *2*) 1000, *3*) 807 °C.

At high concentrations of vacancies clusters are formed: different models of the cluster are discussed in Ref. 77. These defect associations are less mobile than single vacancies, and they show a higher degree of correlation, leading to lower E values at high x. Macroscopic diffusion along free vacancies tends to decrease as the deviation from stoichiometry increases. At a well defined temperature D is independent of x, since the increase in the concentration of free vacancies is balanced by the decrease in mobility and by the increased correlation effect (i.e. by the decrease in f). Lastly, if the temperature is increased still further the higher-order clusters begin to break down, causing D to increase with x.

3. Diffusion of Co in NiO

In order to throw light on the detailed features of impurity diffusion processes, and also to explain the influence of the interaction between impurity cations and defects on the self-diffusion of cations in oxides, Chen and Peterson[78] studied the isotope effect for the diffusion of Co in NiO, and also the simultaneous diffusion of Co and Ni in $(Ni_{1-c}Co_c)O$ crystals. The experimental values of $(f\Delta K)_{Co}$ in NiO increase from 0.45 ± 0.01 and 1179 °C to 0.61 ± 0.01 at 1649 °C. Using the value $\Delta K = 0.78$ obtained for the self-diffusion of Ni in NiO the authors[78] evaluated f_{Co} for the given temperature range (see Fig. 4). These values of f_{Co} were then used to calculate the ratio of the jump frequencies of the impurity ions and the solvent ions, from which was finally obtained the ratio of the diffusion coefficients of Co and Ni (D_{Co}/D_{Ni}) in pure NiO.

The D_{Co}/D_{Ni} values calculated from the diffusion isotope effect agree well with the values obtained directly from experiments on the simultaneous diffusion of Co and Ni in NiO. This agreement between calculation and experiment confirms the validity of the assumptions made in the calculation (including a low value of the energy H_b for the interaction between an impurity cation and a vacancy, i.e. $H_b \ll kT$).

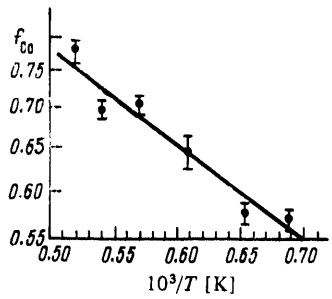


Figure 4. f_{Co} against $1/T$ for the diffusion of Co in NiO.[76]

VII. OTHER APPLICATIONS OF THE DIFFUSION ISOTOPE EFFECT

All the examples considered so far are typical of the practical application of the diffusion isotope effect in detailed studies of migration processes in metals and in ionic crystals. However, the possibilities of the isotopic method are not limited to these systems: the method can be used also to study van-der-Waals and molecular crystals.

Parker and coworkers[79] studied the diffusion of the krypton isotopes $^{78,86}Kr$ in solid argon, and found $E_{86}^{78} = 0.48 \pm 0.25$. This result suggests that the diffusion of Kr in solid Ar involves either a divacancy mechanism or a single vacancy mechanism with $f = 0.78$ and $\Delta K = 0.6$. The low value of ΔK is not surprising, since it can be shown that heavy impurity atoms have very small values of ΔK. Barton[80] calculated the isotope effect for this system theoretically, and obtained $\Delta K = 0.75-0.85$ (a value at the upper limit of experimental results). The calculated value of E_{86}^{78} for the divacancy mechanism is also not too different from the experimental value[79]. However, within the limitations of the model used it is not possible to select the preferred mechanism.

Fox and Sherwood[81] used the mass effect to identify the diffusion mechanism in solid benzene single crystals. The molecules $^{14}C\,^{12}C_5H_6$ and $^{12}C_6\,^2H_5\,^3H$ were used as tracers because their molar volumes are similar (and their spectral characteristics almost identical) to those of ordinary benzene. The authors therefore treated the labelled molecules as "isotopes" of benzene. The measured value $E = 0.8$ suggests mass transport by a single vacancy mechanism, with $f = 0.78$ and $\Delta K = 1$. Similar measurements were carried out on single crystals of naphthalene[82]. The equations for the diffusion isotope effect in solids have been used[83] to interpret data on the isotope effect in liquids. The diffusion of perdeuterobenzene and of ordinary benzene has been studied in chlorobenzene, n-octane, and cyclohexane. The results, which show a negligibly small "isotope effect" for the diffusion of benzene, made the authors conclude[83] that diffusion in these systems is controlled primarily by the viscosity of the solvent.

The diffusion isotope effect has been studied also in glasses (systems in which the structural units have no long-range order). Le Claire[84] observed a small isotope effect for the diffusion of sodium in a sodium silicate glass ($E_{24}^{22} = 0.24$) and concluded that mass transport in this system is by a relay mechanism. Similar measurements were made in other laboratories with the aim of determining the correlation factor or of identifying the mechanism of diffusion in glass[85,86].

A typical application of the diffusion isotope effect to the study of transport processes in disordered crystals was described by Robinson and Peterson[87], who measured the isotope effect for the diffusion of silver along the grain boundaries of metallic silver. The experimental value $\Delta K = 0.46$ can be used to select a series of f and ΔK values compatible with both experiment and theory[88]. The closest agreement between experiment and calculation was obtained for $\Delta K = 0.70-0.76$ and a correlation factor corresponding to the following vacancy–dislocation bond energies: 0.2 eV (vacancy at the centre of the dislocation), and 0.15 eV (vacancy at one interatomic distance from the centre of the dislocation). A measurement[87] of the isotope effect for the diffusion of silver in polycrystalline copper gave much lower values ($E = 0.16$), showing that the diffusion of silver impurity in copper has a high correlation, i.e. that the differences in the vacancy–dislocation bond energy are large. As a result, the silver tends to accumulate along the dislocations.

The separation of isotopes by diffusion has been studied also in geochemistry, because it yields information on the physicochemical conditions of natural processes and on their time scale. The isotopic variations of Mg, Ca, K, and Li in minerals have been examined in detail[89], and the migration parameters obtained have been used to reconstruct the thermal history of the minerals and to determine the temperature and time of their formation.

VIII. METHODS OF MEASURING THE DIFFUSION ISOTOPE EFFECT

According to Eqn.(8) the measurement of the diffusion isotope effect in practice reduces to determining the relative difference between the diffusion coefficients of the migrating isotopes. In order to obtain the E value with a precision of 5% the ratio $\Delta D/D_\beta$ must be measured with an error not exceeding 0.1%. In most experiments the parameters D_α and D_β cannot be measured to better than $\pm(1-2)\%$, and since the difference between the diffusion coefficients is usually between 2 and 3% this difference lies within the experimental uncertainty and is therefore not experimentally detectable.

The problem can be overcome by monitoring the diffusion of the two isotopes simultaneously. Since the diffusion conditions are identical, errors in the measurement of the diffusion temperature and time do not influence the ratio $\Delta D/D_\beta$. In an experiment of this type the precision of the measurement of $\Delta D/D_\beta$ is determined by the precision with which the isotope concentrations c_α and c_β are known. The ratio c_α/c_β can be determined by radio-isotope and mass-spectroscopic techniques to better than 0.1%. The most convenient (and therefore most often used) method is the radioactive indicator methods, which we shall examine in detail.

Mass-spectroscopic methods have been used in geochemical studies to measure the natural abundance ratios of stable isotopes[89]. The methods can be used also to study isotope effects in the diffusion of elements lacking convenient radioactive isotopes. Thus, E_7^6 for the diffusion of $^{6,7}Li$ in Na,[90] AfCl,[70] and TiO_2 [91] has been measured mass-spectrocopically. In this method of analysis the diffusion isotope effect can be calculated by the procedure proposed by Naumov and Ptashnik[70,92]. In the interpretation of mass-spectrometric data on the diffusion isotope effect it is very important to allow for the isotope fractionation which takes place in the ion source during the measurement. Neglect of this factor can lead to spuriously high (ten-fold, or even hundred-fold) results.

By using the radiometric method the concentration of the migrating isotopes can be determined in three ways.

1. If the difference between the half-lives $T_{1/2}^{\alpha}$ and $T_{1/2}^{\beta}$ is fairly large the ratio c_α/c_β can be determined by analysing the time dependence of the total activity.

$$c_{tot} = c_\alpha \exp(-\lambda_\alpha t) + c_\beta \exp(-\lambda_\beta t),$$

where c_{tot} is the measured total activity, λ_α and λ_β are the decay constants, and t is time (measured from the beginning of the experiment).

At present this procedure is the most widely used. If the half-life of one of the isotopes ($T_{1/2}^{\alpha}$, say) is small enough, a second measurement is made at time $t \geq 10T_{1/2}^{\alpha}$, when the short-lived isotope has decayed almost completely and the measured activity corresponds to the concentration of the long-lived isotope c_β. The concentration of the short-lived isotope is then given by the difference $c_\alpha = c_{tot} - c_\beta$.

2. If the isotopes used in the experiment are γ-emitters with their strongest spectral lines at sufficiently different energies, and if the isotopes decay to a significant extent during the measurement, the activity ratio of the isotopes can be expressed as

$$\frac{c_\alpha}{c_\beta} = \frac{(\lambda_\alpha/\lambda_\beta)(A_\alpha/A_\beta)\exp[(\lambda_\alpha - \lambda_\beta)t][1 - \exp(-\lambda_\beta\tau)]}{1 - \exp(-\lambda_\alpha\tau)};$$

where A_α and A_β are the areas under the gamma peak (corrected for background), t is the time elapsed from the beginning of the measurement on a series of samples, and τ is the time of the measurement of one particular sample.

3. If the chosen isotopes emit different radiations (one β-emitter and one γ-emitter, say) it is still possible to determine the concentrations of both isotopes simultaneously by placing the sample between suitable detectors.

We have dealt only with the measurement of the activity ratio of the migrating isotopes (c_α/c_β). We shall now show that this is sufficient for determining E_β^α. In this case of diffusion from a thin layer the concentration of the isotope (c) varies with the depth of penetration (x) and diffusion time (t) according to the expression

$$c = c_0 \exp(-x^2/4Dt),$$

where D is the diffusion coefficient of the isotope. For two isotopes we obtain the ratio

$$\frac{c_\alpha}{c_\beta} = \frac{c_{0\alpha}}{c_{0\beta}} \exp\left[-\frac{x^2}{4D_\alpha t} + \frac{x^2}{4D_\beta t}\right] = \frac{c_{0\alpha}}{c_{0\beta}} \exp\left[\frac{x^2}{4D_\alpha t}\left(\frac{D_\alpha}{D_\beta} - 1\right)\right];$$

$$\ln\frac{c_\alpha}{c_\beta} = \text{const} + \frac{x^2}{4D_\alpha t}\left[\frac{D_\alpha}{D_\beta} - 1\right] = \text{const} - \left[\frac{D_\alpha}{D_\beta} - 1\right]\ln c_\alpha.$$

Thus the relative difference between the diffusion coefficients of the isotopes can be obtained by analysing plots of $\ln(c_\alpha/c_\beta) = f(\ln c_\alpha)$. In this procedure the precision of the determination of the quantity $[D_\alpha/D_\beta - 1]$ depends primarily on the precision with which the relative activities of the isotopes (c_α/c_β) can be measured.

Because of the smallness of the diffusion isotope effect, most workers carry out a blank experiment (in parallel with the measurement of the concentration of the diffusing isotopes) in which the activity of an aliquot of the initial mixture of isotopes is monitored. A zero slope of the $\ln(c_\alpha/c_\beta) = f(\ln c_\alpha)$ plot for the blank experiment confirms that the observed effect arises wholly from diffusion phenomena.

The greatest care is needed in carrying out the isotope experiment. Not less than 10^6 counts should be used in the measurements of activity (in order to minimise the statistical error). In addition to $\ln(c_\alpha/c_\beta) = f(\ln c_\alpha)$ it is useful to plot also the relationship $\ln c_{\alpha,\beta} = f(x^2)$, which should be a straight line. The activity should change by at least three orders of magnitude with depth of penetration, because deviations from normal bulk diffusion, leading to distortions in the linear plot, can only be detected at considerable depths. The blank experiment is an essential part of the procedure. The importance of adhering to all these precautions is well illustrated by published measurements of the isotope effect for the diffusion of Ag in Pb. Herzig and coworkers[93] found $E_{111}^{105} = 1$, but a redetermination of the isotope effect in this system[53] gave $E_{111}^{105} = 0.25$. The latter value of the diffusion isotope effect satisfactorily explains the fast diffusion of Ag in Pb. This very large discrepancy between experimentally measured values of the isotope effect can be ascribed to the failure by Herzig and coworkers[93] to observe all the above precautions.

Isotope diffusion has been studied also in an electric field[59]. In this case the separation of the isotopes is more substantial, and can be used in practice to produce enrichment of the initial mixture with one of the isotopes. The precision of the measurement of the diffusion isotope effect increases with the extent of separation achieved. In these measurements the relative difference between the diffusion coefficients of the isotopes is replaced by its equivalent relative difference between the mobilities of the isotopes ($\Delta D/D_\beta = \Delta\mu/\mu_\beta$). Detailed discussions of the measurement of the diffusion isotope effect with the help of an electric field, and of the advantages of this method, are given in Refs.70 and 92.

---oOo---

In conclusion we note that the importance of the diffusion isotope effect as a new method of gaining information on the details of migration processes in solids is recognised by the inclusion of special chapters on the advantages and applications of this method in all the recently published reviews and monographs devoted to diffusion[94-96].

REFERENCES

1. J.Hladik (Editor), "Physics of Electrolytes" (Translated into Russian), Moscow, 1978.
2. A.S.Nowick and J.J.Burton (Editors), "Diffusion in Solids (Recent Developments)", Academic Press, New York, 1975.
3. J.Manning, "Kinetics of the Diffusion of Atoms in Crystals" (Translated into Russian), Izd.Mir, Moscow, 1971.
4. J.G.Mullen, Phys.Rev., 121, 2649 (1961).
5. C.Zener, "Imperfections in Nearly Perfect Crystals", J.Wiley, New York, 1952.
6. I.Prigogine and T.Bak, J.Chem.Phys., 31, 1368 (1959).

7. S.Rice and H.Frisch, J.Chem.Phys., **32**, 1026 (1960).
8. C.Flynn, Phys.Rev., **171**, 682 (1968).
9. M.D.Feit, Phys.Rev., **B3**, 1223 (1971).
10. M.D.Feit, Phys.Rev., **B5**, 2145 (1972).
11. H.R.Glyde, Phys.Rev., **180**, 722 (1969).
12. B.N.Achar, Phys.Rev., **B2**, 3848 (1970).
13. A.D.Le Claire, Phil.Mag., 14, 1271 (1966).
14. S.Z.Bokshtein (Editor), "Diffuziya v Metallakh s Ob"emno-tsentrirovannoi Reshetkoi" (Diffusion in Body-centred Cubic Metals), Izd.Metallurgiya, Moscow, 1969, p.180.
15. J.Mundy, L.Barr, and F.Smith, Phil.Mag., 14, 785 (1966).
16. N.Nachtrieb, J.Weil, E.Catalano, and A.Lowson, J. Chem.Phys., 20, 1189 (1952).
17. S.Rothman, N.Peterson, and J.Robinson, Phys. Status Solidi, **39**, 635 (1970).
18. R.Brown, J.Vorster, N.March, R.Perrin, and R.Bullough, Phil.Mag., 23, 555 (1971).
19. L.Barr and A.D.Le Claire, Proc.Brit.Ceram.Soc., 1, 109 (1964).
20. R.Brown, Z.Naturforsch., **26a**, 77 (1971).
21. J.Ebisuzaki, W.Kass, and M.O'Keeffe, Phil.Mag., **15**, 1071 (1967).
22. J.Ebisuzaki, W.Kass, and M.O'Keeffe, J.Chem. Phys., **46**, 1375 (1967).
23. J.Ebisuzaki, W.Kass, and M.O'Keeffe, J.Chem. Phys., 49, 3329 (1968).
24. J.Sussmann and J.Wersmann, Phys.Status Solidi, **53(b)**, 419 (1972).
25. R.Katz, M.Guinan, and R.Borg, Phys.Rev., **B4**, 331 (1971).
26. S.Rothman and A.Lascar, J.Phys.Chem.Solids, **33**, 1061 (1972).
27. N.Bakker, Phys.Status Solidi, **31**, 271 (1969).
28. J.Mundy, Phys.Rev., **B3**,2431 (1971).
29. T.Neumann and R.Imm, J.Phys.Chem.Solids, **29**, 1613 (1968).
30. S.Rothman and N.Peterson, Phys.Status Solidi, **35**, 305(1969).
31. V.Irmer and Feller-Kniepmeier, J.Appl.Phys., **43**, 953 (1972).
32. N.Peterson and S.Rothman, Phys.Rev., **163**, 645 (1967).
33. N.Peterson, L.Barr, A.D. Le Claire, J.Phys., C6, 2020 (1973).
34. C.Tomizuka, Symposium "Progress in Very High Pressure Research. Proceedings of the International Conference (France, 1960)", J.Wiley, New York, 1961.
35. R.Hannemann, R.Ogilvie and H.C.Gatos, Trans. AIME, **233**, 691 (1965).
36. M.Beyeler and J.Adda, J.Phys.(Paris), 29, 345 (1968).
37. M.Norton and C.Tomizuka, Bull.Amer.Phys.Soc., **15**, 390 (1970).
38. D.Yoon and D.Lazarus, Phys.Rev., **B5**, 4935 (1975).
39. P.McArdle, Bull.Amer.Phys.Soc., 13, 489 (1968).
40. H.Mehrer and A.Seeger, Phys.Status Solidi, **35**, 313 (1969).
41. R.Simmons and R.Ballufi, Phys.Rev., 129, 1533 (1963).
42. H.Bowden and R.Ballufi, Phil.Mag., **19**, 1001 (1969).
43. P.Reimers and D.Bartdorff, Phys.Status Solidi, **50**, 305 (1972).
44. H.Mehrer and A.Seeger, Phys.Status Solidi, **39**, 647 (1970).
45. N.Peterson, Phys.Rev., **136A**, 568 (1964).
46. C.Walter and N.Peterson, Phys.Rev., **178**, 922 (1969).
47. C.De Gonzalez and N.De Reca, J.Phys.Chem.Solids, **32**, 1067 (1971).
48. J.Mundy, C.Tse, and W.McFall, Phys.Rev., **B13**, 2349 (1976).
49. A.Batra, Phys.Rev., **159**, 487 (1967).
50. E.Stein, H.Mehrer, and A.Seeger, Phys.Status Solidi, (b), 75, 361 (1976).
51. J.Mundy and W.McFall, Phys.Rev., B8, 5477 (1973).
52. J.Mundy and W.McFall, Phys.Rev., B7, 4363 (1973).
53. J.Miller, J.Mundy, L.Robinson, and R.Loess, Phys. Rev., B8, 2411 (1973).
54. J.Miller and W.Edelstein, Phys.Rev., **188**, 1081 (1969).
55. J.Mundy, J.Miller, and S.Rothman, Phys.Rev., B10, 2275 (1974).
56. V.Nelson and R.Friauf, Chem.Solids, 31, 825 (1970).
57. F.Beniere, M.Beniere, and M.Chemla, Chem.Solids, 31, 1205 (1970).
58. K.Tharmalingam and A.Lidiard, Phil.Mag., 6, 1157 (1961).
59. V.B.Ptashnik, Fiz.Tverdogo Tela, 13, 3212 (1971).
60. S.M.Klotzman, J.P.Polikarpova, G.A.Tatarinova, and A.N.Timofeev, Phys.Status Solidi, (b), 63, 153 (1974).
61. H.Abbink and D.Martin, J.Phys.Chem.Solids, 27, 205 (1966).
62. A.N.Murin, I.V.Murin, and V.P.Sivkov, Fiz.Tverdogo Tela, 15, 142 (1973).
63. B.G.Lur'e, A.N.Murin, and I.V.Murin, Vestnik Leningrad.Univ., 4, (22), 131 (1968).
64. M.Tosi and M.Doyama, Phys.Rev., **151**, 642 (1966).
65. N.Peterson and S.Rothman, Phys.Rev., **177**, 1329 (1969).
66. J.Boswara and A.Lidiard, Phil.Mag., **16**, 805 (1967).
67. F.Nicolas, Thesis, Paris, 1971.
68. A.N.Murin, I.V.Murin, V.I.Portnyagin, and A.M.Andreev, Fiz.Tverdogo Tela, 15, 2838 (1973).
69. P.Süptiz, Phys.Status Solidi, 12, 555 (1965).
70. V.B.Ptashnik, Fiz.Tverdogo Tela, 13, 1066 (1971).
71. M.Volpe and J.Reddy, J.Chem.Phys., 53, 1117 (1970).
72. W.Chen, N.Peterson, and W.Reeves, Phys.Rev., **186**, 887 (1969).
73. M.Volpe, N.Peterson, and J.Reddy, Phys.Rev., B3, 1417 (1971).
74. M.Hayakawa, J.Cohen, and T.Reed, J.Amer.Ceram. Soc., **55**, 100 (1972).
75. P.Hembree and J.Wagner, Trans.Met.Soc,AIME, **245**, 1547 (1969).
76. W.Chen and N.Peterson, J.Phys.Chem.Solids, **36**, 1097 (1975).
77. F.Koch and J.Cohen, Acta Cryst., B25, 275 (1969).
78. W.Chen and N.Peterson, J.Phys.Chem.Solids, **33**, 881 (1972).
79. E.Parker, B.Smith, and H.Glyde, Phys.Rev., **188**, 1371 (1969).
80. J.Barton, Phys.Rev., B2, 5010 (1970).
81. R.Fox and J.Sherwood, Trans.Faraday Soc., 67, 3364 (1971).
82. E.Hampton and J.Sherwood, J.Chem.Soc.Faraday Trans., 71, 1392 (1975).
83. J.Shankland, P.Dunlop, and L.Barr, Phys.Rev., B12, 2249 (1975).
84. H.Euring, D.Henderson, and W.Jost (Editors), "Physical Chemistry", Vol.10, Ch.5, Academic Press, New York, 1970.
85. V.A.Zhabrev, V.V.Moiseev, and V.N.Sigaev, Fiz. Khim.Stekla, 1, 475 (1975).
86. C.Lim and D.Day, J.Amer.Ceram.Soc., 60, 473 (1977).
87. J.Robinson and N.Peterson, Surface Sci., 31, 586 (1972).

88. M.Doyama and R.Cotterill, Supl.Jap.Inst.Met., **9**, 55 (1968).
89. A.A.Alferovskii, Thesis, Leningrad, 1974.
90. A.N.Naumov and G.A.Ryskin, Fiz.Tverdogo Tela, 7, 695 (1965).
91. O.Johnson and H.Krause, J.Appl.Phys., **37**, 668 (1966).
92. A.N.Naumov and V.B.Ptashnik Fiz.Tverdogo Tela, 8, 3590 (1966).
93. C.Herzig, T.Neumann, and D.Wolter, Z.Naturforsch., **26a**, 1477 (1971).
94. A.N.Murin, Symposium "Khimiya Nesovershennykh Ionnykh Kristallov" (Chemistry of Imperfect Ionic Crystals), Izd.Leningrad.Univ., 1975, p.270.
95. V.Boldyrev and K.Meier (Editors), "Festkörperchemie (Beitrage aus Forschung und Praxis)", VEB, Leipzig, 1973.
96. B.S.Bokshtein, S.Z.Bokshtein, and A.A.Zhukhovitskii, "Termodinamika i Kinetika Diffuzii v Tverdykh Telakh" (Thermodynamics and Kinetics of Diffusion in Solids), Izd.Metallurgiya, Moscow, 1974.

Leningrad State University

Translated from *Uspekhi Khimii*, **49**, 1990-2031 (1980) U.D.C. 541.144.8

Reversible Recombination of Radicals

I.V.Khudyakov, P.P.Levin, and V.A.Kuz'min

The results of experimental studies on the kinetics of the reversible recombination of radicals in the liquid phase in relation to phenoxy-, C-centred, peroxy-, and nitroxy-radicals and radical-ions are surveyed. It is shown that steric hindrance has a decisive influence on the rate of recombination of many radicals. The influence of the solvent on the kinetics of the reversible recombination is considered and particular attention is given to the influence of the viscosity of the solvent on the kinetics of the recombination of radicals with a distinct anisotropy of their reactivity.
The bibliography includes 181 references.

CONTENTS

I.	Introduction	982
II.	Kinetics of the destruction of radicals	982
III.	Diffusion-limited recombination of radicals	983
IV.	The influence of solvent viscosity on the kinetics of the reversible recombination	984
V.	Phenoxy-radicals	986
VI.	Aromatic C-centred radicals	989
VII.	Peroxy- and nitroxy-radicals	991
VIII.	Radical-ions	992
IX.	Other radicals	994
X.	The influence of the solvent on the kinetics of reversible recombination	996

I. INTRODUCTION

A typical reaction characteristic of all active short-lived radicals is rapid bimolecular recombination (dimerisation, disproportionation, and electron transfer); all other reactions of short-lived radicals compete with it. If the chemical bond formed in the dimer on recombination is weakened owing to the electronic influence of substituents or if the formation of the dimer entails steric hindrance, then the recombination of radicals is reversible†:

$$R + R \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} D. \qquad (1)$$

Comparatively stable radicals, characterised by a high degree of delocalisation of the unpaired electron, also undergo reversible recombination. Radical–dimer systems have been investigated by spectrophotometry, the temperature jump method, flash photolysis, NMR, kinetic EPR, and EPR combined with the rotating sector method. This review considers the results of experimental studies on the kinetics and thermodynamics of reaction (1) in the liquid phase. The study of the kinetics of the reversible recombination of radicals in various media is important for the understanding of the relation between the structure and reactivity of radicals and the influence of the chemical nature of the solvent and the viscosity of the medium on radical reactions. Data for the kinetics of fast reversible recombination reactions are important for the development of a theory of diffusion-controlled processes.

II. KINETICS OF THE DESTRUCTION OF RADICALS

If the radical–dimer system is displaced from the state of equilibrium (for example, by increasing the concentration of radicals with the aid of a light flash), then k_1 and k_{-1} can be obtained from the analysis of the subsequent relaxation of the system to equilibrium[1-6]. Direct or sensitised photochemical oxidation of compounds RH by flash photolysis can lead to the formation of radicals at an initial non-equilibrium concentration $[R]_0$; subsequently the system also relaxes to equilibrium, which makes it possible to determine the corresponding kinetic parameters[1-4,7]. In the majority of studies experiments yielded the values of K and k_1, k_{-1} being determined from the relation $k_{-1} = Kk_1$. The study of temperature relations makes it possible to obtain the thermodynamic parameters of reaction (1). The following relations were used: $K = \exp(\Delta S^\circ/R)\exp(-\Delta H^\circ/RT)$ (the van't Hoff equation) and $k = (k_B T/h)\exp(\Delta S^{\neq}/R)\exp(-\Delta H^{\neq}/RT)$ (the Wynn-Jones and Eyring equation).

The study of the NMR spectra of diamagnetic dimers present in solution in equilibrium with the corresponding radicals permits the determination of k_{-1} and the investigation of the kinetics of all the elementary reactions occurring in the radical–dimer system[8,9].

Together with reaction (1), irreversible radical destruction or irreversible dimer decomposition reactions can occur in the solution. Possible kinetic schemes for the destruction of radicals are described below[10].

Scheme I

$$D \underset{k_1}{\overset{k_{-1}}{\rightleftarrows}} 2R \xrightarrow{k_2} \text{stable products.}$$

When $k_1 \gg k_2$, one obtains

$$-d[R]/dt = 2k_2[R]^2/(1+4k_1[R]/k_{-1}).$$

If $4k_1[R]/k_{-1} \gg 1$, then the radical destruction reaction will obey a first-order law with $k_{obs} = k_2 k_{-1}/2k_1$, while subject to the condition $4k_1[R]/k_{-1} \ll 1$, the radical destruction will follow a second-order law with $k_{obs} = 2k_2$. Thus at high radical concentrations the destruction is a first-order process while at low concentrations it is a second-order process.

Scheme II

$$2R \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} D \xrightarrow{k_2} \text{stable products.}$$

† Here and henceforth it is assumed that $-d[R]/dt = 2k_1[R]^2 - 2k_{-1}[D]$, $K = k_{-1}/k_1$, and $\Delta X^0 = \Delta X^{\neq}_{-1} - \Delta X^{\neq}_1$, where X is a thermodynamic function.

When $k_{-1} \gg k_3$, one obtains,

$$-\mathrm{d}[\mathrm{R}]/\mathrm{d}t = \frac{2k_3k_1[\mathrm{R}]^2}{k_{-1}(1+4k_1[\mathrm{R}]/k_{-1})}.$$

Similarly, when $4k_1[\mathrm{R}]/k_{-1} \gg 1$, the radical destruction obeys a first-order law with $k_{obs} = k_3/2$, and, when $4k_1[\mathrm{R}]/k_{-1} \ll 1$, it obeys a second-order law with $k_{obs} = 2k_3k_1/k_{-1}$.

On the basis of kinetic data alone, it is difficult to distinguish Schemes I and II.

Scheme III

$$2\mathrm{R} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{D}; \quad \mathrm{R} \xrightarrow{k_4} \text{stable products.}$$

When $k_1[\mathrm{R}] \gg k_4$, one obtains

$$-\mathrm{d}[\mathrm{R}]/\mathrm{d}t = k_4[\mathrm{R}]/(1+4k_1[\mathrm{R}]/k_{-1}).$$

When $4k_1[\mathrm{R}]/k_{-1} \gg 1$, the radical destruction obeys a zero-law with $k_{obs} = k_4k_{-1}/4k_1$. When $4k_1[\mathrm{R}]/k_{-1} < 1$, a first-order radical destruction reaction with $k_{obs} = k_4$ should take place.

III. DIFFUSION-LIMITED RECOMBINATION OF RADICALS

The fundamental question which arises from the analysis of the kinetics of the fast recombination of radicals is whether the reaction is diffusion-limited. For bimolecular reactions fully limited by diffusion, the observed rate constant is directly proportional to the quantity T/η, where η is the viscosity of the solvent:

$$k \propto T/\eta. \tag{2}$$

For bimolecular reactions of radicals limited by translational diffusion, we have[15,34,52,64]

$$k = \frac{N}{1000} \cdot \sigma \cdot 4\pi\rho D \simeq \sigma \cdot \frac{8RT}{3000\eta}, \text{ litre mol}^{-1}\text{ s}^{-1},$$

where N is the Avogadro number, $\sigma = 1/4$ is a statistical factor taking into account the fact that only radical pairs which are in the singlet state during the encounter lead to the reaction products, ρ the reaction radius, and D the mutual diffusion coefficient of the radicals. For a reaction between identical radicals [reaction (1)],[15]

$$k_1 = k_{diff} \simeq \sigma \cdot \frac{4RT}{3000\eta}. \tag{3}$$

The choice of the numerical value of the coefficient $4\sigma/3000$ in Eqn.(3) is usually somewhat arbitrary: the questions of the value of σ ($1/4 < \sigma < 1$; see, for example, Nonhebel and Walton[11] and Buchachenko et al.[12]), of the replacement of the coefficient 4/3000 by 4/2000 (see, for example, Tyrrell[13]), etc. have been discussed.

For reactions controlled by translational diffusion, the following expression is valid[1,14]:

$$\Delta H^{\neq}_{diff} = B, \tag{4}$$

where B is the activation energy for the viscous flow of the solvent:

$$\eta = \eta_0 \exp(B/RT).$$

The study of the influence of the viscosity of the solvent on the observed rate of reaction makes it possible to discover, within the framework of the contact model[15], the relations between the rate constants for a diffusion-controlled reaction and the chemical reaction proper within the cage.

According to Noyes[15],

$$1/k_1 = 1/k_{diff} + 1/k_{chem.} \tag{5}$$

It is apparently always possible to select a solvent with sufficiently high viscosity in which the reaction will occur under the diffusion-dependent conditions. The relation $k_{chem} \gg k_{diff}$ and Eqn.(2) then hold. At sufficiently low viscosities deviations from Eqn.(2) may be observed and Eqn.(5) must be used.

The contact model of chemical reactions presupposes the diffusion of the reactants to the site of their contact where the distance between them is ρ and where there is a possibility of a chemical reaction with a rate constant k_{chem}. In the generalised contact model[16,52] account is taken of two important factors.

1. The last step in the process involving the mutual approach of the reactants differs from the previous step owing to the short-range interaction and is described as a jump over a finite distance at a frequency which, like the rate of irreversible process, depends on the solvation interactions of the reactants.

2. The rate of reaction between the reactants on contact is different for their different conformations or mutual orientations.

Allowance for the first condition leads to the subdivision of reactions into three stages: the mutual approach of the reactants to a distance $\rho^* > \rho$, insertion in the first coordination sphere, and the chemical reaction proper. This is reflected in the expression[16]

$$1/k = 1/k'_{diff} + 1/k_{ins} + 1/(gk_{chem}), \tag{6}$$

where $k'_{diff} = 4\sigma\pi\rho^*D$ (ρ^* is the radius of the second coordination sphere), k_{ins} is the rate constant for insertion in the first coordination sphere from the second, and the parameter g characterises the equilibrium radial distribution function. As a result of the introduction of the parameter g, Eqn.(6) takes into account the short-range order and the capacity of the reactants for the formation of complexes with the solvent ($g < 1$) or for the formation of dimers (complexes between the reactants) ($g > 1$), which increase their contact time. Evidently, like k_{diff}, the constant k_{ins} depends on the molecular mobility of the medium. However, k_{ins} can be comparatively small, whereupon the insertion in the first sphere and not translational diffusion limits the process in a viscous medium[16].

The distribution of unpaired electrons in radicals is in most cases anisotropic; the reactivity of radicals is therefore also anisotropic. The anisotropy of the reactivity is characterised by the geometrical steric factor f_g, equal to the probability of the occurrence of a mutual orientation favourable for recombination at the instant of the first contact on formation of the diffusional pair. It is usually assumed that the reactant is spherical and that the reaction region on the surface of the sphere is bounded by a circle characterised by an angle θ (the angle between the radius of the sphere bounding the reaction region and the radius directed to its centre). For bimolecular reactions between identical species, we then have $f_g = \sin^4(\theta/2)$. The anisotropy of the reactivity is partly or completely averaged out as a result of the rotational and translational movement of the reactants during their encounter (contact time)[17-21,32]. In the general case one can write for bimolecular reactions limited by molecular mobility

$$k = \sigma 4\pi\rho D f_{eff},$$

where f_{eff} is the effective steric factor and $f_g < f_{eff} \leq 1$.

The relations between f_{eff} and f_g have been considered in various theoretical studies[18–21,32].

A rigorous solution of the diffusional problem for a bimolecular reaction between anisotropic molecules (taking into account particular assumptions) usually has no simple analytical form and is carried out by numerical methods[19,20,32]. An approximate solution susceptible to an experimental test has been put forward[21]:

$$1/k = 2\,[\sigma k'_{chem}(1-\cos\theta)]^{-1} + 2\,[k_{diff}(1-\cos\theta)\theta]^{-1}, \quad (7)$$

where k'_{chem} is the recombination rate constant for a favourable mutual orientation of the reactants in the cage.

If it is assumed that the anisotropy of the reactivity is averaged out as a result of rare rotations of the reactant by large angles, the solution of the diffusional problem leads to the expression[12,18]

$$1/k = (\sigma f_g k'_{chem})^{-1} + (1 + f_g q^{1/2})\,[(1 + q^{1/2}) f_g k_{diff}]^{-1}, \quad (8)$$

where q is the ratio of the contact time in the formation of the pair and the characteristic rotational diffusion time ($q = \tau_c/\tau_{rot}$). For quantitative estimates, $q = 6$ has been used[14].

Analysis of experimental data for the kinetics of the rapid recombination of many radicals (see Sections IV–X) shows that steric hindrance in recombination, characterised by the quantity f_g, has a decisive influence on k_1.

Like k_1, the constant k_{-1} depends on k_{diff} (and hence on viscosity)[22–24]:

$$1/k_{-1} = 1/k_{diss} + k_{chem}/(k_{diss} k_{diff}), \quad (9)$$

or, in the case of anisotropic reactants[14,18],

$$1/k_{-1} = 1/k_{diss} + k_{chem}(1 + f_g q^{1/2})\,[(1 + q^{1/2})\, k_{diss}\, k_{diff}]^{-1}, \quad (10)$$

where k_{diff} is the elementary rate constant for the association of dimers into radicals in the cage.

IV. THE INFLUENCE OF SOLVENT VISCOSITY ON THE KINETICS OF THE REVERSIBLE RECOMBINATION

The study of the influence of solvent viscosity on the kinetics of fast reversible radical recombination reactions is important for tests of theoretical ideas concerning diffusion-controlled reactions (see Section III).

The influence of the viscosity of the medium on the kinetic and thermodynamic parameters of the reversible recombination of phenoxy-radicals has been studied[1,14,16,24–27]. Binary mixtures of solvents, with widely differing viscosities but of a similar chemical type, have been used, which made it possible to vary smoothly the viscosity over a wide range; under these conditions, other parameters of the binary mixtures changed only slightly. Fig.1 presents the variation of k_1 with the viscosity of the solvent for phenoxy-radicals of different structures (see Table 1). It follows from the data in Fig.1 that the kinetics of the recombination of radicals (I)–(V) obey Eqn.(2) as well as the relations $k_1 \propto T/\eta^{0.8}$ and $k_1 \propto T/\eta^{1.2}$; the majority of the constants k_1 are smaller than the values of k_{diff} calculated by Eqn.(3) (the discrepancy between the k_1 and k_{diff} is within an order of magnitude).

Table 1. Kinetic and thermodynamic parameters of reaction (1) involving phenoxy-radicals in solvents with different viscosities at 20 °C.[14,25]

Radical	Substituents in radical	Solvent	$10^{-8}k_1$, l mol^{-1} s^{-1}	k_{-1}, s^{-1}	$10^8 K_1$, mol l^{-1}	$\Delta H_1^{\neq}$	$\Delta H_{-1}^{\neq}$	ΔH^0	$-\Delta S_1^{\neq}$	$\Delta S_{-1}^{\neq}$	ΔS^0
(I)	4-methoxy-2,6-diphenyl	methanol	12	840	70	1.5	11.2	9.7	11	−7	4
	"	toluene	7.5	150	20	3.0	14.0	11.0	7	0	7
	"	DBP	0.30	6.0	20	6.0	13.6	7.6	2	—	—
	"	CH–M	0.15	1.2	8.0	8.6	13.8	5.2	−5	−10	−15
(II)	4-phenyl	toluene	7.0	0.0070	0.0010	2.2	24	22	9	16	25
	"	DBP	0.6	0.00060	0.0010	5.5	30	25	3	32	35
(III)	2-phenyl	toluene	6.0	—	$\sim 5\cdot10^{-4}$	1.6	—	—	12	—	—
	"	DBP	0.23	—	$\sim 5\cdot10^{-4}$	5.8	—	—	4	—	—
(IV)	2,4-diphenyl	toluene	3.4	5.5	1.62	1.6	17.8	16.2	13	6	19
	"	DBP	0.23	0.12	0.51	5.1	24.6	19.5	6	22	28
(V)	2,6-diphenyl	toluene	2.5	0.010	0.0042	0.5	22	21	17	7	24
	"	DBP	0.17	0.00024	0.0014	5.4	28	23	6	23	29
(VI)	2-methoxy	toluene	5.7	—	—	1.9	—	—	10	—	—
	"	DBP	0.20	—	—	7.2	—	—	1	—	—
(VII)	2,6-dimethoxy	toluene	4.0	12	3.0	1.7	13.0	11.3	18	−14	4
	"	DBP	0.25	0.5	2.0	5.7	21.7	16.0	−5	15	20
(VIII)	2,6-diphenyl-4-diphenylmethyl	toluene	0.80	2.5	3.2	2.5	17.0	14.5	12	3	15
	"	DBP	0.14	0.21	1,5	4.0	20.0	16.0	11	8	19
(IX)	2,4,6-triphenyl	methanol	0.60	4200	7000	—	—	—	—	—	—
	"	E	0.15	450	3000	—	—	—	—	—	—
(X)	2,6-di-t-butyl	toluene	0.60	—	—	1.0	—	—	17	—	—
	"	DBP	0.05	—	—	5.1	—	—	9	—	—
(XI)	2,6-di-t-butyl-4-methyl	toluene	0.45	112	250	−1.0	16.5	17.5	25	9	34
	"	DBP	0.075	6.75	90	3.0	19.5	16.5	15	13	28

Note. ΔH and ΔS are expressed in kcal mol^{-1} and cal mol^{-1} K^{-1} respectively; the average errors of the determinations are 20% in the constants, ±0.5 kcal mol^{-1} in ΔH, and ±2 cal mol^{-1} K^{-1} in ΔS. The viscosities are 0.58 for methanol, 0.59 for toluene, 18.4 for dibutyl phthalate (DBP), 19.9 for ethylene glycol (E), and 24.5 cP for the 5 : 1 (by volume) cyclohexanol–methanol (CH–M) mixture.

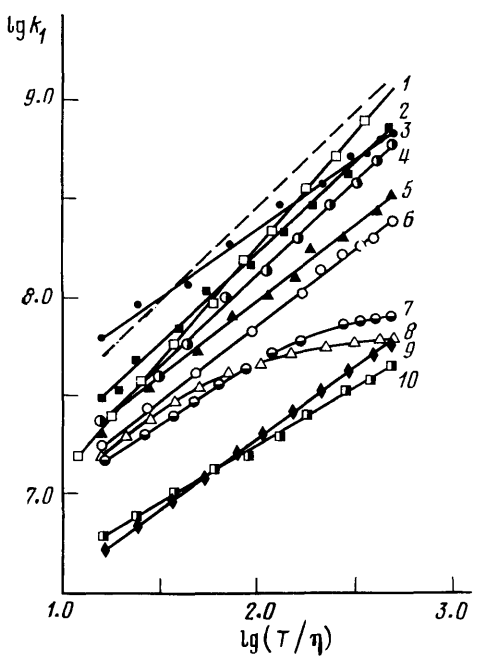


Figure 1. Relations between lg k_1 and lg (T/η) at 20 °C (η in cP) for phenoxy-radicals of different structure[1,14] [1) and 2) (I); 3) (II); 4) (III); 5) (IV); 6) (V); 7) (VIII); 8) (IX); 9) (X); 10) (XI)] in methanol–cyclohexanol (curve *1*), methanol–ethylene glycol (curve *8*), and toluene–dibutyl phthalate (curves *2–7*, *9*, and *10*) mixtures. Dashed curve—relation predicted by Eqn.(3). The names of the radicals are given in Table 1.

The discrepancy between the theoretical and experimental values of the rate constant for a diffusion-controlled reaction can apparently amount to not more than an order of magnitude due to the following causes: the lack of validity of the application of the Stokes–Einstein law; the uncertainty in the numerical value of the statistical factor σ (see Section III); the lack of validity of the assumption that the hydrodynamic radius is equal to half the reaction radius[5,16]. Thus the recombination of radicals (I)–(V) in a given range of viscosities is limited mainly by translational diffusion.

The rates of recombination of radicals (VIII) and (IX) (Fig.1) depend on the viscosity, but the reaction occurs under conditions intermediate between kinetic and diffusion-dependent. Numerical values of k_{chem} have been obtained[1,14] for these radicals using Eqn.(5) (Fig.2). For radicals characterised by linear relations between $\lg k_1$ and $\lg(T/\eta)$ (Fig.1), $k_{chem} \gg k_{diff}$ (Fig.2). The recombination of radicals (VIII) and (IX) in the cage apparently involves the overcoming of an activation barrier, since the given radicals form complexes with molecules of aromatic solvents (see Section X). The recombination probably involves desolvation, which is accompanied by the expenditure of a definite amount of energy.

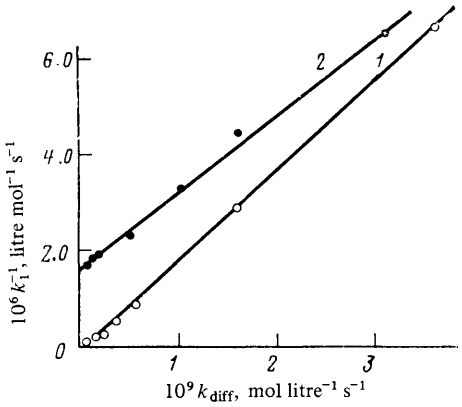


Figure 2. Relations between k_1^{-1} and k_{diff}^{-1} at 20 °C ($k_{diff} = 8RT/3000\eta$): 1) radical (I) in methanol–cyclohexanol mixture; 2) radical (IX) in methanol–ethylene glycol mixture[1].

The values of k_1 obtained for radicals (X) and (XI) are smaller by two orders of magnitude than k_{diff} (Table 1). The steric hindrance generated by the t-butyl groups leads to a low value of f_g for the recombination of radicals[7,14,25]. The value of f_g estimated by Eqn.(8) for 2,6-di-t-butylphenoxy-radicals is ~0.03.[14]

Eqn.(4) holds for radicals whose recombination is limited by translational diffusion[1,14,25]. For the recombination of radicals which occurs in only some of the encounters between the radicals in solution (for a low value of f_g), low and even negative $\Delta H_1^{\neq}$ are observed (Table 1 and Refs.7–9, 14, 25, and 28). In order to account for the low observed values of $\Delta H_1^{\neq}$, it is usually assumed that the recombination of radicals takes place not in one but in at least two stages[14,28]:

$$PhO^{\cdot} + PhO^{\cdot} \rightleftarrows (PhO^{\cdot} \ldots PhO^{\cdot}) \rightarrow \text{dimer} . \qquad (11)$$

The formation of the complex should promote the averaging of the anisotropy of the reactivity as a result of the increase of the lifetime of the radical pair[14]. The radicals in the complex are apparently linked by dipole–dipole and dispersion interactions, which are not rigorously directional and do not prevent the rotation of the radicals relative to one another. The conversion of the complex into the dimer apparently involves the rotation of the radicals relative to one another in the complex and the rate of this reaction is inversely proportional to the viscosity[14]. The observed $\Delta H_1^{\neq}$ can then be expressed as follows[14]:

$$\Delta H_1^{\neq} \simeq \Delta H_c^{\circ} + B, \qquad (12)$$

where ΔH_C° is the heat of formation of the complex and B is the activation energy for the viscous flow of the solvent. Furthermore, $\Delta H_C^{\circ} < 0$ and $\Delta H_1^{\neq} < B$.

The relations in Fig.1 have a slope less than unity for the majority of radicals. This type of relation is predicted by the theory of diffusion-controlled reactions taking into account the rotation of the reactants[19], subject to the condition that the distribution of the reaction centre over the surface of a sphere is described by a smooth and not a stepped function. This hypothesis corresponds to reality to a greater extent than the hypothesis of a centre with sharply outlined boundaries[14].

The constants k_{-1} for radicals (I)–(XI) also depends strongly on the viscosity (Table 1, Fig.3). The dependence of $\lg k_{-1}$ on $\lg(T/\eta)$ is then of the same type as the corresponding relations between $\lg k_1$ and $\lg(T/\eta)$ (cf. Figs.1 and 3). This is consistent with the theory of diffusion-controlled reactions [see Eqns.(9) and (10)].[18,22–24] The rate constants for the decomposition of the dimers of radicals (VIII) and (IX) in the cage have been obtained[24].

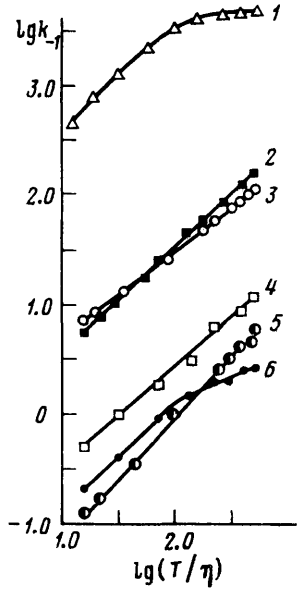
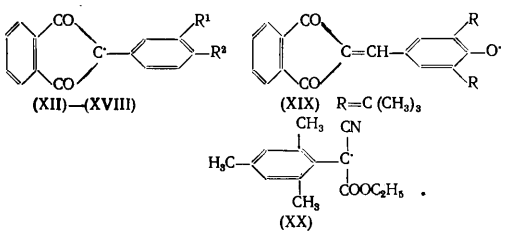


Figure 3. Relations between $\lg k_{-1}$ and $\lg(T/\eta)$ for the dissociation of the dimers of phenoxy-radicals[14,24] at 20 °C (η in cP): 1) radical (IX) in methanol–ethylene glycol mixture; 2)–6) radicals (I), (XI), (VII), (V), and (VIII) respectively in toluene–dibutyl phthalate mixture.

The relations between k_1 and η (Fig.4) have been obtained for C-centred and phenoxy-radicals having the following structures[5]:



Here R^1 = H and R^2 = $N(CH_3)_2$ (XII), R^1 = H and R^2 = $N(C_2H_5)_2$ (XIII), R^1 = H and R^2 = $N(n\text{-}C_3H_7)_2$ (XIV), R^1 = H and R^2 = $N(n\text{-}C_4H_9)_2$ (XV), R^1 = H and R^2 = $N(C_6H_5)_2$ (XVI), R^1 = R^2 = OCH_3 (XVII), and R^1 = Br and R^2 = $N(CH_3)_2$ (XVIII). Table 2 presents the kinetic and thermodynamic parameters of reaction (1) involving radicals (XII)–(XX) in chlorobenzene.

Table 2. Kinetic and thermodynamic parameters of reaction (1) involving C-centred and phenoxy-radicals (XII)–(XX) in chlorobenzene at 20 °C.[5]

Radical	$10^{-7}k_1$, l mol^{-1} s^{-1}	$10^{-6}k_{chem}$, l mol^{-1} s^{-1}	10^4k_{-1}, s^{-1}	10^9K, mol l^{-1}	$\Delta H_1^{\neq}$	$\Delta H_{-1}^{\neq}$	ΔH^0	$-\Delta S_1^{\neq}$	$\Delta S_{-1}^{\neq}$	ΔS^0
(XII)	80	1.3	0.9	0.11	2.3	20.1	17.8	10	2	12
(XIII)	50	0.7	2.5	0.5	3.5	19.5	16.0	6	5	11
(XIV)	30	0.55	2.7	0.9	3.4	22.5	19.1	8	13	21
(XV)	35	0.65	1.75	0.5	3.6	20.3	16.7	7	4	11
(XVI)	45	100	0.016	0.0035	2.5	14.7	12.2	10	−25	−15
(XVII)	180	100	—	—	2.9	—	—	6	—	—
(XVIII)	250	100	—	—	3.0	—	—	5	—	—
(XIX)	0.055	0.00055	93	17000	3.1	18.4	15.3	22	7	29
(XX)	0.06	5	0.48	80	2.8	15.2	12.4	21	−13	8

Note. ΔH and ΔS are expressed in kcal mol^{-1} and cal mol^{-1} K^{-1} respectively; the errors of the determinations are 20% in k_1 and k_{chem}, 20% in K, 40% in k_{-1}, ±0.5 kcal mol^{-1} in ΔH, and ±2 cal mol^{-1} K^{-1} in ΔS.

The relations presented in Fig.4 for radicals (XVI)–(XVIII) are represented by straight lines with a slope of unity. The values of k_1 obtained for these radicals differ by not more than a factor of 2 from k_{diff} [Eqn.(3)] and $\Delta H_1^{\neq}$ is close to B (see Table 2). The recombination of radicals (XVI)–(XVIII) is limited by translational diffusion.

The recombination of radicals (XII)–(XV) for $\eta \geqslant 5$ cP takes place under diffusion-dependent conditions and the recombination for $\eta \leqslant 2$ cP takes place under kinetic conditions (Fig.4). The values of k_{chem} have been obtained for these radicals (Table 2). The recombination of radicals (XIX) takes place under kinetic conditions over the entire range of viscosities (Fig.4 and Table 2). The values of ΔH_1 obtained for the recombination of radicals (XIX) in toluene[5] and chlorobenzene (Table 2) exceed the corresponding values of B for solvents[5].

The constant k_1 for radical (XX) in the range of viscosities 2–18.4 cP varies with the viscosity in accordance with Eqn. (2), but the values of k_1 obtained for this radical are smaller than the corresponding k_{diff} almost by three orders of magnitude (Fig.4). The structural formula of radical (XX) shows that the reaction centre is strongly shielded by substituents and the radical is characterised by a pronounced anisotropy of reactivity ($f_g < 10^{-3}$). The recombination takes place when the necessary mutual orientation of the reactants is achieved on attainment of the radius of contact, which apparently occurs only in a few encounters out of a thousand between radicals (XX) in solution. It is only possible that the recombination of radicals (XX) is limited by the rate of insertion in the first coordination sphere [see Eqn.(6)].[5,16]

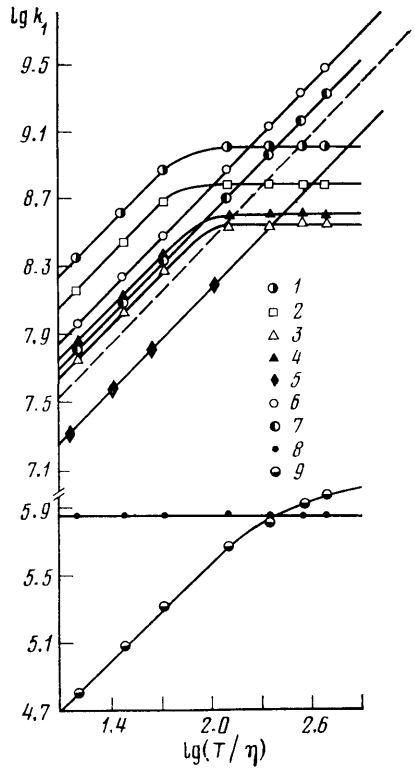
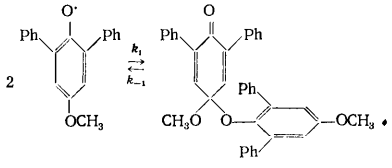


Figure 4. Relations between $\lg k_{-1}$ and $\lg(T/\eta)$ at 20 °C (η in cP) for aromatic C-centred and phenoxy-radicals in toluene–dibutyl phthalate mixture[5]: 1) (XII); 2) (XIII); 3) (XIV); 4) (XV); 5) (XVI); 6) (XVII); 7) (XVIII); 8) (XIX); 9) (XX). Dashed line—relation predicted by Eqn.(3). The formulae of the radicals are given in the text.

V. PHENOXY-RADICALS

The principal channel for the destruction of phenoxy-radicals in solutions in the absence of radical acceptors involves their reaction with one another. The fastest stage in this reaction is usually recombination. The C–C or C–O bond formed as a result of recombination is fairly weak (ΔH° = 10–30 kcal mol^{-1}; see, for example, Khudyakov et al.[29]). The recombination of phenoxy-radicals is therefore reversible, for example:



In many cases a fairly high value of $K = 10^{-8}$–10^{-3} mol litre^{-1} is then observed (see, for example, Khudyakov et al.[29]).

The structures of dimerising phenoxy-radicals as well as the structures and physicochemical properties of the phenoxy-radical dimers have been considered in a number of reviews and monographs[11,30,31,33,116,169]. However, numerous studies on the kinetics and thermodynamics of the reversible recombination of the radicals have been published recently and these will be considered in the present section.

1. The Structures of Dimerising Phenoxy-Radicals

Different 2,4,6-substituted phenoxy-radicals, whose substituents do not contain reactive hydrogen atoms, can exist for a long time in solution in equilibrium with their dimers. 2,6-Di-t-butyl-4R-phenoxy-radicals[8,9,35–42,176,181], 2,6-diphenyl-4R-phenoxy-radicals[1–3,29,43–47], polyhalogenophenoxy-radicals[48,49], certain naphthoxy-radicals[50,170], radicals derived from phenanthrenols[51], and other phenoxy-radicals[181] are involved in equilibrium (1) in solution.

The equilibrium constant depends significantly on the steric hindrance due to the substituents and also on the influence of the substitutents on the electronic structures of the radical and the dimer. For example, the steric hindrance generated by the t-butyl groups in the 2,4,6-tri-t-butylphenoxy-radical precludes the formation of its dimers in solution even at −100 °C.[53,177] The 2,6-di-t-butyl-4-phenylradical[54] and the 2,6-di-t-butyl-4-methoxyphenoxy-radical[55] are also monomeric in solution. However, the replacement of one t-butyl group in the 2,4,6-tri-t-butylphenoxy-radical in the *ortho*-position by a benzene ring or a t-butoxy-group, which give rise to a smaller steric hindrance, makes the radical capable of the formation of dimers in the solution[56–59]. Sterically hindered phenoxy-radicals readily form dimers with sterically unhindered phenoxy-radicals[60–63,65–72].

If the substituent in the *ortho*- or *para*-position in a 2,4,6-substituted phenoxy-radical contains reactive hydrogen atoms, then the reaction between such radicals leads to the formation of stable products as a result of disproportionation. The disproportionation reaction can involve reversible dimerisation as an intermediate stage if the substituents in the phenoxy-radical do not give rise to an appreciable steric hindrance. For example, the disproportionation of the 2,6-di-t-butyl-4-methylphenoxy-radical[7,73–75], the 2,4,6-trimethylphenoxy-radical[73], the 4-methyl-2,6-diphenylphenoxy-radical[75], and the 2,6-diphenyl-4-diphenylmethylphenoxy-radical[7,75] takes place in this way.

The observed decrease of the equilibrium concentration of phenoxy-radicals as a result of the disproportionation reaction [after the establishment of equilibium (1)] obeys a first-order law when the condition $[\overline{PhO^{\cdot}}] \gg K/4$ holds (see Section II). The observed destruction of radicals was described in terms of a first-order law for the disproportionation of a series of 2,6-di-t-butyl-4R-phenoxy-radicals, where R = C_2H_5,[76] CH_2OCH_3, CH_2OCOCH_3, etc.[77,78] Consequently the fast reaction (1) takes place simultaneously with the disproportionation reaction.

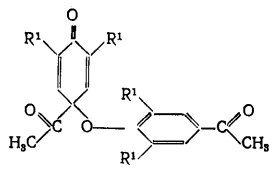
The disproportionation of the 3,6-di-t-butyl-2-hydroxyphenoxy- and 2,6-diphenyl-4-(4′-hydroxy-3′,5′-diphenylphenoxy)phenoxy-radicals has been investigated[79,80]. It was suggested on the basis of kinetic data that the disproportionation reaction is accompanied by reversible recombination.

Phenoxy-radicals without substituents in the *ortho*- or *para*-positions recombine with formation of stable dimeric products. Metastable dimers having the structure of a diketone or quinol are formed in this reaction and then enolise irreversibly with formation of the final products. The formation of metastable dimers is also reversible[25,28,29,81,82].

2. The Structures of Phenoxy-Radical Dimers

The dimerisation of phenoxy-radicals leads to the formation of C–O or C–C bonds. O–O dimers cannot be stable, since the high stabilisation energy of phenoxy-radicals (17.5 kcal mol^{-1}),[83] due to the delocalisation of the unpaired electron, leads to a low dissociation energy of the O–O bond[53].

On formation of the C–O bonds, the corresponding dimers have the structure of quinol ethers. This structure has been established reliably for dimers formed on recombination of the 2,4,6-tri-t-butylphenoxy-radical with various sterically unhindered phenoxy-radicals[60–63,65]. Dimerisation takes place via the carbon atom in the *para*-position in the 2,4,6-tri-t-butylphenoxy-radical with formation of a "heat-to-tail" structure. Quinol ethers are formed on dimerisation of the majority of 2,4,6-substituted phenoxy-radicals. The "head-to-tail" structures have been attributed to the dimers of 2,6-di-t-butylphenoxy-radicals containing the substituents CH_3,[84] OCOR,[35,37] and COR [8,9,35–37] (where R = alkyl) in the *para*-position, for example:



The dimers of the 2,4,6-triphenylphenoxy- [85,86] and 4-methoxy-2,6-diphenylphenoxy-radicals[87] have the same structure. The structure of quinol ethers has also been attributed to the dimers of radicals derived from phenanthrenol[51].

The dimerisation of 2,6-di-t-butyl-4R-phenoxy-radicals can also entail the formation of a C–O bond involving the carbon atom in the *ortho*-position. Such a structure has been postulated, for example, for the dimer of the radical with R = CO_2X (X = alkyl).[37] The third possible structure of dimers, where recombination results in the formation of a C–C bond involving the carbon atoms in the *para*-position (a "tail-to-tail" structure), is believed to be feasible for the dimers of the 2,6-di-t-butyl-4-ethoxycarbonylphenoxy-,[36] 2,6-di-t-butyl-4-diethylphosphinylphenoxy-, and 2,6-di-t-butyl-4-diethylphosphinodithionylphenoxy-radicals[88] and also in the case of the 6-t-butoxy-2,4-di-t-butylphenoxy-[59] and 2,4-di-t-butyl-6-phenylphenoxy-radicals[56]. The formation of an N–N bond on dimerisation of the 2,6-di-t-butyl-4-cyanophenoxy-radical has been postulated[30]. 2,6-Dialkyl-phenoxy-radicals containing the β-phthalylvinyl substituted in the *para*-position [e.g. radical (XIX)] dimerise with formation of a C–C bond[172].

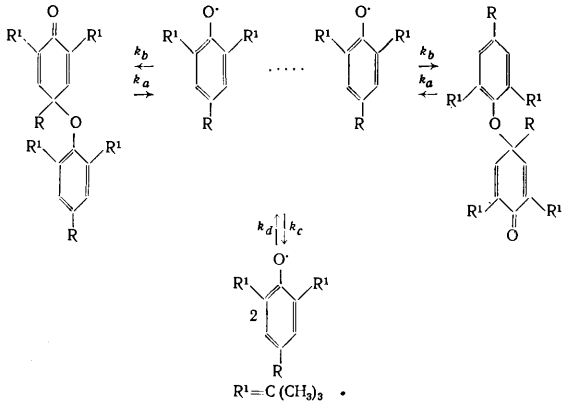
The structure of the primary dimers formed on dimerisation of phenoxy-radicals without substituents in the *ortho*- or *para*-positions can be postulated on the basis of the structure of the final stable dimerisation products. Depending on the positions and bulk of the substituents and on the nature of the solvent, the transfer or elimination of hydrogen atoms can then result in the formation of C–O or C–C bonds[11,30].

The probability of the formation of C–C bonds on dimerisation increases in dimethylformamide (DMF) and in acids compared with non-polar solvents (and also on raising the temperature)[89], which can be explained by the increase of the stability of the primary dimers with a C–C bond and by the decrease of the stability of the primary dimers with a C–O bond with increase of solvent polarity[29]. For example, 2,6-diphenylphenol is oxidised in solvents of low polarity to 2,6-diphenyl-4-(2′,6′-diphenylphenoxy)phenol[89]; consequently the primary dimer has the structure of a quinol ether of the "head-to-tail" type. However, in DMF and in acids the product is the corresponding diphenoquinone[89], which shows that the primary dimers have the "tail-to-tail" structure.

3. Kinetics of the Reversible Recombination of Phenoxy-Radicals

The rate constants for the recombination of phenoxy-radicals (k_1) and for the dissociation of the resulting dimers (k_{-1}) depend significantly on the chemical nature, bulk, and positions of the substituents in the benzene ring (Table 3).

Recombination reaction. The kinetics of the recombination of 2,6-di-t-butyl-4R-phenoxy-radicals have been investigated by NMR,[8,9] flash photolysis[14,25], and EPR [176] (Tables 1 and 3). The following mechanism of reaction (1) with participation of 2,6-di-t-butyl-4R-phenoxy-radicals has been proposed[9] on the basis of NMR data:



The dissociation of the dimer with a rate constant k_a results in the formation of an intermediate of unknown structure—a complex between the radicals. The complex can be reconverted into the initial dimer with a rate constant k_b, or into a dimer in which the radicals have changed places (also with a rate constant k_b), or it can dissociate into two free radicals with a rate constant k_c. The radicals recombine to a

Table 3. Kinetic and thermodynamic parameters of reaction (1) involving phenoxy-radicals at 20 °C.

Radical	Substituents in radical	Solvent	$10^{-8}k_1$, l mol^{-1} s^{-1}	k_{-1}, s^{-1}	10^8K, mol l^{-1}	$\Delta H_1^{\neq}$	$\Delta H_{-1}^{\neq}$	$\Delta H°$	$-\Delta S_1^{\neq}$	$\Delta S_{-1}^{\neq}$	$\Delta S°$	References
(I)	4-methoxy-2,6-diphenyl	1-propanol	7.0	280	40	5.0	15	9.8	0	4	4	1
(II)	4-phenyl	hexane	55	—	—	0.2	—	—	12	—	—	29
(III)	2-phenyl	hexane	18	—	—	0.0	—	—	15	—	—	29
(IV)	2,4-diphenyl	hexane	18	1.3	0.074	0.5	22.5	22.0	13	20	33	29
(V)	2,6-diphenyl	hexane	8	—	—	0.5	—	—	15	—	—	29
(VI)	2-methoxy	hexane	17	—	—	0.5	—	—	13	—	—	90
(VII)	2,6-dimethoxy	hexane	4.3	11	2.6	0.2	7.2	7.0	18	—29	—11	90
(VIII)	2,6-diphenyl-4-diphenylmethyl	hexane	7.5	3.0	0.40	0.5	18.0	17.5	15	6	21	29
(X)	2,6-di-t-butyl	hexane	0.85	—	—	0.5	—	—	19	—	—	29
(XI)	2,6-di-t-butyl-4-methyl	hexane	1.1	50	45	—1.5	21.5	23.0	25	24	49	29
(XXI)	4-ethoxy-2,6-diphenyl	hexane	22	315	14	0.5	17.5	17.0	14	14	28	29
(XXI)	4-ethoxy-2,6-diphenyl	1-propanol	3.5	1000	300	4.0	14	9.6	5	4	7	1
(XXII)	2,6-diphenyl-4-stearyloxy	hexane	20	200	10	0.0	19.0	19.0	15	20	35	29
(XXII)	2,6-diphenyl-4-stearyloxy	1-propanol	1.9	1000	500	4.0	14	9.5	6	4	8	1
(XXIII)	4-acetoxy-2,6-diphenyl	hexane	22	—	—	0.5	—	—	14	—	—	29
(XXIV)	4-methyl-2,6-diphenyl	hexane	11	0.23	0.020	1.5	27.0	25.5	11	34	45	29
(XXV)	4-chloromethyl-2,6-diphenyl	hexane	13	0.027	0.0020	0.5	28.5	28.0	13	37	50	29
(XXVI)	2,6-diphenyl-4-(2′,6′-diphenylphenoxy)	hexane	0.5	30	60	1.0	16.5	15.5	20	6	26	29
(XXVII)	2,6-dicyclohexyl-4-phenyl	1-propanol	0.27	1100	4000	—	—	—	—	—	—	1
(XXVIII)	4-acetyl-2,6-di-t-butyl	deuterochloroform*	0.0077	14	3600	1.0	9.1	9.1	30	—14	16	9
(XXVIII)	4-acetyl-2,6-di-t-butyl	acetone-*d**	0.0070	3.5	1000	—4.6	7.0	11.6	48	—25	23	9
(XXVIII)	4-acetyl-2,6-di-t-butyl	carbon disulphide*	0.030	11	700	—3.5	6.8	10.3	41	—24	18	9
(XXIX)	2,6-di-t-butyl-4-(2′,2′-dimethylpropionyl)	deuterochloroform*	—	—	500000	—	—	6.9			17	9
(XXX)	methyl 3,5-di-t-butyl-4-hydroxybenzoate***	deuterochloroform*	0.050	2100	8500	—1.6	10.0	11.6	33	—5	28	9
(XXXI)	ethyl 3,5-di-t-butyl-4-hydroxybenzoate***	deuterochloroform*	0.077	190	4800	—0.4	8.5	8.8	27	—12	15.5	9
(XXXI)	ethyl 3,5-di-t-butyl-4-hydroxybenzoate***	acetone-*d**	0.067	35	1000	—2.8	9.2	12.0	37	—12	25	9
(XXXI)	ethyl 3,5-di-t-butyl-4-hydroxybenzoate***	carbon disulphide*	0.133	120	1900	—2.8	8.1	10.9	37	—14	22	9
(XXXII)	cyclohexyl 3,5-di-t-butyl-4-hydroxybenzoate***	deuterochloroform*	0.0007	15	43000	1.8	9.0	7.2	28	—14	13	9
(XXXIII)	2,6-di-t-butyl-4-cyano	deuterochloroform*	—	—	70000	—	—	6.1	—	—	9.3	9
(XXXIV)	4-methoxy**	chlorobenzene	0.27	0.027	0.1	0.5	20.3	19.8	28	—2	26	28
(XXXV)	4-t-butyl**	chlorobenzene	0.23	$5.2\cdot10^{-4}$	0.0023	—0.7	25.4	26.1	24	5	29	28
(XXXVI)	3-ethoxycarbonyl**	chlorobenzene	0.22	$3.4\cdot10^{-6}$	$1.54\cdot10^{-5}$	—0.2	28.8	30	26	5	31	28
(XXXVII)	3,5-dimethyl**	chlorobenzene	—	$1.4\cdot10^{-4}$	—	—	27.3	—	—	8	—	71
(XXXVIII)	4-bromo**	chlorobenzene	—	$5.5\cdot10^{-5}$	—	—	27.1	—	—	6	—	71
(XXXIX)	2,4,6-trichloro**	chlorobenzene	—	0.08	—	—	21.7	—	—	4	—	71

Note. *Dimerisation at −23 °C. **1 : 1 recombination with the 2,4,6-tri-t-butylphenoxy-radical at 60 °C. ***Complete name of the radical.

ΔH and ΔS are expressed in kcal mol^{-1} and cal mol^{-1} K^{-1} respectively. The average errors of the determinations are 20% in k_1, 20% in k_{-1}, 30% in K, ±0.5 kcal mol^{-1} in ΔH, and ±2 mol^{-1} K^{-1} in ΔS.

complex with a rate constant k_d. When the above complexes are stationary and $k_b \gg k_c$ (the validity of this assumption has been confirmed by experimental data[9]), we have $k_{-1} = k_a k_c / 2k_b$ and $k_1 = k_d$. The exchange of magnetically-non-equivalent parts in a dimer is called a "flip-flop" process and is characterised by a rate constant $k_a/2$.

We may note that the quantities k_1 (and k_d) are lower by several orders of magnitude than k_{diff} (Table 3), i.e. the given complex between the radicals is by no means formed in every encounter between them in solution. It may be that the formation of the complex is a non-elementary reaction, since negative values of $\Delta H_1^{\neq}$ ($\Delta H_d^{\neq}$) are observed (Table 3). The hypothesis of the existence of complexes between sterically hindered phenoxy-radicals makes it possible to explain also the low and even negative values of $\Delta H_1^{\neq}$ (Tables 1 and 3) observed for these radicals (Section IV). It can be assumed that the recombination of phenoxy-radicals takes place in the same way as the recombination of the "related" benzyl radicals[28]. Quantum-chemical calculations have shown that, when benzyl radicals approach one another to a distance of 2.9 Å, a "sandwich" type complex between the radicals is energetically favourable, while at shorter distances the "head-to-head" structure is preferred, which is converted into the final recombination product (bibenzyl).[28]

The quantity k_1 increases significantly when the t-butyl groups in the *ortho*-positions in the phenoxy-radical are replaced by benzene rings or methoxy-groups (Table 3). The decreased shielding of the oxygen atom of the phenoxy-radical by the benzene rings compared with t-butyl groups can be understood if one takes into account the fact that the phenyl group can rotate freely and, for angles of rotation close to 90° relative to the plane of the phenoxy-ring, the steric hindrance is small.

The dimerisation reactions of mono- and di-phenylphenoxy- and 4-alkoxy-2,6-di-phenylphenoxy-radicals are limited mainly by translational diffusion (see Section IV). The data in Table 3 show that, with increase of the number of carbon atoms in the hydroxyalkyl substituent in the 4-alkoxy-2,6-diphenylphenoxy-radical, k_1 decreases, which may be caused by the fact that, with increase of the bulk of the radical, the area of the reaction region apparently remains virtually unchanged; as a result, f_g and the rate constant diminish. On replacement of the hydroxyalkyl substituent by the phenyl substituent, a further decrease of k_1 is observed, which is due to the increase of steric hindrance on dimerisation of the radicals. The constant k_1 becomes smaller still on replacement of phenyl substituents in the *ortho*-positions by the more bulky cyclohexyl groups (Table 3).

Thus the steric hindrance generated by substituents in the phenoxy-radical has a decisive influence on the kinetics of their recombination.

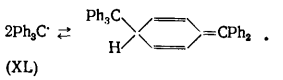
The dissociation of dimers. The rate constant for the dissociation of the dimers of 2,6-diphenyl-4R-phenoxy-radicals (k_{-1}) as well as $\Delta H_{-1}^{\neq}$ depend significantly on the nature of the substituent (Table 3). The quantity k_{-1} diminishes and $\Delta H_{-1}^{\neq}$ increases with enhancement of the electron-accepting capacity of the substituent. A similar relation has been observed for the dissociation of the 1:1 complexes formed by the 2,4,6-tri-t-butyl-phenoxy-radical with sterically unhindered phenoxy-radicals[28,71].

The constants k_{-1} for the dissociation of the complexes of the 2,4,6-tri-t-butylphenoxy-radical with *meta*- and *para*-substituted phenoxy-radicals are correlated with the parameters σ^+ of the substituents, the correlation having $\rho = -3.3$.[71] The ratio of the constant k_{-1} for the above 1:1 complexes ("dimers") to the rate constant for the abstraction of a hydrogen atom by the 2,4,6-tri-t-butylphenoxy-radical from the corresponding sterically unhindered phenol is almost independent of the substituent. Comparatively high values of k_{-1} have been observed[71] for radicals with substituents in the *ortho*-position; here $\Delta H_1^{\neq}$ were lower than the values expected on the basis of the electronic influence of the substituents. The explanation is that the *ortho*-substituents give rise to steric hindrance on dimerisation. The quinol ethers formed from the 2,4,6-tri-t-butylphenoxy-radical and *ortho*-substituted phenoxy-radicals are therefore less stable. For example, the strain energy of the C–O bond formed on dimerisation of the 2,6-dimethylphenoxy- and 2,4,6-trichlorophenoxy-radicals is 5 kcal mol^{-1}.[71]

VI. AROMATIC C-CENTRED RADICALS

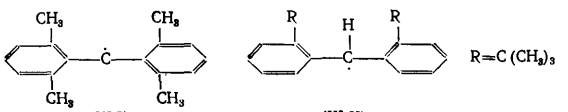
Different C-centred radicals with aryl substituents exist in solution in equilibrium with their dimers[5,6,91,92]. Phenyl substituents (±*E*-substituents) greatly facilitate the dissociation of substituted ethanes into arylmethyl radicals, stabilising the latter. The difference between the equilibrium constants for the mono-, di-, and tri-arylmethyl radicals can be explained by the method of perturbed molecular orbitals[93]. However, one should bear in mind that the steric hindrance in the recombination of radicals plays a more important role than the electronic effects; for this reason, hexa-arylethanes do not exist[93,94].

The triphenylmethyl radicals (XL) recombine reversibly with formation of 1-di-phenylmethylene-4-triphenylmethyl-2,5-cyclohexadiene[95–97]:

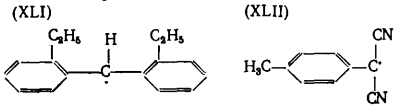


(XL)

The kinetic and thermodynamic parameters of reaction (1), which takes place with participation of the arylmethyl radicals (XX) and (XL)–(XLVII) are presented in Table 4.

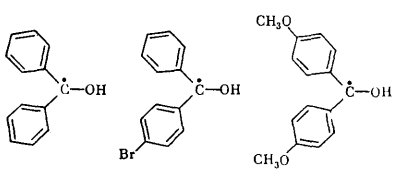


(XLI) (XLII)



(XLIII) (XLIV)

The activation energy for the dimerisation of radicals (XL) is satisfactorily consistent with the familiar general relation between the activation energy and the heat of reaction $E = 11.5 - 0.25|Q|$, kcal mol^{-1}.[96]



(XLV) (XLVI) (XLVII)

After the radical (XL) had been obtained[98], different derivatives and analogues of the triphenylmethyl radical were synthesised. The properties of these radicals have been described in numerous reviews and monographs[11,91,92,94,101,109,169]. The values of K for triphenylmethyl radicals with different substituents have been obtained[102–104]. The following conclusions can be reached on the basis of experimental data[102–104] for the stability of substituted triphenylmethyl radicals: (1) the stability of the radicals increases with increase of the bulk and number of substituents in the *ortho*-, *para*-, and *meta*-positions; (2) the stability of the radicals is very high when bulky substituents are present in all three benzene rings in the *para*-positions.

The observed regularities can be explained mainly by steric factors. Thus, despite the fact that the introduction of *ortho*-substituents increases the deviation of the benzene rings from the plane and reduces the degree of delocalisation of the unpaired electron, the constant K then increases, since the *ortho*-substituents hinder recombination[102,103].

The degree of delocalisation of the unpaired electron does not influence K. Furthermore, steric models have shown that in many arylmethyl radicals the aromatic rings have been rotated by a specific angle (and do not lie in a single plane) owing to the repulsion of the *ortho*-protons or *ortho*-substituents[92]. As a result of this, the delocalisation of the unpaired electron among the benzene rings takes place to only a small extent or not at all.

Table 4. Kinetic and thermodynamic parameters of reaction (1) involving C-centred aromatic radicals.

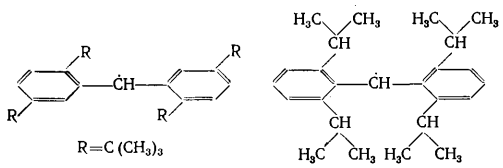
Radical	Solvent	t, °C	k_1, l mol^{-1} s^{-1}	k_{-1}, s^{-1}	K, mol l^{-1}	$\Delta H_1^{\neq}$	$\Delta H_{-1}^{\neq}$	ΔH^0	$-\Delta S_1^{\neq}$	$\Delta S_{-1}^{\neq}$	ΔS^0	Refs.
(XX)	α-chloronaphthalene	20	—	—	—	—	14.5	—	—	—13	—	107
(XL)	*m*-xylene	25	70	0.048	$6.8\cdot10^{-4}$	7.5	18.4	10.9	25	—3	22	97
(XL)	toluene	20	$3.5\cdot10^{2}$	0.25	$7.0\cdot10^{-4}$	6.4	17.8	11.2	26	—3	23	96
(XLI)	*m*-xylene	25	24	$1.1\cdot10^{-6}$	$4.6\cdot10^{-7}$	0.3	22.3	22.0	51	—6	45	97
(XLII)	*m*-xylene	25	9	$1.4\cdot10^{-5}$	$1.6\cdot10^{-6}$	5.0	24.7	19.7	36	4	40	97
(XLIII)	*m*-xylene	25	10	$1.6\cdot10^{-4}$	$1.6\cdot10^{-5}$	7.0	19.0	12.0	30	—12	18	97
(XLIV)	chlorobenzene	20	$5.0\cdot10^{7}$	0.08	$1.6\cdot10^{-9}$	6.8	15.9	9.1	—2	—8	—10	5
(XLIV)	α-chloronaphthalene	20	—	—	—	—	26	—	—	—14	—	107
(XLV)	benzene	30	$1.8\cdot10^{9}$	$5\cdot10^{-10}$	$2.8\cdot10^{-19}$	0.4	32.9	32.5	12	12	24	110
(XLV)	isopropyl alcohol	30	$1.1\cdot10^{8}$	$1.3\cdot10^{-8}$	$1.2\cdot10^{-16}$	4.3	26.7	22.4	5	—3	2	110
(XLVI)	benzene	30	$2.5\cdot10^{8}$	$8\cdot10^{-10}$	$3.2\cdot10^{-18}$	1.7	33.1	31.4	11	13	24	110
(XLVI)	isopropyl alcohol	30	$4.6\cdot10^{7}$	$1.6\cdot10^{-8}$	$3.5\cdot10^{-16}$	5.1	29.1	24.0	4	5	9	110
(XLVII)	benzene	30	$6.3\cdot10^{9}$	$1\cdot10^{-9}$	$1.6\cdot10^{-19}$	—1.1	24.7	25.8	14	12	26	110

Note. ΔH and ΔS are expressed in kcal mol^{-1} and cal mol^{-1} K^{-1} respectively. The average errors of the determinations are 20% in k_1, 20% in k_{-1}, 30% in K, ±0.5 kcal mol^{-1} in ΔH, and ±2 cal mol^{-1} K^{-1} in ΔS.

The introduction of substituents in the *para*-position also gives rise to certain difficulties in dimerisation via the *para*-carbon atoms (the second reaction centre)[102]. The *meta*-substituents are in the *ortho*-positions relative to the second reaction centre and act analogously to substituents in the *ortho*-position relative to the central carbon atom[102,104].

The influence of substituents on K is determined solely by their bulk and number. Regardless of whether they are donors or acceptors, substituents exert the same influence on the equilibrium[102,103]. Triphenylmethyl radicals containing both methoxy-groups and chlorine atoms in all the *ortho*-positions relative to the central carbon atom have been isolated in a pure state[101].

Analogous conclusions are applicable to diarylmethyl radicals. Equilibrium shifts towards the radicals when they contain sterically bulky substituents; for example, the dimer of the bis-2,5-di-t-butylphenylmethyl radical is fully dissociated in solution[105]. Bis-2,6-di-isopropylphenylmethyl radicals do not dimerise either[106].

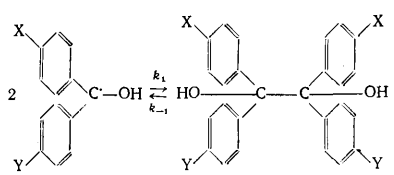


The reversible recombination of triphenylmethyl and diarylmethyl radicals (XL)–(XLIII) has been studied by EPR and that of the monoarylmethyl radicals (XX) and (XLIV) has been investigated by flash photolysis and NMR (Table 4). The values of k_1 for radicals (XL)–(XLIV) are lower than $k_{diff} \approx 5 \times 10^9$ litre mol^{-1} s^{-1} and $\Delta H_1^{\neq}$ differs significantly from the activation energy for the viscous flow of *m*-xylene and chlorobenzene ($B \approx 2.0$ kcal mol^{-1}) (Table 4). The recombination of radicals (XL)–(XLIV) takes place in the kinetic region.

The very low rate constants for the recombination of radicals (XL)–(XLIII) are caused by steric hindrance, as shown by the large negative values of $\Delta S^{\neq}$ (Table 4). Owing to the steric hindrance due to the *ortho*-substituents, the recombination of the diarylmethyl radicals (XLI)–(XLIII) also leads to the formation of a dimer having the ethane and not the cyclohexadiene structure[97]. In the recombination of the radical (XX) via the α-carbon atom the steric hindrance is so great (see Section III) that an asymmetric dimer linked by a C–N bond is formed[107].

For the decomposition of the molecules into complex fragments, the average value of the pre-exponential factor A is 10^6 s^{-1} ($\Delta S_{-1}^{\neq} \approx 11$–$12$ kcal mol^{-1} K^{-1}).[108] Smaller values of $\Delta S_{-1}^{\neq}$ have been obtained for the decomposition of the dimers of radicals (XX) and (XL)–(XLIV) (Table 4). The steric hindrance in the transition state of the decomposition of the dimers apparently hinders the rocking and torsional vibrations relative to the bond undergoing dissociation, which leads to a decrease of $\Delta S_{-1}^{\neq}$ compared with the average value of this quantity[5,6,53].

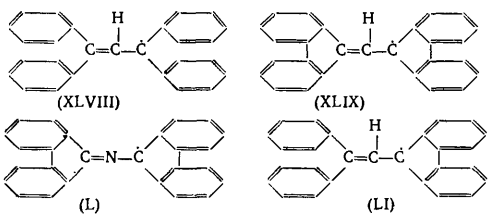
The ketyl radicals formed in the decomposition of benzopinacols can be regarded as substituted diphenylmethyl radicals. Benzopinacol, 4,4″-dibromobenzopinacol, and 4,4′,4″,4‴-tetramethoxybenzopinacol exist in benzene and isopropyl alcohol in equilibrium with the corresponding ketyl radicals at 80–141 °C:[110]



X, Y = H or substituent.

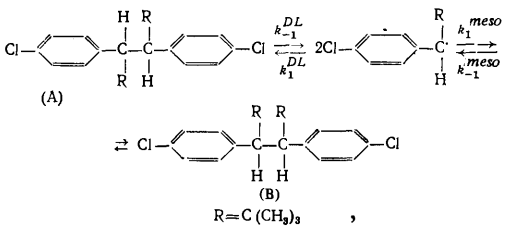
The kinetic and thermodynamic parameters obtained for reaction (1) involving ketyl radicals are listed in Table 4. Values of $\Delta H_1^{\neq}$ smaller than the corresponding values of B for the solvents were observed (2.9 and 6.4 kcal mol^{-1} for benzene and isopropyl alcohol respectively). It is extremely likely that the recombination of unsubstituted ketyl radicals (XLV) is limited by diffusion[110].

The recombination of tetraphenylallyl and related radicals has been studied by EPR and spectrophotometric methods[111]:



It was established that, in contrast to radicals (XLIX)–(LI), radical (XLVIII) does not form dimers in solution [benzene and ether, from −60° to 50 °C (20 °C)]. $\Delta H° = 12.2 \pm 0.4$, 8.9 ± 0.3, and 14.7 kcal mol^{-1} were obtained for radicals (XLIX), (L), and (LI) respectively. The bond in the dimer is formed between the α-carbon atoms or between the α- and γ-carbon atoms of the allyl groups. The inability of radical (XLVIII) to form a dimer can be explained by steric hindrance[111]. The extents of steric hindrance for radicals (XLIX) and (L) are the same and the differences between the $\Delta H°$ are then caused by the differences between the degrees of delocalisation of the unpaired electron.

Sterically hindered radicals can recombine diastereoselectively and exist in solution in equilibrium with two stereoisomeric dimers, for example[112]:



where (A) = DL-3,4-di-(*p*-chlorophenyl)-2,2,5,5-tetramethylhexane and (B) = *meso*-3,4-di-(*p*-chlorophenyl)-2,2,5,5-tetramethylhexane. The 1-(*p*-chlorophenyl)2,2-dimethylpropyl radicals, obtained on thermal decomposition of the corresponding azo-compound in 1-methylnaphthalene with 10 vol.% of thiophenol, are in equilibrium at ~300 °C with the *meso*- and DL-dimers; at 135 °C the ratio DL-dimer/*meso*-dimer equals 1.7.[112]

Like many C-centred radicals with phenyl substituents, 2-arylindan-1,3-dionyl radicals exist in solution in equilibrium with their dimers[5,6]. The interest in 2-arylindan-1,3-dionyl radicals increased recently, because they are effective inhibitors of liquid-phase oxidation processes[113]. The kinetic and thermodynamic parameters of reaction (1) involving the 2-arylindan-1,3-dionyl radicals (XII)–(XVIII) are listed in Table 2. Evidently the equilibrium constant depends significantly on the nature of the substituent in the phenyl fragment of radicals (XII)–(XVIII) (Table 2). In the recombination of radicals (XII)–(XVIII) (or the dissociation of the corresponding dimers), containing the phthaloyl fragment, the steric hindrance can be regarded as virtually identical and the difference between the values of *K* is therefore caused by electronic effects. In the dissociation of a dimer of similar structure, the C–C dimer of radical (XIX), equilibrium (1) is strongly displaced towards the formation of radicals compared with radicals (XII)–(XVIII) (Table 2). This is related to the fact that dissociation of the dimer (XIX) leads to the formation of relatively stable radicals, in which the unpaired electron is delocalised over the system of π-bonds, including the *p* orbital of the oxygen atom. The introduction of a bromine atom in the *ortho*-position relative to the dimethylamino-group in 1,2-bis-(4′-dimethylaminophenyl)diphthaloylethane fully displaces the equilibrium in this instance [radical (XVIII)] towards the formation of the dimer. The bromine atom displaces the dimethylamino-group from the plane of the ring, which leads to the breakdown of conjugation between the unshared electron pair of the nitrogen atom and the phenylindandionyl fragment[114] and hence reduces the degree of delocalisation of the unpaired electron.

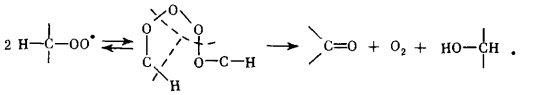
Comparison of the kinetic and thermodynamic parameters of reaction (1) for the dimers of radicals (XII)–(XVIII) (Table 2), triphenylmethyl radicals (Table 4), and phenoxy-radicals (Tables 1 and 3) shows that the dimers of radicals (XII) to (XVIII) dissociate much less and are characterised by higher bond dissociation energies.

VII. PEROXY- AND NITROXY-RADICALS

Tertiary peroxy-radicals are in equilibrium with the corresponding tetroxides at low temperatures[99,100,115–119]:

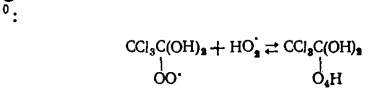
$$RO_2^{\cdot} + RO_2^{\cdot} \rightleftarrows ROOOOR \rightarrow \underset{\text{(cage)}}{[RO^{\cdot}\ldots O_2\ldots{}^{\cdot}OR]} .$$

The reactions were investigated by EPR. The values of *K* and $\Delta H°$ obtained for the peroxy-radicals are listed in Table 5. The data in this table show that the values of K, $\Delta H°$, and $\Delta S°$ depend little on the nature of the alkyl groups[100]. Consequently, the difference between the rates of chain termination on recombination of tertiary peroxy-radicals is caused mainly by the difference between the rates of the irreversible decomposition of the tetroxide[118]. The irreversible destruction of the tertiary alkylperoxy-radicals is negligible at $t < -115$ °C. There is evidence for the reversible formation of tetroxides from secondary peroxy-radicals[117–119]:



However, the thermodynamic parameters of the reversible formation of these tetroxides could not be obtained in view of the low concentration of the radicals and their rapid irreversible destruction even at $t < -115$ °C.[117,118] This mechanism of the destruction of secondary peroxy-radicals has been criticised by Benson[100].

The occurrence of reversible cross-recombination of the following radicals has been demonstrated by kinetic measurements[120]:

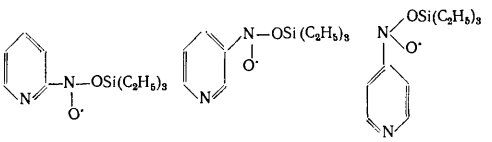


The equilibrium is displaced towards the formation of radicals (water, $t \cong 20$ °C). The tetroxide decomposes with liberation of oxygen.

The destruction of the phosphoranylperoxy-radical $C(CH_3)_3O(RO)_3POO^{\cdot}$, where R = CH_3, C_2H_5, or iso-C_3H_7, in cyclopropane takes place in the same way as the destruction of alkylperoxy-radicals[121]. In the range from −70° to −45 °C the destruction of these radicals obeys a first-order law and at $t < -90$ °C a second-order law. $k_1 \cong 10^4$ litre mol^{-1} has been obtained for three phosphoranylperoxy-radicals in

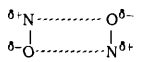
cyclohexane at −90 °C and $\Delta H_1^{\neq} = 4$ kcal mol^{-1} and $k_1 = 3 \times 10^4$ litre mol^{-1} s^{-1} (−90 °C) have been found for $C(CH_3)_3O(CH_3O)_3$. .POO· in the temperature range between −116° and −89 °C.[121]

Nitroxy-radicals of different structure also dimerise reversibly in solution[122–127,167]. Table 5 presents the kinetic and thermodynamic parameters of the dimerisation of nitroxy-radicals of different structure, obtained by EPR. It has been shown[127] that the destruction of nitroxy-radicals having the structure



in triethylsilane at temperatures in the range from −33° to 25 °C obeys a first-order law. It has been observed that the radicals are in equilibrium with diamagnetic dimers and that their destruction proceeds in accordance with Scheme II (see Section II).[127]

The thermodynamic parameters of the dimerisation of nitroxy-radicals in isopentane are close to the corresponding parameters of the reversible recombination of t-alkylperoxy-radicals in alkanes[116], for example of t-butylperoxy-radicals in isopentane (Table 5). However, the recombination of nitroxy-radicals leads to the formation of dimers via a 4-centre bond[122]



and not via the O—O linkage.

VIII. RADICAL-IONS

Despite electrostatic repulsion, radical-ions dimerise reversibly in solution[128–134]. The dimerisation of radical-ions was first described in detail by Michaelis and Schubert[135], who analysed titration curves. The dimerisation reaction is usually accompanied by the electron transfer reaction between radical-ions, but, having selected the appropriate conditions, it is possible to suppress fully one of these reactions[135].

The following relation is valid for the reversible dimerisation of many aromatic radical-anions[136]:

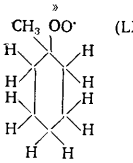
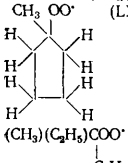
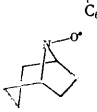
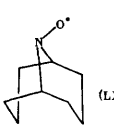
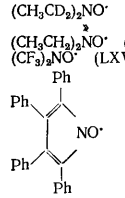
$$\Delta G^0 = \Delta\xi_\pi + \text{const},$$

where $\Delta\xi_\pi$ is the change in the energy of π-electrons.

The dimerisation of ion pairs is a well known phenomenon, which is induced by Coulombic attraction[137]. Electrostatic forces promote the formation of π−π′ bonds between suitable reactants, which results in the formation of ion pair dimers having fundamentally new properties compared with electrostatically linked ion pairs[137].

The zinc-octaethylporphyrin radical-cations (LXX) form diamagnetic dimers in a 10:1 (by volume) methanol–chloroform mixture in the temperature range between −20° and 50 °C.[138] The reaction was investigated by optical spectroscopy, EPR, NMR, and the temperature jump method (Table 6). The porphyrin rings in the dimer are located in parallel planes and are linked by a π−π′ bond[138] formed as a result of the overlap of half-filled orbitals. This bond [bond dissociation energy 17 kcal mol^{-1} (Table 6)] is stronger than the usual covalent bond in "hexaphenylethane" [11 kcal mol^{-1} (Table 4)].

Table 5. Thermodynamic parameters of the reversible dimerisation of peroxy- and nitroxy-radicals.

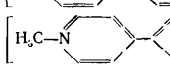
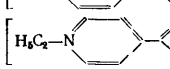
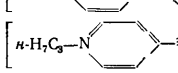
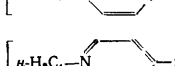
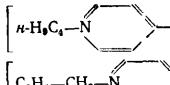
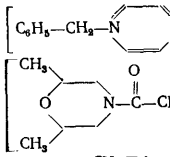
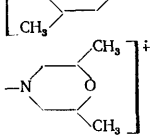
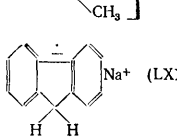
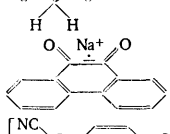
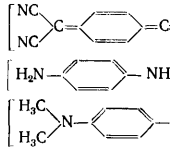
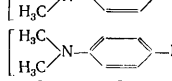
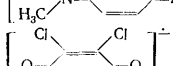
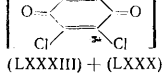
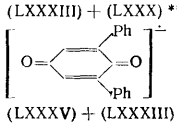
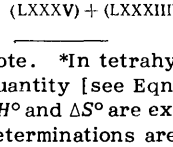
Radical	Solvent	K, mol l^{-1}	ΔH^0	ΔS^0	Refs.
$(CH_3)_3COO\cdot$ (LII)	CH_2Cl_2 *	$4.9\cdot10^{-6}$	6	—	115
»	CF_2Cl_2	—	8.8	34	116, 117
»	CF_2Cl_2	—	8.0	31	116, 117
»	isopentane	—	8.4	30	116, 117
$(CH_3)_2C(C_2H_5)OO\cdot$ (LIII)	2-methylbutane	$1.5\cdot10^{-5}$	8.9	36	118
»	CF_2Cl_2	—	7.5	29	116, 117
$(CH_3)_2C(C_3H_7)OO\cdot$ (LIV)	2-methylpentane	$6.7\cdot10^{-5}$	8.9	39	118
$(CH_3)_2C(CH(CH_3)_2)OO\cdot$ (LV)	isopentane	—	8.6	33	116, 117
$CH_3C(C_2H_5)_2OO\cdot$ (LVI)	3-methylpentane	$5.5\cdot10^{-5}$	9.7	44	118
$CH_3C(CH(CH_3)_2)_2OO\cdot$ (LVII)	2,3-dimethylbutane	$5.3\cdot10^{-5}$	8.2	34	118
$(CH_3)_2C(C(CH_3)_3)OO\cdot$ (LVIII)	2,2,3-trimethylbutane	$7.7\cdot10^{-5}$	8.7	38	118
$(CH_3)_2C(C_6H_5)OO\cdot$ (LIX)	cumene	$3.1\cdot10^{-6}$	11.2	48	118
»	CF_2Cl_2	—	9.2	32	116, 117
»	CF_2Cl_2	—	10.6	—	116, 117
 (LX)	CF_2Cl_2	—	7.0	35	116, 117
$(CH_3)_2C(CH_2C(CH_3)_3)OO\cdot$ (LXI)	CF_2Cl_2	—	7.8	31	116, 117
 (LXII)	CF_2Cl_2	—	8.0	30	116, 117
$(CH_3)(C_2H_5)C(C_6H_5)OO\cdot$ (LXIII)	CF_2Cl_2	—	11.0	—	116, 117
 (LXIV)	isopentane**	0.2	8.2	25	122
ditto	$CFCl_3$+10% isopentane**	0.5	5.6	17.5	122
»	CCl_4 **	0.9	—	—	122
 (LXV)	isopentane**	1.0	8.5	28.6	122
$(CH_3CD_2)_2NO\cdot$ (LXVI)	isopentane**	0.63	7.6	24.8	123
»	CF_2Cl_2 **	0.018	2.6	0.1	123
$(CH_3CH_2)_2NO\cdot$ (LXVII)	CF_2Cl_2 **	0.34	6	18	123, 126
$(CF_3)_2NO\cdot$ (LXVIII)	CF_2Cl_2 **	0.45	2.4	6.5	124
 (LXIX)	CH_2Cl_2 **	0.001	13	30	125

Note. *−95 °C; **25 °C—in the remaining cases −120 °C. ΔH and ΔS are expressed in kcal mol^{-1} and cal mol^{-1} K^{-1}. The average errors of the determination are 30% in K, ±0.5 kcal mol^{-1} in ΔH, and ±5 cal mol^{-1} K^{-1} in ΔS.

The reversible dimerisation of the radical-cations of substituted viologens (1,1'-di-R,4,4'-bipyridylium monocations) (LXXI)–(LXXVII) in methanol at temperatures between −90° and 40 °C was investigated by EPR.[129,139,140] Table 6 presents the thermodynamic parameters obtained for these radicals. With increase of the size of the radical-cation, the reaction becomes more endothermic and its entropy increases. At room temperature the entropy of reaction has the dominant influence and, with increase in the size of the radical, the equilibrium shifts towards the formation of radicals. A linear relation has been observed between $\Delta H°$ and $\Delta S°$.[139]

It was to be expected that $\Delta S° > 0$ for the decomposition of dimers; however, the data in Table 6 show that the majority of radical-cations $\Delta S° < 0$, which means that the opposite

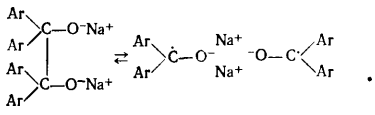
Table 6. Kinetic and thermodynamic parameters of reaction (1) involving radical-ions and ion pairs.

Radical ion or ion pair	Solvent	t, °C	k_1, l mol^{-1} s^{-1}	k_{-1}, s^{-1}	K, mol l^{-1}	$\Delta H°$	$\Delta S°$	Refs.
Radical-cation of zinc-octaethylporphyrin (LXX)	10:1 (by volume) methanol–chloroform	20	$1.3\cdot10^8$	$5.0\cdot10^3$	$4\cdot10^{-5}$	17.5	38	138
 (LXXI)	methanol	−13.5	—	—	$4.3\cdot10^{-3}$	1.0	−8.3	139
 (LXXII)	methanol	25	—	—	$1.5\cdot10^{-3}$	1.6	−7.7	139
 (LXXIII)	methanol	−11	—	—	$8.7\cdot10^{-4}$	2.0	−6.3	139, 140
 (LXXIV)	methanol	−10	—	—	$1.0\cdot10^{-3}$	2.5	−3.8	139
 (LXXV)	methanol	−12.5	—	—	$7.2\cdot10^{-4}$	3.0	−2.5	139
 (LXXVI)	methanol	−20	—	—	$7.2\cdot10^{-4}$	5.5	7.5	139
  (LXXVII)	methanol	−11	—	—	$6.3\cdot10^{-4}$	10.8	27.5	129
 (LXXVIII)	dimethoxyethane	23	—	—	$2\cdot10^{-3}$	−2.5	−29	144
 (LXXIX)	tetrahydrofuran	20.9	$1.0\cdot10^{4}$*	—	$1.96\cdot10^{-2}$	6	13	137
 (LXXX)	water + 0.2 M LiCl	15	$3.5\cdot10^8$	$9.0\cdot10^4$	$2.5\cdot10^{-4}$	10.4	18	130, 145
 (LXXXI)	1:2 ether–alcohol	~−100	—	—	—	8	—	131
 (LXXXII)	1:2 ether–alcohol	~−100	—	—	—	10	—	131
 (LXXXIII)	1:2 ether–alcohol	~−150	—	—	—	5	—	131
 (LXXXIV)	ethanol	−139	—	—	$5.0\cdot10^{-4}$	4.5	18.7	132
(LXXXIII) + (LXXX) **	acetonitrile	23	$6\cdot10^9$	$4\cdot10^8$	$7\cdot10^{-2}$	−4	−17	147
 (LXXXV) *** (LXXXV) + (LXXXIII)	acetonitrile	20	$5\cdot10^9$	$5.5\cdot10^8$	$1.1\cdot10^{-8}$	2.4	−20	148

Note. *In tetrahydropyran at 25 °C. ** Here k_{-1} is expressed in litre mol^{-1} s^{-1} and K is a dimensionless quantity [see Eqn.(13)]. *** See Eqn.(14).
$\Delta H°$ and $\Delta S°$ are expressed in kcal mol^{-1} and cal mol^{-1} K^{-1} respectively. The average errors of the determinations are 20% in k_1, k_{-1}, and K, ±0.5 kcal mol^{-1} in $\Delta H°$, and ±2 cal mol^{-1} K^{-1} in $\Delta S°$.

effect, causing an increase of entropy on dimerisation of two monomeric species, operates; this involves the removal of solvent molecules from the solvation shell of the radical-cation on dimerisation. With increase of the size of the radical-cation, the forces maintaining solvent molecules near it are weakened and ΔS° diminishes on desolvation during the dimerisation process. On this basis, one can assume that the radicals dimerise via a "plane-to-plane" mechanism, this type of dimerisation ensuring effective desolvation. By analogy with earlier studies[138,141], Evans et al.[139,140] suggested that the radicals in the diamagnetic dimer are linked by a $\pi-\pi'$ bond. Kosower and Cotter[142] postulated that the dimer (LXXII) is a biradical. The strongest bond between the viologen radical-cations is formed on dimerisation of (LXXVII) (Table 6). This behaviour can be due to the greater degree of delocalisation of the unpaired electron in (LXXVII), which ensures a more effective overlap between the π-type molecular orbitals of the radical-cations[140]. The reversible dimerisation of (LXXII) has also been observed by Blandmer et al.[143]

Apparently all alkali metal derivatives of aromatic ketyls are involved in equilibrium (1) in etheral solutions[144], which has been investigated by EPR and spectrophotometric methods. The ketyl dimer can have different structures and, depending on the solvent, can be paramagnetic or diamagnetic[144]. In non-polar solvents mainly the reversible conversion of the diamagnetic dimer into the paramagnetic dimer is observed:



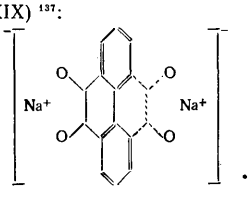
In ethers the paramagnetic dimer is formed preferentially. The data for equilibrium (1) involving sodium fluorenyl (LXXVIII) are presented in Table 6.

The sodium salts of radical-anions (ion pairs) of 9,10-phenanthrenequinone (LXXIX) and acetonaphthoquinone form diamagnetic dimers linked by a $\pi-\pi'$ bond[137]:

$$2(PhQ^{\cdot-}, Na^+) \rightleftarrows (D^{2-}, 2Na^+) .$$

The reactions were investigated by stopped flow and spectrophotometric methods (Table 6). The following structure has been postulated for the dimer (LXXIX):[137]

(LXXIX)[137]:



The tetracyanoquinodimethane radical-anions (LXXX) dimerise reversibly in aqueous and aqueous alcoholic solutions at room temperature[130,145]. The value of k_1 obtained by the temperature jump method (Table 6) is smaller by a factor of 5 than that calculated by the Debye formula taking into account the electrostatic repulsion. It may be that reaction (1) is diffusion-limited[145].

p-Phenylenediamine bromide (LXXXI), *N*,*N*-dimethyl-*p*-phenylenediamine perchlorate (Wurster's red) (LXXXII), and *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine perchlorate (Wurster's blue) (LXXXIII) dimerise reversibly in solution (Table 6), being apparently linked to a single counterion[131]:

$$2R^{\dot{+}} + X^- \rightleftarrows (R_2X)^+.$$

The weak binding of radical (LXXXIII) is caused by the steric repulsion of the methyl groups: this radical is present in solution at room temperature as the monomer[131].

The radical-anions of quinones are involved in reversible dimerisation reactions at reduced temperatures, apart from the disproportionation reaction via one-electron transfer[132]. Table 6 presents data for the chloranil radical-anion (LXXXIV).

Radical-anions and radical-cations undergo rapid reversible electron transfer reactions with one another:

$$R^{\dot{+}} + Q^{\dot{-}} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} R + Q. \qquad (13)$$

For example, Table 6 presents data for reaction (13) involving radicals (LXXXIII) and (LXXX) obtained by the temperature jump method. This reaction can include a stage in which a charge-transfer complex (CTC) is formed:

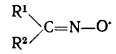
$$R^{\dot{+}} + Q^{\dot{-}} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CTC \rightleftarrows R + Q. \qquad (14)$$

For example, the formation of both the corresponding radical-anions and CTC has been observed in polar solvents[148]. The kinetic and thermodynamic parameters of reaction (14) with participation of (LXXXIII) and the 2,6-diphenyl-1,4-benzoquinone radical-anion (LXXXV) have been obtained by flash photolysis and spectrophotometry (Table 6). The constant k_1 agrees satisfactorily with the rate constant for a reaction between charged radicals limited by translational diffusion[148].

IX. OTHER RADICALS

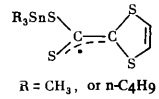
1-Alkyl-4-methoxycarbonylpyridyl radicals (LXXXVI)–(LXXXVIII) (Table 7) dimerise reversibly in isopentane at temperatures between −207° and −63 °C.[141,174] The reaction has been investigated spectrophotometrically. It has been suggested that the radical dimers are charge-transfer complexes[141] and it has been shown[149] that the irreversible destruction of 4-carbamoyl-1-methylpyridyl radicals in acid aqueous solution is preceded by reversible dimerisation[149]. Certain pyridyl radicals disproportionate reversibly via the transfer of a single electron[173].

Diaryliminoxy-, alkylaryliminoxy-, and dialkyliminoxy-radicals having the structure



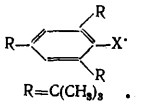
dimerise reversibly in benzene with formation of N–N, N–O, and C–O bonds[10]. Sterically unhindered dialkyliminoxy-radicals are involved in an equilibrium which is displaced towards the dimers. For the majority of the diaryliminoxy-, alkylaryliminoxy-, and sterically hindered dialkylimonoxy-radicals, the equilibrium is displaced towards the radicals. For these radicals, ΔH° = 15–20 kcal mol^{-1} in toluene[10]. Irreversible reactions also take place in the system[10].

The 1-thioallyl radicals, having the structure



and obtained from tetrathiofulvalene, have been investigated by EPR.[150] It was established that these sterically hindered radicals are in equilibrium with diamagnetic dimers in toluene at 25 °C and below. The dimer is probably formed via the S–S coupling reaction[150].

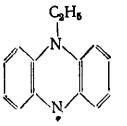
The recombination of 2,4,6-tri-t-butyl-substituted benzyl (LXXXIX), phenylaminyl (LXL), phenylthiayl (LXLI), and phenoxy-radicals in hydrocarbons as well as di-t-butyl peroxide has been investigated by EPR:[53]



The radicals are isoelectronic and are characterised by the same extent of steric hindrance around the reaction centre. It has been established that the benzyl radicals recombine irreversibly to form bibenzyl (Table 7). The phenylaminyl radical is in equilibrium with the corresponding dimer (hydrazine) at room temperature (Table 7). The data in Table 7 show that the recombination of sterically hindered phenylaminyl radicals is slower by four orders of magnitude than that of benzyl radicals. The phenylthiyl radicals in solution are in equilibrium with the corresponding disulphide (Table 7).

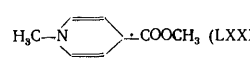
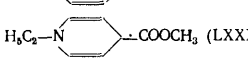
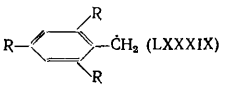
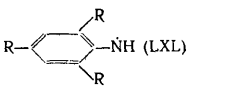
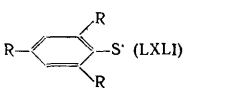
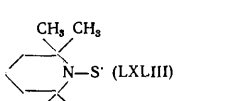
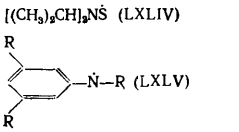
The difference between the reactivities of radicals (LXXXIX)–(LXLI) is due to the difference between the dissociation energies of the bonds formed on "head-to-head" recombination. The dissociation energy of the bonds in the dimers varies in the sequence C–C > S–S > N–N > O–O; the O–O bond dissociation energy is apparently close to zero[53]. With increase of the strength of the bond formed, the rate of recombination of radicals also increases, which can be accounted for on the basis of Hammond's postulate. Indeed the more exothermic the reaction, the greater the similarity between the transition state and the reactants. For sufficiently exothermic reactions, the bond can then be formed over a comparatively large distance between the reactants, where the influence of t-butyl groups is small[53]. The values of $\Delta S_{-1}^{\neq}$ are much smaller than the "normal" value (see Section VI) for radicals (LXL) (Table 7) and (LXXXIX).[53]

The study of the absorption spectra and magnetic susceptibility of *N*-ethylphenazyl



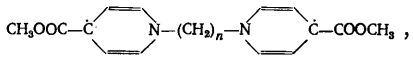
(solvent 2 : 1 alcohol–ether) showed that the radicals dimerise reversibly at low temperatures (~–180 °C); the radicals in the dimer are located in parallel planes[146].

Table 7. Kinetic and thermodynamic parameters of reaction (1) involving radicals of different structure.

Radical	Solvent	t, °C	k_1, l mol^{-1} s^{-1}	k_{-1}, s^{-1}	K, mol l^{-1}	$\Delta H_1^{\neq}$	$\Delta H_{-1}^{\neq}$	ΔH^0	$\Delta S_1^{\neq}$	$\Delta S_{-1}^{\neq}$	ΔS^0	Refs.
 (LXXXVI)	isopentane	–196	—	—	$1.4\cdot10^{-4}$	—	—	—	—	—	—	141
 (LXXXVII)	isopentane	–196	—	—	$2.9\cdot10^{-5}$	—	—	—	—	—	—	141
 (LXXXVIII)	isopentane	–196	—	—	$1.2\cdot10^{-4}$	—	—	—	—	—	—	141
 (LXXXIX)	di-t-butyl peroxide	24	$5\cdot10^{8}$	—	—	—	—	—	—	—	—	53
 (LXL)	di-t-butyl peroxide	20	$3\cdot10^{4}$	7.5	$2.5\cdot10^{-4}$	2.0	15.0	13.1	–32	–5	27	53
 (LXLI)	iso-octane	18	—	—	$1.7\cdot10^{-12}$	—	—	23.3	—	—	27	53
$(CH_3)_3\dot{C}Se\dot{C}[C(CH_3)_3]_2$ (LXLII)	pentane	–15 ÷ –50	—	—	—	—	—	18.2	—	—	37.5	152
 (LXLIII)	t-butylbenzene	25	$8.3\cdot10^{8}$	$3\cdot10^{-3}$ **	$1.5\cdot10^{-12}$	3.4	13	28	–7	20	27	153
$[(CH_3)_2CH]_2N\dot{S}$ (LXLIV)	t-butylbenzene	11	$6.0\cdot10^{8}$	$5\cdot10^{-7}$ **	$1\cdot10^{-15}$	3.4	27	24	–7	9	16	153
 (LXLV)	methylcyclohexane	–13.8	1,6	—	$6.0\cdot10^{-6}$ ***	–2.2	29	31.2	–65	8	73	154

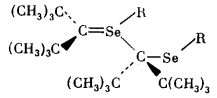
Note. *At 71 °C. **Calculated from the formula $k_{-1} = Kk_1$. ***At 47.7 °C.
ΔH and ΔS are expressed in kcal mol^{-1} and cal mol^{-1} K^{-1} respectively. The errors of the determinations of the various quantities differ markedly and are given in the original papers.

Biradicals can form diamagnetic dimers. Pyridyl biradicals having the structure



where $n = 3$ or 4, exhibit a significantly smaller paramagnetism than expected[151,174]. The ends of the pyridyl radicals are involved in intermolecular association and form a singlet (diamagnetic) species. There is virtually no association of radicals with $n = 2$, 5, and 10.[151,174]

The bimolecular reactions of the radicals $RSeC[C(CH_3)_3]_2$, where R = CH_3, $(CH_3)_3C$ (LXLII), CF_3, C_6H_5, $(n\text{-}C_4H_9)_3Si$, $(CH_3)_3Sn$, $(CH_3)_3Ge$, $(CH_3)_3CO$, or $(CH_3)_3CS$, have been investigated by EPR.[152] The majority of these radicals (possibly all of them) are in equilibrium with diamagnetic dimers at low temperatures. The dimers apparently have a "head-to-tail" structure:



The data for radicals (LXLII) are presented in Table 7. Together with reversible recombination, the irreversible destruction of the radicals takes place. The destruction follows a first-order law in conformity with Scheme II (Section II).

The 2,2,6,6-tetramethylpiperidinylthiyl radical (LXLIII) and the diisopropylaminothiyl radical (LXLIV) have been obtained[153] by the photolysis of the corresponding disulphides in the resonator of the EPR spectrometer. The equilibrium

$$2R_2NS^{\cdot} \rightleftarrows R_2NSSNR_2$$

is established at 40–130 °C. The destruction of radicals (LXLIII) and (LXLIV) at room and lower temperatures obeys a second-order law in t-butylbenzene (Table 7); the rate of reaction is apparently limited by diffusion.

The recombination of the radicals $R_2NS^{\cdot}$ differs from the recombination of the related dialkylnitroxy-radicals $R_2NO^{\cdot}$ by the fact that it takes place via a "head-to-head" mechanism with formation of a stronger bond (Table 7). The nitroxy-radical dimers have a bond dissociation energy not exceeding 13 kcal mol^{-1} (Table 5).

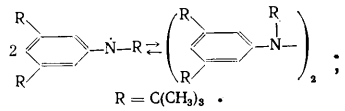
Like arylethanes and the dimer (XL) (Section VI), arylhydrazines dissociate reversibly into diarylaminyl radicals on heating or irradiation:

$$2Ar_2N^{\cdot} \rightleftarrows Ar_2N{-}NAr_2 .$$

This reaction has been described in monographs[11,101,168,169] and reviews[178,180]. The EPR spectra of diarylaminyl radicals containing the electron-donating substitutents $N(CH_3)_2$, CH_3O, and CH_3 in the aromatic ring have been recorded[179].

On thermal dissociation of arylhydrazines, not all substituents capable of delocalising the unpaired electron increase the degee of dissociation. The following sequence based on the influence of the substitutents is observed: $N(CH_3)_2 > OCH_3 > CH_3 > H > COOC_2H_5 > CN > NO_2$.[178] This sequence of substituents shows that the dissociation of substituted hydrazines is determined mainly by the interaction within the hydrazine molecule (the interaction of the unshared electron pair with the substituents in the *para*-position) and much less so by the delocalisation of the unpaired electron in the radical[178].

The *N*-3,5-tri-t-butylphenylaminyl radical (LXLV) recombines reversibly to a dimer at temperatures between −13° and −103 °C in methylcyclohexane (Table 7):[154]



R = $C(CH_3)_3$.

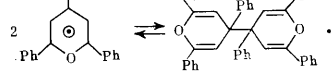
The reaction was investigated by EPR. At low temperatures ($t < -13$ °C) the equilibrium is fully displaced towards the formation of the dimer; the radical can be regenerated by photolysis and the kinetics of its destruction can be studied.

The value of $\Delta H°$ obtained (Table 7) is close to the dissociation energy of the N–N bond in hydrazobenzene (37.7 kcal mol^{-1}) [154] and the introduction of t-butyl groups into hydrazobenzene should reduce this quantity. The value of $\Delta S°$ obtained for this radical is extremely high compared with $\Delta S°$ for phenoxy- (Tables 1 and 3), nitroxy- (Table 5), triphenylmethyl (Table 4), and arylindan-1,3-dionyl (Table 2) radicals as well as radical-ions (Table 6). The given dimer is sterically hindered to an extremely large extent as a result of the coupling reaction and its decompositon leads to the possibility of the free rotation of the t-butyl groups.

The negative values of $\Delta H_1^{\neq}$ obtained for the recombination of radicals (LXLV) were observed also for other radicals—phenoxy (Tables 1 and 3) and nitroxy-radicals[123], and were interpreted on the assumption of an equilibrium preceding the slowest stage of the reaction. The high negative value of $\Delta S_1^{\neq}$ (Table 7) indicates a very rigid transition state in the recombination reaction. In fact the rate of recombination is controlled by the activation entropy.

The appreciable shielding of the N atom in aminyl radicals leads to the formation of dimers linked by C–N and even C–C bonds[155,178].

The 2,4,6-triphenylpyranyl radicals recombine reversibly to a dimer in acetonitrile at temperatures between −40° and 30 °C:[156]



The reaction was investigated by EPR and ultraviolet spectroscopy. $\Delta H_1^{\neq} = 6.4$ kcal mol^{-1} was obtained.

X. THE INFLUENCE OF THE SOLVENT ON THE KINETICS OF REVERSIBLE RECOMBINATION

The solvent is known to have a significant influence on the rates of radical reactions in the liquid phase[157]. The solvent viscosity, the formation of complexes by radicals with the solvent, and specific and non-specific solvation influence the reactivity of radicals. The difference between the degrees of solvation of the radicals and the dimer influences the constant of equilibrium (1). The rate of reaction (−1) in polar solvents depends on the ratio of the dipole moments of the transition states in this reaction. The influence of the solvent on reaction (1) for radicals of different classes is examined below.

1. Phenoxy-Radicals

The influence of specific solvation on the kinetics of the reversible recombination of phenyl-, methoxy-, and t-butylphenoxy-radicals has been studied in detail[1,7,25–27,29,75,90,158].

Tables 8 and 9 present the kinetic and thermodynamic parameters of reaction (1) involving phenoxy-radicals in various solvents.

Table 8. Kinetic and thermodynamic parameters of reaction (1) involving phenoxy-radicals in different solvents at 20 °C.

Solvent	$10^{-8}k_1$, l mol^{-1} s^{-1}	k_{-1}, s^{-1}	10^8K, mol l^{-1}	$\Delta H_1^{\neq}$	$\Delta H_{-1}^{\neq}$	ΔH^0	$-\Delta S_1^{\neq}$	$\Delta S_{-1}^{\neq}$	ΔS^0
				(I) [1]					
Hexane	32	80	2.5	0.5	12.8	12.3	12	—5	7
Carbon tetrachloride	8.5	50	5.5	2.5	14.8	12.3	3	0	8
Toluene	7.5	150	20	3.0	14.0	11.0	7	0	7
Dioxan	3	120	40	3.0	14.4	11.4	9	1	10
Methanol	12	840	70	1.5	11.2	9.7	11	—7	4
Acetonitrile	6	720	120	2.0	10.5	8.5	11	—9	2
Chloroform	2	250	130	2.0	10.0	8.0	13	—13	0
DMF	5	800	160	—	—	—	—	—	—
				(II) [25]					
Carbon tetrachloride	14	—	—	0.3	—	—	14	—	—
Toluene	7.0	0.0070	0.001	2.2	24	22	9	16	25
Benzene	6.5	—	—	2.3	—	—	9	—	—
THF	6.0	—	—	1.9	—	—	10	—	—
Chlorobenzene	3.2	0.096	0.03	3.2	19	17	11	8	19
Chloroform	2.0	—	—	2.0	—	—	9	—	
Dichloromethane	3.8	—	—	1.1	—	—	14	—	
Acetone	8.0	—	—	0.7	—	—	14	—	
Acetonitrile	10	0.06	0.006	0.5	22	21	14	11	25
Acetic acid	3.6	—	—	2.3	—	—	13	—	
Formic acid	4.5	—	—	1.3	—	—	13	—	
				(IV) [25]					
Carbon tetrachloride	3.1	0.71	0.23	1.6	22.3	20.7	13	18	31
Toluene	3.4	5.5	1.62	1.6	17.8	16.8	13	6	19
Benzene	3.0	2.4	0.81	1.5	20.7	19.2	13	15	28
THF	2.2	3.0	1.38	1.8	19.0	17.2	13	9	22
Chlorobenzene	2.2	2.3	1.03	1.9	20.9	19.0	12	16	28
Chloroform	1.4	6.6	4.71	2.6	17.2	14.6	11	5	16
Dichloromethane	2.2	8.0	3.62	1.2	18.7	17.5	15	11	26
Acetone	2.4	6.5	2.71	1.3	17.8	16.5	14	7	21
Acetonitrile	5.5	9.7	1.77	0.9	16.0	15.1	14	2	16
Acetic acid	2.0	17	8.7	2.2	18.7	16.5	12	12	24
Formic acid	3.0	—	—	1.7	—	—	12		
				(V) [25]					
Carbon tetrachloride	2.3	—	—	0.2	—	—	18	—	—
Toluene	2.5	0.010	0.0042	0.5	22	21	17	7	24
Benzene	2.0	—	—	1.7	—	—	13	—	—
THF	3.0	—	—	0.9	—	—	15	—	—
Chlorobenzene	1.3	0.014	0.011	1.1	20	19	16	1	17
Chloroform	0.36	—	—	1.1	—	—	19	—	—
Dichloromethane	1.1	—	—	0.1	—	—	20	—	—
Acetone	3.8	—	—	0.6	—	—	16	—	—
Acetonitrile	7.0	0.049	0.0070	0.4	15	15	15	—11	4
Acetic acid	2.2	—	—	1.7	—	—	13	—	—
Formic acid	3.0	—	—	2.0	—	—	11	—	—
				(VII) [90]					
Carbon tetrachloride	11	22	2.0	1.5	8.6	7.1	10	—22	—12
Toluene	4.0	12	3.0	1.7	13.0	11.3	19	—14	4
Benzene	7.2	17	2.3	1.0	12.0	11.0	13	—11	2
THF	2.6	2.5	0.96	0.8	15.8	15.0	17	—2	15
Chlorobenzene	6.7	10	1.5	0.8	12.6	11.8	13	—9	4
Chloroform	2.5	27	11	2.0	14.9	14.7	19	0	19
Dichloromethane	5.6	26	4.7	1.2	16.7	15.5	14	6	20
Acetone	0.97	0.87	1.0	3.2	21.0	17.8	11	14	25
Acetonitrile	6.1	4.6	0.75	0.2	20.1	19.9	17	14	31
Acetic acid	1.5	3.5	2.3	1.6	15.6	14.0	11	2	13
Formic acid	0.60	—	—	3.0	—	—	21	—	—
				(VIII) [7, 75]					
Toluene	0.80	2.5	3.2	2.5	17.0	14.5	12	3	15
Benzene	0.50	3.5	7.1	2.5	17.5	15.0	13	5	18
Chloroform	0.20	1.2	6.0	4.5	17.5	13.0	8	3	11
Acetonitrile	1.7	4.0	2.4	1.0	15.0	14.0	16	—3	13
				(XI) [7, 75]					
Toluene	0.45	112	250	—1.0	16.5	17.5	25	9	34
Benzene	0.7	110	160	—0.5	17.0	17.5	23	10	33
				(XXIV) [7,75]					
Benzene	3.1	0.85	0.28	1.5	22.0	20.5	14	19	33
Chloroform	0.9	2.8	3.1	2.5	17.5	15.0	13	5	18
Acetonitrile	4.7	6.1	1.3	0.5	17.5	17.0	17	6	23
Formic acid	2.7	3.0	1.1	2.0	20.0	18.0	12	9	23

Note. ΔH and ΔS are expressed in kcal mol^{-1} and cal mol^{-1} K^{-1} respectively. The average errors of the determinations are 20% in k_1, 30% in k_{-1}, 30% in K, ±0.5 kcal mol^{-1} in ΔH, and ±1 cal mol^{-1} K^{-1} in ΔS. See also Table 13.

Table 9. The rate and equilibrium constants for reaction (1) involving radical (IX) in various solvents at 20 °C.[1,27]

Solvent	k_1, l mol^{-1} s^{-1}	k_{-1}, s^{-1}	K, mol l^{-1}	Solvent	k_1, l mol^{-1} s^{-1}	k_{-1}, s^{-1}	K, mol l^{-1}
Hexane	5.4	1600	300	t-Butyl alcohol	0.175	525	3 000
Carbon tetrachloride	1.75	1750	1 000	Acetonitrile	0.26	2900	11 000
Toluene	0.7	2100	3 000	Isopropyl alcohol	0.55	1650	3 000
Benzene	0.65	2600	4 000	1-Butanol	0.62	2500	4 000
Dioxan	0.19	3000	16 000	1-Propanol	0.81	3200	4 000
Chlorobenzene	0.11	2000	18 000	Ethanol	0.86	2600	3 000
Chloroform	0.050	1100	22 000	DMF	0.095	1400	15 000
Pyridine	0.022	550	25 000				

Note. The average errors of the determinations are 10% in k_1, 20% in K, and 30% in k_{-1}. See also Table 1.

The recombination reaction. V-shaped relations between k_1 and the empirical parameter E_T, characterising the solvent polarity, have been observed for phenylphenoxy-radicals (Tables 8 and 9).[1] The above relations are more pronounced for radicals whose recombination takes place under kinetic conditions [radicals (VIII) and (IX)] than for phenylphenoxy-radicals whose recombination is limited by diffusion[1,90]. This fact is consistent with the general observation that the solvent has a more significant influence on slow reactions than on fast reactions.

Phenylphenoxy-radicals form charge-transfer complexes with solvent molecules. The charge-transfer bands in the spectra of solutions of radical (IX) in different solvents have been observed.[159] The solvation of the radicals leads as a rule to a decrease of their diffusion coefficient and possibly to shielding of the reaction centre, which entails a decrease of k_1. Furthermore, the recombination of radicals is accompanied by the dissociation of complexes, which increase $\Delta H_1^{\neq}$. As a consequence, k_1 diminishes with increase of E_T from 31 (hexane) to 40 (chloroform). In chloroform k_1 has the lowest value; chloroform molecules form complexes with phenoxy-radicals as a result of interaction with the oxygen atom or the π-electrons of the benzene rings[158].

The causes of the increase of k_1 in solvents with $E_T > 40$ are less clear. DMF, acetonitrile, and alcohols have high dielectric constants and an unshared electron pair; alcohols are capable of forming hydrogen bonds with phenoxy-radicals. The redistribution of charges on the atoms of phenoxy-radicals due to their specific solvation by these solvents apparently promotes a rapid attainment of the required orientation for the recombination of the radicals in the cage[1,158]. As a result of this, the constant k_1 should increase. The V-shaped relation between k_1 and E_T for the recombination of radicals (VIII) and (IX) under kinetic conditions can be explained as follows[1,27,90]. The recombination of the radicals is accompanied by the dissociation of the complexes, which increases $\Delta H_1^{\neq}$. At the same time the decomposition of the complexes increases the degree of disorder and hence the activation entropy $\Delta S_1^{\neq}$. Since $\Delta H_1^{\neq}$ and $T\Delta S_1^{\neq}$ have opposite signs as components of $\Delta G_1^{\neq}$, the observed relation can occur when, on changing the solvent, k_1 is initially influenced predominantly by the change in $\Delta H_1^{\neq}$ and then by the change in $\Delta S_1^{\neq}$.

Polar solvents can also solvate the molecules of the dimers as a result of which the recombination of the radicals is not accompanied by the dissociation of the complexes[90]. Indeed, the recombination of radicals (VIII) is accompanied by an increase of $\Delta H_1^{\neq}$ in the sequence hexane < toluene (benzene) < chloroform (Tables 3 and 8), owing to the increase of the stability of the radical–solvent complex. At the same time an increase of $\Delta S_1^{\neq}$ is observed (compensation effect). However,

in a polar solvent (acetonitrile) low values of $\Delta H_1^{\neq}$ and $\Delta S_1^{\neq}$ are observed. In this case the dimer molecules as well as the radical are solvated and the solvation energies of the radical and the dimer are similar[90].

The influence of the composition of the binary mixture on k_1 for phenylphenoxy-radicals has been studied[1,26,27] using binary mixtures of solvents corresponding to different branches of the V-shaped relation between k_1 and E_T as well as binary mixtures one of the components of which was chloroform. The low value of k_1 in chloroform is caused by the specific solvation of the radical by the solvent and not by the properties of the medium as a "continuum"[1]. It was suggested that in binary hexane–chloroform and carbon tetrachloride–chloroform mixtures hexane and carbon tetrachloride do not form complexes with phenoxy-radicals (PhO$^{\cdot}$), while chloroform (S) forms 1 : 1 solvate complexes (PhO$^{\cdot}_S$):

$$PhO^{\cdot} + S \underset{}{\overset{K_{RS}}{\rightleftharpoons}} PhO^{\cdot}_S,$$

$$PhO^{\cdot} + PhO^{\cdot} \xrightarrow{k_1} \text{dimer},$$

$$PhO^{\cdot} + PhO^{\cdot} \xrightarrow{k_{RS}} \text{dimer},$$

$$PhO^{\cdot}_S + PhO^{\cdot}_S \xrightarrow{k_{SS}} \text{dimer}.$$

The kinetic parameters for which the given scheme describes the observed dependence of k_1 on the chloroform concentration in the binary mixture were estimated[1]:

$K_{RS}=0.9\pm0.2$ litre mol^{-1}, $k_{RS}=(1.2\pm0.5)\cdot10^7$ litre mol^{-1} s^{-1}

[radical (IX) in a chloroform–hexane mixture];

$K_{RS}=0.45\pm0.10$ litre mol^{-1}, $k_{RS}=(9.0\pm2.0)\cdot10^6$ litre mol^{-1} s^{-1}

[radical (IX) in a chloroform–carbon tetrachloride mixture];

$K_{RS}=0.18\pm0.05$ litre mol^{-1}, $k_{RS}=(2.0\pm1.0)\cdot10^8$ litre mol^{-1} s^{-1}

[radical (I) in a chloroform–carbon tetrachloride mixture]. In all cases $k_{SS} \ll k_{RS}^1$.

The above ideas proved to be inapplicable to binary mixtures containing an alcohol. The relations between $k_1\eta$ and the compositions of such binary mixtures showed maxima and minima[1,90], which is due to the fact that the mixtures have a complex structure which varies with the component ratio. The solutions differ significantly from regular solutions and there is a possibility of microlayer formation in the mixture. When methanol is diluted with carbon tetrachloride or chloroform, the fraction of alcohol dimers and trimers, which form more stable complexes with the radicals, increases[1].

The rate of the diffusion-controlled recombination of radicals reflects the changes in the structure of the solution as a function of its composition. In these mixtures the microviscosity differs significantly from the macroviscosity and the changes in k_1 are determined by the behaviour of excess thermodynamic functions. Thus the study of the rate of diffusion-controlled recombination reactions constitutes together with spin exchange in binary mixtures, a method for the quantitative study of phenomena of this kind[1].

The constants k_1 for t-butyl- and methoxy-phenoxy-radicals depend only slightly on the chemical nature of the solvent (Table 8). The data of Kuz'min et al.[160] permit the conclusion that the k_1 for the *o*-methylphenoxy-radical also depends on the nature of the solvent only slightly. Thus specific solvation has a significant influence on the recombination of only those phenoyx-radicals which contain aryl substituents.

It has been observed that k_1 for the *o*-methylphenoxy-radical diminishes with increase of the ionic strength of the aqueous solution[161], but this is apparently caused by the increased viscosity of the medium.

Dissociation reaction of the dimers. The solvent also has a significant influence on k_{-1}. For example, k_{-1} for radical (I) increases by more than an order of magnitude with increase of solvent polarity (Table 8). An analogous solvent effect was observed for radical (XXIV) (Table 8). For dimers with a "head-to-tail" structure, $\Delta H_{-1}^{\neq}$ decreases with increased solvent polarity [radicals (I), (VIII), (IX), and (XXIV); Tables 8 and 9]. Under these conditions, k_{-1} either increases [radicals (I) and (XXIV)] or depends only slightly on the solvent [radicals (VIII) and (IX)] due to the compensation effect.

The influence of the solvent on $\Delta H_{-1}^{\neq}$ has been examined[29] as a function of the ratio of the dipole moments of the transition state ($\mu^{\neq}$) and the initial dimer (μ_d). 2,6-Diphenyl-4R-phenoxy-radicals form dimers having the structure of quinol ethers ("head-to-tail"). An increase of the solvating capacity of the solvent lowers $\Delta H_{-1}^{\neq}$ for such dimers, since in this case $\mu^{\neq} > \mu_d$. The dimerisation of radicals (VII) results in the formation of C–C dimers ("tail-to-tail"). In this case $\mu^{\neq} < \mu_d$ and the increase of the solvating capacity of the solvent leads to an increase of $\Delta H_{-1}^{\neq}$ (Table 8).

2. Aromatic C-Centred Radicals

The values of K for the triphenylmethyl radical (XL) and its substituted derivatives in various solvents have been determined calorimetrically[162–164,175] and the constants k_{-1} have been obtained in experiments involving the addition of oxygen or nitric oxide to the dimer (Table 10). The values of k_{-1} obtained[162,175] for radical (XL) in 28 solvents at 0 °C varied from 1.1×10^{-3} to 4.2×10^{-3} s^{-1}.

Table 10. The equilibrium constants and enthalpies of reaction (1) involving radical (XL) in various solvents at 20 °C.[163]*

Solvent	$10^4\cdot K$, mol l^{-1}	ΔH^0, kcal mol^{-1}	Solvent	$10^4\cdot K$, mol l^{-1}	ΔH^0, kcal mol^{-1}
Propionitrile	1.20	11.1	Ethylene dibromide	3.90	11.4
Ethyl benzoate	1.67	12.0	Benzene	4.10	11.3
Acetophenone	1.70	11.5	Chloroform**	6.90	10.5
Dioxan	2.50	11.6	Carbon disulphide***	19.2	11.0
Bromobenzene	3.70	11.5			

Note. *See also Table 4; **$k_{-1} = 0.219$ s;[164] $k_1 = 3.2\times10^2$ litre mol^{-1} s^{-1}; ***$k_{-1} = 0.252$ s^{-1};[164] $k_1 = 1.3\times10^2$ litre mol^{-1} s^{-1}.
The errors of the determinations are ~5% in K and k_{-1}, ~10% in k_1, and ±0.3 kcal mol^{-1} in ΔH^0.

A relation of the Brønsted type, $\ln k = \alpha \ln K + \text{const.}$, is known to hold for a number of reactions[165]. It has been shown[165] that the relation holds satisfactorily for the dissociation of the dimer of (XL) in various solvents and $\alpha = 0.2$. According to the author, the transition state in the decomposition reaction resembles the dimer more than the radicals. The initial dimer and the transition state cannot interact with the solvent for steric reasons[165]. The influence of the solvent on the kinetics of

reaction (1) with participation of 2-aryl-indan-1,3-dionyl radicals having structures (XII) and (XVI) has been studied[166]. The values of k_1 for radical (XII) differ insignificantly in all the solvents investigated (Table 11).

Table 11. Kinetic and thermodynamic parameters of reaction (1) involving radicals (XII) in various solvents at 20 °C.[166]

Solvent	10^7 k_1, l mol^{-1} s^{-1}	10^2 k_{-1}, s^{-1}	10^6 K, mol l^{-1}	$\Delta H_1^{\neq}$	ΔH_{-1}	ΔH^0	$-\Delta S_1^{\neq}$	$\Delta S_{-1}^{\neq}$	ΔS^0
Toluene	10.5	2	$1.9 \cdot 10^{-1}$	3.5	24.2	20.7	3.9	16.2	20.1
Chloroform	8	7	$9.1 \cdot 10^{-1}$	2.6	21.9	19.3	7.5	10.9	18.4
Acetic acid	3.75	11.5	3.1	2.3	21.0	18.7	9.7	9.0	19.1
Tetrachloroethane	3.6	16	4.5	2.0	19.9	17.9	10.2	6.7	17.1
DMF	7.5	45	6.0	1.0	18.0	17.0	12.6	2.0	14.7

Note. ΔH and ΔS are expressed in kcal mol^{-1} and cal mol^{-1} K^{-1}. The errors of the determinations are 10% in k_1, 20% in K, 30% in k_{-1}, ±0.5 kcal mol^{-1} in ΔH, and ±2 cal mol^{-1} K^{-1} in ΔS; see also Table 2.

The linear relation observed[166] between $\Delta H_1^{\neq}$ and $\Delta S_1^{\neq}$ is apparently a consequence of purely random experimental errors. Generally speaking, the range of variation of $\Delta H_1^{\neq}$ for reaction (1) is very insignificant compared with the errors in the determination of this quantity; as a result, it is difficult to demonstrate the existence of an isokinetic relation for reaction (1). A V-shaped relation between k_1 and the parameter E_T has been observed[166] for radical (XVI) containing phenyl substituents, as for phenylphenoxy-radicals[1,25].

The constant K for radical (XLV) increases by a factor of 430 at 30 °C on transfer from benzene to isopropyl alcohol (Table 4).[110] This is caused by the specific solvation of the radical in isopropyl alcohol with formation of hydrogen bonds. The heats of formation of the benzopinacol dimer in benzene and isopropyl alcohol are approximately the same. According to estimates, the solvation of the above radical in isopropyl alcohol is more exothermic by 3–7 kcal mol^{-1} than in benzene[110]. The quantity $\Delta(\Delta S)$ for solvation is 10.8 cal mol^{-1} K^{-1} on transfer from benzene to toluene. Such values are usually observed on formation of a hydrogen bond with oxygen-containing acceptors[110].

3. Other Radicals

The thermodynamic parameters $\Delta H°$ and $\Delta S°$ for the dimerisation of the nitroxy-radicals (LXIV) and (LXVI) (Table 5) depend on the solvent. In isopentane, which is a poor solvent for nitroxy-radicals and their dimers, the thermodynamic parameters for the above two radicals are similar (Table 5). The radicals are more polar than the dimers and, on transfer from isopentane to polar solvents such as $CFCl_3$ and CF_2Cl_2, $\Delta H°$ and $\Delta S°$ diminish[122,123] (Table 5).

The solvent can solvate the radicals and dimers to different extents as a consequence of the difference in the steric hindrance around the active centre in the radical and the dimer. In the paramagnetic dimers of aromatic sodium ketyls two sodium ions are surrounded by two large ketyl anions and the solvation is therefore hindered[144]. In the monomer more space is available for solvent molecules and the radical pair is solvated to a greater extent than the dimer. The difference between the degrees of order in the solvent for the monomer and dimer is reflected in the negative values of $\Delta S°$ (−29 – −37 cal mol^{-1} K^{-1}).[144]

The thermodynamic parameters of equilibrium (1) involving the tetracyanoquinodimethane radical-anion (LXXX) in aqueous ethanol have been determined[128] and it has been established that $\Delta G°$ decreases with increase of the ethanol content, while $\Delta H°$ and $\Delta S°$ pass through a maximum. These relations have been explained on the basis of the proposed model of solvation: water molecules are more strongly attracted to the radical-anion dimer than ethanol molecules. The Li^+, Na^+, and K^+ counterions do not have an appreciable influence on the dimer–monomer equilibrium and are apparently not present in the vicinity of the anions.

---o0o---

Thus the reversible recombination of radicals in solution with formation of dimers is a fairly general phenomenon, characteristic of organic radicals of different classes, such as the arylmethyl, phenoxy-, alkylperoxy-, iminoxy-, nitroxy-, diarylaminyl, and many others. Numerous radicals present in solution at an appreciable concentration are not stable monomers and are involved in a dynamic equilibrium with the corresponding diamagnetic dimers. The solutions of these radicals are usually coloured and give rise to an EPR signal. The solutions do not obey the Beer–Lambert–Bouguer law. Heating or irradiation of the solutions increase the concentration of radicals.

In the study of the magnetic susceptibilities of solutions of organic free radicals, a deviation from the Curie law, caused by the equilibrium between the paramagnetic monomers and the diamagnetic dimers, is frequently observed.

Together with the reversible recombination reaction, irreversible radical disproportionation or dimer decomposition reactions can take place in solution. The decrease of the steady-state concentration of radicals frequently obeys a kinetic first-order law under these conditions. The dimers undergoing reversible decomposition have found a practical application as photochromic and thermochromic compounds[171] and also as effective inhibitors[113].

REFERENCES

1. I.V.Khudyakov, P.P.Levin, V.A.Kuzmin, and C.R.H.I.de Jonge, Int.J.Chem.Kinetics, **11**, 357 (1979).
2. V.A.Kuzmin, I.V.Khudyakov, P.P.Levin, A.S.Tatikolov, and N.M.Emanuel, "Proceedings of the IInd Conference on the Degradation and Stabilisation of Polymers, Arnhem,1976", p.123.
3. I.V.Khudyakov, P.P.Levin, V.A.Kuz'min, and C.R.H.I.de Jonge, Izv.Akad.Nauk SSSR, Ser.Khim., 1303 (1977).
4. V.A.Kuzmin, I.V.Khudyakov, P.P.Levin, N.M.Emanuel, C.R.H.I.de Jonge, H.J.Hageman, M.E.F.Biemond, F.P.B.van der Maeden, and W.J.Mijs, J.Chem.Soc., Perkin Trans.II, 1540 (1979).
5. I.V.Khudyakov, A.I.Yasmenko, and V.A.Kuzmin, Int.J.Chem.Kinetics, **11**, 621 (1979).
6. I.V.Khudyakov, A.I.Yasmenko, A.P.Khardin, A.I.Prokof'ev, and V.A.Kuz'min, Izv.Akad.Nauk SSSR, Ser.Khim., 1499 (1978).
7. I.V.Khudyakov, C.R.H.I.de Jonge, P.P.Levin, and V.A.Kuz'min, Izv.Akad.Nauk SSSR, Ser.Khim., 1492 (1978).

8. D.J.Williams and R.Kreilick, J.Amer.Chem.Soc., **89**, 3408 (1967).
9. D.J.Williams and R.Kreilick, J.Amer.Chem.Soc., **90**, 2775 (1968).
10. J.L.Brokenshire, J.R.Roberts, and K.U.Ingold, J.Amer.Chem.Soc., **94**, 7040 (1972).
11. D.C.Nonhebel and J.C.Walton, "Free-Radical Chemistry: Structure and Mechanism" (Translated into Russian), Izd.Mir, Moscow, 1977.
12. A.L.Buchachenko, R.Z.Sagdeev, and K.M.Salikhov, "Magnitnye i Spinovye Effekty v Khimicheskikh Reaktsiyakh" (Magnetic and Spin Effects in Chemical Reactions), Izd.Nauka, Novosibirsk, 1978.
13. H.J.V.Tyrrell, "Diffusion and Heat Flow in Liquids", Butterworth, London, 1961, Chapter 6.
14. P.P.Levin, I.V.Khudyakov, and V.A.Kuzmin, Int.J. Chem.Kinetics, **12**, 147 (1980).
15. R.M.Noyes, "Progress in Reaction Kinetics", Pergamon Press, London, 1961, Vol.1, p.129.
16. A.I.Burshtein, I.V Khudyakov, and P.P.Levin, Izv. Akad.Nauk SSSR, Ser.Khim., 261 (1980).
17. A.I.Burshtein and B.I.Yakobson, Chem.Phys., **28**, 415 (1978).
18. K.M.Salikhov, Teor.Eksper.Khim., **13**, 731 (1977).
19. K.Sŏlc and W.H.Stockmayer, Int.J.Chem.Kinetics, **5**, 733 (1973).
20. K.S.Schmitz and J.M.Schurr, J.Phys.Chem., **76**, 534 (1972).
21. J.M.Schurr and K.S.Schmitz, J.Phys.Chem., 80, 1934 (1976).
22. J.M.Schurr, Biophys.J., **10**, 700 (1970).
23. O.G.Berg, Chem.Phys., **31**, 47 (1978).
24. S.F.Burlatsky, P.P.Levin, I.V.Khudyakov, V.A.Kuzmin, and A.A.Ovchinnikov, Chem.Phys.Letters, **66**, 565 (1979).
25. P.P.Levin, I.V.Khudyakov, and V.A.Kuz'min, Izv. Akad.Nauk SSSR, Ser.Khim., 255 (1980).
26. I.V.Khudyakov, T.A.Kokrashvili, P.P.Levin, and V.A.Kuz'min, Izv.Akad.Nauk SSSR, Ser.Khim., 2364 (1977).
27. P.P.Levin, I.V.Khudyakov, I.A.Khardina, and L.N.Rygalov, Izv.Akad.Nauk SSSR, Ser.Khim., 2605 (1977).
28. L.R.Mahoney and M.A.DaRooge, J.Amer.Chem.Soc., **97**, 4722 (1975).
29. I.V.Khudyakov, A.I.Yasmenko, V.A.Kuz'min, P.P.Levin, and A.P.Khardin, Neftekhimiya, **18**, 716 (1978).
30. E.R.Altwicker, Chem.Rev., **67**, 475 (1967).
31. I.V.Khudyakov and V.A.Kuz'min, Uspekhi Khim., **44**, 1748 (1975) [Russ.Chem.Rev., No.10 (1975)].
32. R.Samson and J.M.Deutsch, J.Chem.Phys., **68**, 285 (1978).
33. V.D.Pokhodenko, "Fenoksil'nye Radikaly" (Phenoxy-Radicals), Izd.Naukova Dumka, Kiev, 1969.
34. F.S.Sarvarov and K.M.Salikhov, React.Kinet.Catal. Letters, **4**, 33 (1976).
35. A.Z.Rieker, Z.Naturforsch., **21b**, 647 (1966).
36. T.Matsuura, A.Nishinaga, and H.J.Cahnmann, J.Org. Chem., **27**, 3620 (1962).
37. E.Müller, A.Rieker, R.Mayer, and K.Scheffler, Annalen, **645**, 36 (1961).
38. E.Müller, H.B.Stegmann, and K.Scheffler, Annalen, **645**, 79 (1961).
39. K.Scheffler, Z.Elektrochem., **65**, 439 (1961).
40. K.Scheffler and H.B.Stegmann, Z.Elektrochem., **67**, 864 (1963).
41. H.B.Stegmann, K.Scheffler, and E.Müller, Annalen, **677**, 59 (1964).
42. E.Müller, H.B.Stegmann, and K.Scheffler, Annalen, **657**, 5 (1962).
43. I.V.Khudyakov, P.P.Levin, C.R.H.I.de Jonge, and K.-M.Beckman, Izv.Akad.Nauk SSSR, Ser.Khim., 1655 (1977).
44. K.Dimroth, Angew.Chem., **72**, 714 (1960).
45. K.Dimroth, F.Kalk, and G.Neubauer, Chem.Ber., **90**, 2058 (1957).
46. K.Dimroth, F.Kalk, R.Sell, and K.Schlömer, Annalen, **624**, 51 (1959).
47. K.Dimroth and G.Neubauer, Angew.Chem., **69**, 65 (1957).
48. E.Müller, A.Rieker, and W.Beckert, Z.Naturforsch., **17b**, 367 (1962).
49. R.Read, J.Amer.Chem.Soc., **80**, 219 (1958).
50. A.Rieker, N.Zeller, K.Schurr, and E.Müller, Annalen, **697**, 1 (1966).
51. E.Müller, K.Schurr, and K.Scheffler, Annalen, **627**, 132 (1959).
52. A.I.Burshtein, Uspekhi Khim., **47**, 212 (1978) [Russ. Chem.Rev., No.2 (1978)].
53. D.Griller, L.R.C.Barclay, and K.U.Ingold, J.Amer. Chem.Soc., **97**, 6151 (1975).
54. E.Müller, A.Schick, and K.Scheffler, Chem.Ber., **92**, 474 (1959).
55. K.Scheffler, Z.anal.Chem., **181**, 456 (1960).
56. E.Müller, A.Schick, R.Mayer, and K.Scheffler, Chem. Ber., **93**, 2649 (1960).
57. E.Müller, H.Eggensperger, B.Teissier, and K.Scheffler, Z.Naturforsch., **18b**, 984 (1963).
58. E.Müller, H.Eggensperger, B.Teissier, and K.Scheffler, Z.Naturforsch., **19b**, 1079 (1964).
59. E.Müller, K.Ley, and G.Schlechter, Chem.Ber., **90**, 1530 (1957).
60. H.D.Becker, J.Org.Chem., **29**, 3068 (1964).
61. H.J.Cahnmann and T.Matsuura, J.Amer.Chem.Soc., **82**, 2050 (1960).
62. T.Matsuura and A.Nishinaga, J.Org.Chem., **27**, 3072 (1962).
63. E.Müller, K.Ley, and G.Schlechter, Angew.Chem., **69**, 204 (1957).
64. A.I.Burshtein and B.I.Yakobson, Khim.Vys.Energii, **14**, 291 (1980).
65. E.Müller, A.Riecker, and A.Schick, Annalen, **673**, 40 (1964).
66. A.L.Buchachenko, M.B.Neiman, O.R.Sukhanova, and Yu.G.Mamedova, Zhur.Fiz.Khim., **37**, 113 (1963) [Russ. J.Phys.Chem., No.1 (1963)].
67. M.A.DaRooge and L.R.Mahoney, J.Org.Chem., **32**, 1 (1967).
68. L.R.Mahoney, F.C.Ferris, and M.A.DaRooge, J.Amer. Chem.Soc., **91**, 3883 (1969).
69. L.R.Mahoney, J.Amer.Chem.Soc., **89**, 1895 (1967).
70. L.R.Mahoney and M.A.DaRooge, J.Amer.Chem.Soc., **89**, 5619 (1967).
71. L.R.Mahoney and M.A.DaRooge, J.Amer.Chem.Soc., **92**, 890 (1970).
72. A.I.Prokof'ev, N.A.Malysheva, N.N.Bubnov, S.P.Solodovnikov, and M.I.Kabachnik, Izv.Akad.Nauk SSSR, Ser.Khim., 511 (1976).
73. S.A.Weiner and L.R.Mahoney, J.Amer.Chem.Soc., **94**, 5029 (1972).
74. R.D.Parnell and K.E.Russell, J.Chem.Soc., Perkin Trans.II, 161 (1974).
75. I.V.Khudyakov, C.R.H.I.de Jonge, P.P.Levin, and V.A.Kuzmin, "Proceedings of the IIIrd Conference on

the Degradation and Stabilisation of Polymers, Moscow, 1977", p.104.
76. A.I.Brodskii, V.D.Pokhodenko, V.A.Khizhnyi, and N.N.Kalibabchuk, Dokl.Akad.Nauk SSSR, **169**, 339 (1966).
77. V.A.Khizhnyi, I.A.Spirina, Ya.A.Gurvich, E.L.Styskin, I.N.Gorodetskaya, and V.D.Pokhodenko, Zhur. Obshch.Khim., **11**, 2079 (1975).
78. V.A.Khizhnyi, I.A.Spirina, Ya.A.Gurvich, O.F.Starikova, I.D.Pletneva, I.N.Gorodetskaya, and V.D.Pokhodenko, Zhur.Obshch.Khim., **11**, 2074 (1975).
79. B.L.Tumanskii, S.P.Solodovnikov, A.I.Prokof'ev, N.N.Bubnov, and M.I.Kabachnik, Izv.Akad.Nauk SSSR, Ser.Khim., 1309 (1977).
80. I.V.Khudyakov, S.F.Burlatskii, B.L.Tumanskii, and V.A.Kuz'min, Izv.Akad.Nauk SSSR, Ser.Khim., 2153 (1978).
81. L.R.Mahoney and S.A.Weiner, J.Amer.Chem.Soc., **94**, 585 (1972).
82. L.R.Mahoney and S.A.Weiner, J.Amer.Chem.Soc., **94**, 1412 (1972).
83. A.J.Colussi, F.Zabel, and S.W.Benson, Int.J.Chem. Kinetics, **9**, 161 (1977).
84. H.D.Becker, J.Org.Chem., **30**, 982 (1965).
85. K.Dimroth and A.Berndt, Angew.Chem., **76**, 434 (1964).
86. K.Dimroth, Chem.Ber., **101**, 2519 (1968).
87. C.R.H.I.de Jonge, H.J.Hageman, W.G.V.Huysmans, and W.J.Mijs, J.Chem.Soc., Perkin Trans.II, 1276 (1973).
88. E.Müller, H.Eggensperger, and K.Scheffler, Annalen, **658**, 103 (1962).
89. C.R.H.I.de Jonge, H.M.van Dort, W.G.B.Huysmans, R.W.M.van Berkel, M.A.P.J.Heemskerk, and W.J.Mijs, "Proceedings of the Ist Conference on the Degradation and Stabilisation of Polymers, Moscow, 1975", p.17.
90. P.P.Levin, Candidate's Thesis, Institute of Chemical Physics, USSR Academy of Sciences, Moscow, 1979.
91. A.R.Forrester, J.M.Hay, and R.H.Thomson, "Organic Chemistry of Stable Free Radicals", Acad.Press, London, 1968.
92. V.D.Sholle and E.G.Rozantsev, Uspekhi Khim., **12**, 2176 (1973) [Russ.Chem.Rev., No.12 (1973)].
93. M.Dewar and R.Dogherty, "Theory of the Perturbations of Molecular Orbitals in Organic Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1977, pp.183, 213.
94. D.V.Ioffe and L.S.Efros, Reaktsionnaya Sposobnost' Organicheskikh Soedinenii, Tartu, **9**, 1165 (1972).
95. H.Lankamp, W.T.Nauta, and C.MacLean, Tetrahedron Letters, 249 (1968).
96. F.S.D'yachkovskii, N.N.Bubnov, and A.E.Shilov, Dokl.Akad.Nauk SSSR, **122**, 629 (1958).
97. K.H.Fleurke and W.T.Nauta, Rec.Trav.chim., **85**, 86 (1966).
98. M.Gomberg, Ber., **33**, 3150 (1900).
99. K.U.Ingold, Accounts Chem.Res., **2**, 1 (1969).
100. P.S.Nangia and S.W.Benson, Int.J.Chem.Kinetics, **12**, 29, 43 (1980).
101. V.A.Rodionov and E.G.Rozantsev, "Dolgozhivushchie Radikaly" (Long-lived Radicals), Izd.Nauka, Moscow, 1972.
102. C.S.Marvel, M.B.Mueller, C.M.Himeli, and J.F.Kaplan, J.Amer.Chem.Soc., **61**, 2771 (1939).
103. C.S.Marvel, J.Whitson, and H.W.Johnston, J.Amer. Chem.Soc., **66**, 415 (1944).
104. W.Theilacker and M.Eward, Annalen, **594**, 214 (1955).
105. W.Theilacker and F.Koch, Angew.Chem.Int.Ed., **5**, 246 (1966).
106. K.H.Fleurke and W.T.Nauta, Rec.Trav.chim., **84**, 1059 (1965).
107. H.A.P.de Jongh, C.R.H.I.de Jonge, H.J.M.Sinnge, W.J.de Klein, W.G.B.Huysmans, and W.J.Mijs, J.Org. Chem., **37**, 1960 (1972).
108. S.W.Benson, "Thermochemical Kinetics, Wiley, New York–London, 1976, Chapter 3.
109. K.U.Ingold, in "Free Radicals", Vol.1 (Edited by J.K.Kochi), Wiley, 1973, p.37.
110. S.A.Weiner, J.Amer.Chem.Soc., **93**, 6978 (1971).
111. K.Watanabe, J.Yamauchi, H.Ohya-Nishiguchi, and Y.Deguchi, Bull.Chem.Soc.Japan, **47**, 274 (1974).
112. K.-H.Eichin, K.J.McCullough, H.-D.Beckhaus, and C.Rüchardt, Angew.Chem.Int.Ed., **17**, 934 (1978).
113. L.M.Pisarenko, Candidate's Thesis, Institute of Chemical Physics, USSR Academy of Sciences, Moscow, 1975.
114. I.T.Poluektov, V.V.Moiseev, I.F.Gainullin, and A.I.Yasmenko, Zhur.Org.Khim., **11**, 1300 (1975).
115. P.D.Bartlett and G.Guaraldi, J.Amer.Chem.Soc., **89**, 4799 (1967).
116. J.A.Howard, Adv.Free-Radical Chem., 4, 49 (1972).
117. K.Adamic, J.A.Howard, and K.U.Ingold, Canad.J. Chem., **47**, 3803 (1969).
118. J.E.Bennett, D.M.Brown, and B.Mile, Trans.Faraday Soc., **66**, 397 (1970).
119. G.A.Russell, J.Amer.Chem.Soc., **79**, 3871 (1957).
120. T.Eriksen, A.Henglein, and K.Stockhausen, J.Chem. Soc., Faraday Trans.I, 337 (1973).
121. C.B.Watts and K.U.Ingold, J.Amer.Chem.Soc., **94**, 2528 (1972).
122. G.D.Mendenhall and K.U.Ingold, J.Amer.Chem.Soc., **95**, 6390 (1973).
123. D.F.Bowman, T.Gillan, and K.U.Ingold, J.Amer.Chem. Soc., **93**, 6555 (1971).
124. W.D.Blackley and R.R.Reinhard, J.Amer.Chem.Soc., **87**, 802 (1965).
125. R.Ramasseul, A.Rassat, G.Rio, and M.-J.Scholl, Bull. Soc.chim.France, 215 (1971).
126. K.Adamic, D.F.Bowman, T.Gillan, and K.U.Ingold, J.Amer.Chem.Soc., **93**, 902 (1971).
127. L.Lunazzi, G.Placucci, and N.Ronchi, J.Chem.Soc., Perkin Trans.II, 1132 (1977).
129. A.G.Evans, J.C.Evans, and M.W.Backer, J.Chem.Soc., Perkin Trans.II, 1310 (1975).
130. R.H.Boyd and W.D.Phillips, J.Chem.Phys., **43**, 2927 (1965).
131. K.Uemura, S.Nakayama, Y.Seo, K.Suzuki, and Y.Ooshika, Bull.Chem.Soc.Japan, **39**, 1348 (1966).
132. N.Sakai, I.Shirotani, and S.Minomura, Bull.Chem.Soc. Japan, **44**, 675 (1971).
133. T.Yamazaki and K.Kimura, Bull.Chem.Soc.Japan, **44**, 298 (1971).
134. K.Kimura, H.Yamade, and H.Tsubomura, J.Chem.Phys., **48**, 440 (1968).
135. L.Michaelis and M.P.Schubert, Chem.Rev., **22**, 437 (1938).
136. B.J.McClelland, Chem.Rev., **64**, 301 (1964).
137. T.L.Staples and M.Swarz, J.Amer.Chem.Soc., **92**, 5022 (1970).
138. J.H.Furhop, P.Wassar, D.Reisner, and D.Mauzerall, J.Amer.Chem.Soc., **94**, 7996 (1972).
139. A.G.Evans, J.C.Evans, and M.W.Baker, J.Chem.Soc., Perkin Trans.II, 1787 (1977).
140. A.G.Evans, J.C.Evans, and M.W.Baker, J.Amer.Chem. Soc., **99**, 5882 (1977).
141. M.Itoh and S.Nagakura, J.Amer.Chem.Soc., **89**, 3959 (1967).

142. E.M.Kosower and J.L.Cotter, J.Amer.Chem.Soc., **86**, 5524 (1964).
143. M.J.Blandmer, M.F.Fox, M.C.R.Symons, and G.S.P.Verma, Chem.Comm., 844 (1966).
144. N.Hirota and S.I.Weissman, J.Amer.Chem.Soc., **86**, 2538 (1964).
145. A.Yamagishi, Y.Iida, and M.Fujimoto, Bull.Chem.Soc. Japan, **45**, 3482 (1972).
146. K.H.Hausser and J.N.Murrell, J.Chem.Phys., **27**, 500 (1957).
147. A.Yamagishi, F.Watanabe, and T.Masui, Chem.Comm., 273 (1977).
148. P.P.Levin, I.V.Khudyakov, and V.A.Kuz'min, Dokl. Akad.Nauk SSSR, **246**, 144 (1979).
149. E.M.Kosower, A.Teurstein, and A.J.Swallow, J.Amer. Chem.Soc., **95**, 6127 (1973).
150. D.Forrest and K.U.Ingold, J.Amer.Chem.Soc., **100**, 3868 (1978).
151. M.Itoh and E.M.Kosower, J.Amer.Chem.Soc., **90**, 1843 (1968).
152. J.C.Scaino and K.U.Ingold, J.Amer.Chem.Soc., **99**, 2079 (1977).
153. B.Maillard and K.U.Ingold, J.Amer.Chem.Soc., **98**, 520 (1976).
154. S.F.Nelson and R.T.Landis, J.Amer.Chem.Soc., **95**. 8707 (1973).
155. F.A.Neugebauer, H.Fischer, S.Bamberger, and H.O.Smith, Chem.Ber., **105**, 2694 (1972).
156. V.B.Panov, M.V.Nekhoroshev, and O.Yu.Okhlobystin, Dokl.Akad.Nauk SSSR, **243**, 372 (1978).
157. N.M.Emanuel', G.E.Zaikov, and Z.K.Maizus, "Rol' Sredy v Radikal'no-Tsepnykh Reaktsiyakh Okisleniya Organicheskikh Soedinenii" (The Role of the Medium in Radical-Chain Oxidation Reactions of Organic Compounds), Izd.Nauka, Moscow, 1973.
158. I.V.Khudyakov, C.R.H.I.de Jonge, P.P.Levin, and V.A.Kuz'min, Izv.Akad.Nauk SSSR, Ser.Khim., 444 (1977).
159. M.L.Khidekel', G.A.Razuvaev, E.N.Novikova, L.A.Smirnova, and A.P.Khrushch, Izv.Akad.Nauk SSSR, Ser.Khim., 1530 (1964).
160. V.A.Kuz'min, I.V.Khudyakov, and N.M.Emanuel', Dokl.Akad.Nauk SSSR, **206**, 1154 (1972).
161. I.V.Khudyakov and V.A.Kuz'min, Khim.Vys.Energii, **8**, 171 (1974).
162. K.Ziegler, P.Orth, and K.Weber, Annalen, **504**, 131 (1933).
163. K.Ziegler and L.Ewald, Annalen, **473**, 163 (1929).
164. K.Ziegler, Annalen, **504**, 130 (1933).
165. J.E.Leffler, Science, **117**, 340 (1953).
166. A.I.Yasmenko, I.V.Khudyakov, and V.A.Kuz'min, Izv. Akad.Nauk SSSR, Ser.Khim., 529 (1980).
167. D.Pilo Veloso and A.Rassat, J.Chem.Research (**S**), 106, 186 (1979).
168. F.A.Neugebauer, "Organic N-Centered Radicals and Nitroxide Radicals", Springer Verlag, 1979.
169. E.G.Rozantsev and V.D.Sholle, "Organicheskaya Khimiya Svobodnykh Radikalov" (The Organic Chemistry of Free Radicals), Izd.Khimiya, Moscow, 1979.
170. F.P.A.Zweegers and C.A.G.O.Varma, J.Phys.Chem., **83**, 1821 (1979).
171. G.Eigenmann, "Photochromism. Techniques of Chemistry", Vol.3 (Edited by G.H.Brown), Wiley, 1971, p.433.
172. I.T.Poluektov, V.V.Moiseev, and I.F.Gaimulin, Dokl. Akad.Nauk SSSR, **218**, 123 (1974).
173. M.Mohammad, A.Y.Khan, M.Iqbal, R.Iqbal, and M.Razzaq, J.Amer.Chem.Soc., **100**, 7658 (1978).
174. E.Kosower, in "Free Radicals in Biology", Vol.2 (Edited by W.Pryor) (Translated into Russian; translation edited by N.M.Emanuel'), Izd.Mir, Moscow, 1979, p.7.
175. K.Ziegler, A.Seib, K.Knoevenagel, P.Herte, and F.Andreas, Annalen, **551**, 150 (1942).
176. M.R.Skurko, V.A.Khiznyi, V.D.Pokhodenko, S.S.Zlotskii, P.S.Belov, D.L.Rakhmankulov, U.B.Imashev, and R.A.Karakhanov, Dokl.Akad.Nauk SSSR, **248**, 376 (1979).
177. A.B.Jaffe and R.W.Kreilick, Chem.Phys.Letters, 32, 572 (1975).
178. W.C.Danen and F.A.Neugebauer, Angew.Chem.Int.Ed., **14**, 783 (1975).
179. F.A.Neugebauer and P.H.H.Fischer, Chem.Ber., 98, 844 (1965).
180. S.F.Nelson, in "Free Radicals", Vol.2 (Edited by J.K.Kochi), Wiley, 1973, p.527.
181. F.R.Hewgill and G.B.Howie, Austral.J.Chem., **31**, 1061 (1978).

Institute of Chemical Physics,
USSR Academy of Sciences,
Moscow

Translated from *Uspekhi Khimii*, **49**, 2032-2063 (1980) U.D.C. 541.49 + 535.34:548.735

The Spectra and Structure of Transition Metal Complexes with Tetradentate Macrocyclic Ligands

K.B.Yatsimirskii and Ya.D.Lampeka

A systematic account is given of data on the structures and spectroscopic properties of transition metal complexes with synthetic tetradentate macrocyclic ligands. The principal types of the structures of such complexes are specified. On the basis of the analysis of electronic absorption spectra, a conclusion is reached concerning the mutual influence of the ligands, which is expressed by a consistent variation of the spectrochemical parameters.
The bibliography includes 191 references.

CONTENTS

I.	Introduction	1003
II.	The structure of complexes with macrocyclic ligands	1003
III.	Absorption spectra of iron complexes	1008
IV.	Absorption spectra of cobalt complexes	1010
V.	Spectra of nickel(II) complexes	1014
VI.	Spectra of other transition metal complexes	1015
VII.	The mutual influence of the ligands in macrocyclic complexes	1016

I. INTRODUCTION

Macroheterocyclic compounds represent the structural elements of many important natural metal complexes such as haem, vitamin B_{12}, chlorophyll, and others. The chemistry of these compounds has now been thoroughly investigated[1] and many complexes of porphyrins and corrins have been synthesised *in vitro*[2,3]. Only high-intensity bands, associated with intraligand transitions and (or) charge-transfer bands, which mask the $d-d$ transition bands, have been observed in the electronic spectra of compounds of this type. The problems of the spectroscopy of porphyrin complexes have been described in detail in a monograph[4].

The chemistry of synthetic ligands, i.e. ligands which are not encountered in living nature and which constitute models of natural macrocycles, has developed vigorously during the last decade. There have been a number of reviews devoted to various aspects of the chemistry of metal complexes with ligands of this type[5-8], but the problems of the spectroscopy of these compounds have been considered only briefly in Busch's review[5] published in 1967.

This review deals with the crystal structures and electronic absorption spectra of complexes formed by metal ions having unfilled d shells with synthetic tetradentate macrocyclic ligands containing either donor atoms of one kind (nitrogen or sulphur) or donor atoms of different kinds (nitrogen, sulphur, and oxygen). The compounds under consideration include also complexes with ligands having a large number of donor atoms, among which only four are involved in coordination. Attention is concentrated on the absorption spectra associated with the excitation of the d electrons of the metal ions, which precludes the inclusion of porphyrin and corrin complexes in this review. The review covers the literature up to 1977 inclusive.

The ligands are designated using the namenclature proposed by Busch and coworkers[9,10], which we believe to be most suitable, despite some ambiguity.

Macrocyclic ligands, whose complexes are considered in this review, and their names are given in Fig.1. Other most frequently encountered names of individual ligands are given in brackets.

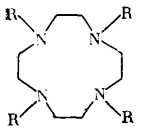
II. THE STRUCTURE OF COMPLEXES WITH MACROCYCLIC LIGANDS

In the majority of the complexes dealt with in this review the donor atoms of the macrocyclic ligand occupy the equatorial plane in the coordination sphere of the metal. This type of coordination enables the ligand to assume the most convenient conformation to which corresponds the minimum strain in the macroring. However, in such coordination another source of strain in the macroring is generated. The maximum overlap of the metal orbitals with the occupied donor orbitals of the ligand is observed when the latter are directed along the diagonals of the tetragon formed by the donor atoms. In the ligands considered below the size of the macroring prevents the ligands from assuming such a conformation and the incorporation of the metal ion in the plane of the donor atoms therefore leads to the occurrence of strain in the donor atom–carbon atom bonds.

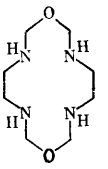
The "ideal" metal–donor atom distances have been calculated as a function of the size of the macroring[11] by the ligand strain minimisation method. It follows from the results that a 14-membered macrocyclic ligand will experience the minimum strain on coordination to the cobalt(III) ion and that in the case of nickel(II), high-spin complexes a 15-membered macrocycle is most suitable. However, this does not rule out the possibility of the formation of planar complexes of these ions with ligands having larger or smaller macrorings. It has been suggested[12] that nickel can form such complexes even with 12-membered macrorings, but these complexes are in all probability of the low-spin type.

The picture becomes somewhat more complex when the macrocyclic ligand has different donor atoms or donor atoms of the same kind but of different chemical nature (for example amino- and imino-nitrogen atoms). In this case the metal–donor atom bond length will depend on the type of donor atom. In complexes of ligands of this type the metal ion may not be located in the centre of the plane of the donor atoms.

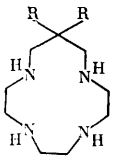
The types of the fundamental structures discovered in transition metal complexes with macrocyclic ligands (henceforth these complexes will be referred to, for brevity, as



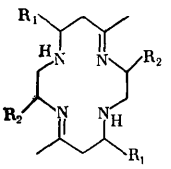
R = H; [12] aneN4(cyclen)
R = $CH_2C_6H_5$; N - $(CH_2C_6H_5)_4$[12] aneN4(tricyclen)



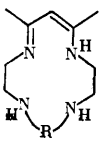
[14] aneN4O2



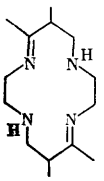
R = H; [13] aneN4
R = CH_3; Me_2[13] aneN4



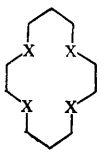
$R_1 = R_2 = H$; Me_2[14] 4, 11 dieneN4
$R_1 = C_6H_5$; $R_2 = H$; Me_2Ph_2[14] dieneN4
$R_1 = CH_3$; $R_2 = H$; 5, 7, 12, 14 Me_4[14] dieneN4
$R_1 = H$; $R_2 = CH_3$; 3, 5, 10, 12 Me_4[14] dieneN4
$R_1 = (CH_3)_2$; $R_2 = H$; Me_6[14] dieneN4 (1,7CT)
$R_1 = (CH_3)_2$; $R_2 = CH_3$; Me_8[14] dieneN4



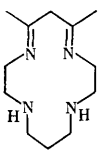
R = —$(CH_2)_2$—; Me_2[13] dieneN4
R = —$(CH_2)_3$—; Me_2[14] 5, 7 dieneN4



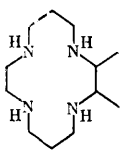
6, 7, 13, 14 Me_4[14] dieneN4



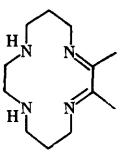
X = NH; [14] aneN4(cyclam)
X = NCH_3; N - Me_4[14]aneN4(TMC)
X = S; [14]aneS4



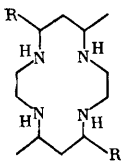
Me_2[14] 4,7 dieneN4



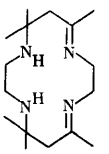
2, 3 Me_2[14] aneN4(DMC)



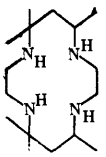
Me_2[14] 1,3 dieneN4(DIM)



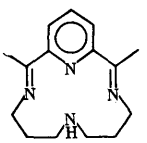
R = H; 5, 12 Me_2[14] aneN4
R = C_2H_5; Me_2Et_2[14] aneN4
R = $(CH_3)_2$; Me_6[14] aneN4(tet a/b)



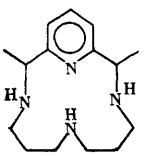
Me_6[14] 4,14 dieneN4(1.4CT)



5, 7, 7, 12, 12, 14 Me_6[14] aneN4(tet c/d)

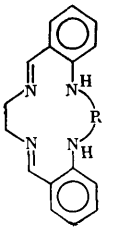


Me_2py[14] dieneN4(CR)



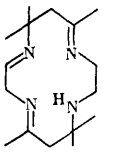
Me_2py[14] aneN4(CRH)

Figure 1. The macrocyclic ligands (the numerical indication of the positions of the substituents or double bonds is used only in the presence of several isomers).

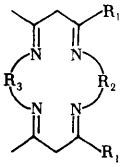


R = —$(CH_2)_2$—; Bz_2[14] dieneN$_4$

R =  ; Bz_2Pyr[14] dieneN$_4$



Me_6[14] trieneN$_4$

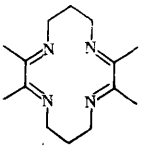


R_1 = H; R_2 = R_3 = —$(CH_2)_2$—; Me_2[14] tetraeneN$_4$

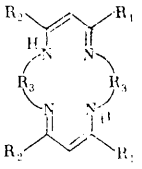
R_1 = H; R_2 = —$(CH_2)_2$—; R_3 = —$(CH_2)_3$—; Me_2[15] tetraeneN$_4$

R_1 = H; R_2 = R_3 = —$(CH_2)_3$—; Me_2[16] tetraeneN$_4$

R_1 = CH_3; R_2 = R_3 = —$(CH_2)_3$—; Me_4[14] 4, 7, 11, 14 tetraeneN$_4$



Me_4[14] tetraeneN$_4$(TIM)

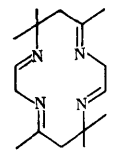


R_1 = R_2 = CH_3; R_3 = —$(CH_2)_2$—; Me_4[14]4, 6, 11, 13 tetraeneN$_4$

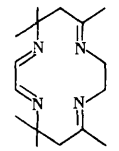
R_1 = R_2 = H; R_3 = —C_6H_4—; Bz_2[14] tetraeneN$_4$

R_1 = H; R_2 = CH_3; R_3 = —C_6H_4—; Me_2Bz_2[14] tetraeneN$_4$

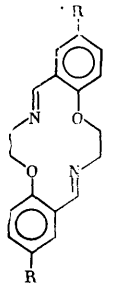
R_1 = R_2 = CH_3; R_3 = —C_6H_4—; Me_4Bz_2[14] tetraeneN$_4$



Me_6[14] tetraeneN$_4$

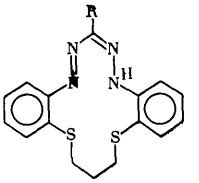


Me_6[14]4, 8, 10, 14 tetraeneN$_4$



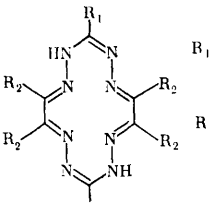
R = H; Bz_2[14] dieneN$_2$O$_2$

R = OCH_3; $(CH_3OC_6H_3)_2$[14] dieneN$_2$O$_2$

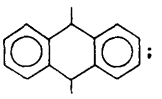


R = H; Bz_2[14] dieneN$_4$S$_2$

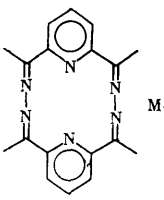
R = $(CH_2)_3OH$; $OprBz_2$[14] dieneN$_4$S$_2$



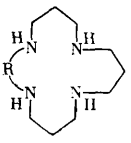
R_1 = H; R_2 = CH_3; Me_4[14] hexaeneN$_8$

R_1 = $(CH_2)_7CH_3$; R_2R_2 =  ;

Oct_2Antr_2[14] hexaeneN$_8$

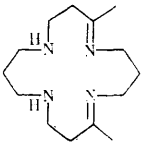


Me_4py_2[14] tetraeneN$_6$

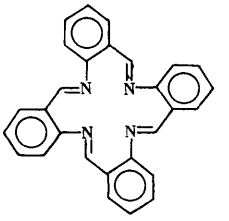


R = —$(CH_2)_2$—; [15] aneN$_4$

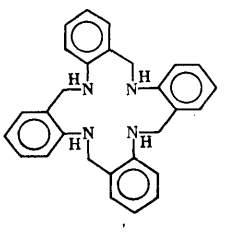
R = —$(CH_2)_3$—; [16] aneN$_4$



Me_3[16] dieneN$_4$



Bz_4[16] tetraeneN$_4$(TAAB)



Bz_4[16] aneN$_4$(TAABH$_8$)

Figure 1 (contd.)

macrocyclic complexes), are presented in Fig.2. Structure A is characteristic of the majority of nickel(II) complexes. Apart from nickel, complexes of this kind have been found only for copper(II)[13,14] and cobalt(II).[15] Structure B is obtained when the diameter of the plane of the macroring is too small for the given metal ion and the rigidity of the ligand prevents it from assuming another conformation more suitable for coordination. For complexes with a coordination number (C.N.) of 5 there is a possibility of structures of types C, D, and E. The structure of the complex in each specific case is determined by the characteristics of the structure of the macrocyclic ligand. Complexes having structure F are probably most common, but their X-ray diffraction analysis has been carried out in only a limited number of instances. Structure G is obtained when additional bidentate and monodentate ligands are involved in coordination apart from the macrocyclic ligands. In the last case[16] the structure is determined by the small size of the macroring, as a result of which the metal ion cannot be accommodated in the centre of the plane of the donor atoms.

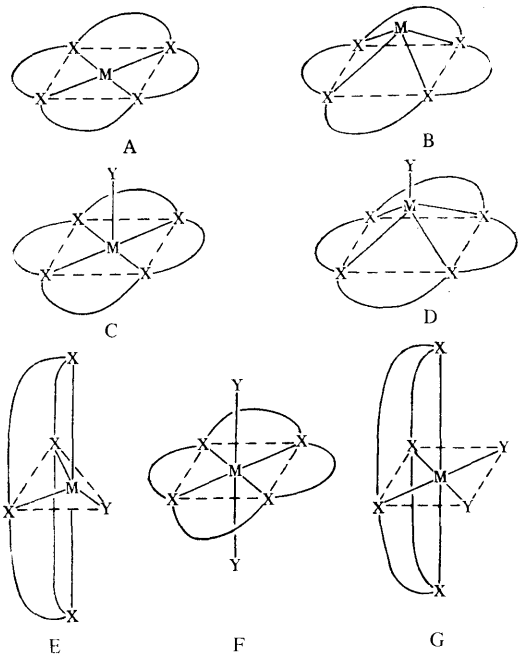


Figure 2. The types of structures of transition metal complexes with macrocyclic ligands (X = donor atoms of macrocyclic ligands; Y = donor atoms of additional ligands).

proton. However, the difference between the last two types of donor atoms is in many cases abolished owing to the conjugation in the six-membered chelate ring. If the complex formation reaction takes place with substitution of a proton at the nitrogen atom, then the imino- and ionic nitrogen atoms become equivalent. Subsequently they will be designated by N_{cov}. The equivalence of these two types of donor atoms in complexes of the above type has been confirmed by X-ray diffraction data (Table 1) and X-ray electronic spectroscopic data[37]. An analogous phenomenon has been observed also in porphyrin and phthalocyanine complexes[38,39]. In all probability the structures of such complexes are represented more correctly by formula I rather than II [in relation to compound No.18 (Table 1)].

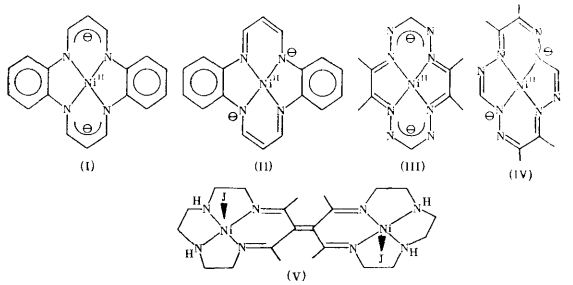


Table 1. The nickel–donor atom distances (in Å) in square planar complexes.

No.	Compound	Ni–N_{am}	Ni–N_{im}	Ni–N_{cov}	Ni–other atoms*	Refs.
1	Ni(Me$_2$[13]dieneN$_4$)ClO$_4$	1.88	—	1.83	—	12
2	Ni(Me$_2$[13]aneN$_4$)(ClO$_4$)$_2$	1.87	—	—	—	17
3	Ni(5,12Me$_2$[14]aneN$_4$)(ClO$_4$)$_2$	1.93	—	—	—	18
4	Ni(Me$_2$Et$_2$[14]aneN$_4$)(ClO$_4$)$_2$	1.98	—	—	—	19
5	Ni(Me$_6$[14]aneN$_4$)(ClO$_4$)$_2$	1.93	—	—	—	20
6	Ni(Me$_2$py[14]aneN$_4$)(ClO$_4$)$_2$	1.88	—	—	1.80 (N_{py})	21
7	Ni(5,7,12,14Me$_4$[14]dieneN$_4$)(ClO$_4$)$_2$	1.93	1.88	—	—	22,23
8	Ni(3,5,10,12Me$_4$[14]dieneN$_4$)(ClO$_4$)$_2$	1.94	1.91	—	—	24
9	Ni(Me$_6$[14]4,14dieneN$_4$)(ClO$_4$)$_2$	1.97	1.89	—	—	25
10	Ni(Me$_6$[14]dieneN$_4$)(ClO$_4$)$_2$	1.90	1.86	—	—	26
11	Ni(Me$_6$[14]dieneN$_4$)(NCS)$_2$	1.92	—	—	—	27
12	Ni(Me$_6$[14]dieneN$_4$)(ClO$_4$)$_2$	1.93	1.89	—	—	28
13	Ni(Bz$_2$[14]dieneN$_4$)	—	—	1.86	—	15
14	Ni(Bz$_2$Pyr[14]dieneN$_4$)	—	—	1.85	—	15
15	Ni(Bz$_2$[14]dieneN$_4$S$_2$)ClO$_4$	—	—	1.84	2.18 (S)	29
16	Ni(OprBz$_2$[14]dieneN$_4$S$_2$)ClO$_4$	—	—	1.83	2.16 (S)	30
17	Ni(Me$_6$[14]4,8,10,14tetraeneN$_4$)(ClO$_4$)$_2$	—	1.89	—	—	31
18	Ni(Bz$_2$[14]tetraeneN$_4$)	—	—	1.87	—	32
19	Ni(Me$_2$Bz$_2$[14]tetraeneN$_4$)	—	—	1.85	—	33
20	Ni(Me$_4$[14]hexaeneN$_8$)	—	1.82	—	1.78 (N_{ion})	34
21	Ni([14]aneS$_4$)(BF$_4$)$_2$	—	—	—	2.17 (S)	35
22	Ni(Bz$_4$[16]tetraeneN$_4$)(BF$_4$)$_2$	—	1.88	—	—	36

*Here N_{py} is the nitrogen atom of pyridine.

1. Nickel(II) Complexes

The majority of nickel(II) complexes investigated by X-ray diffraction have a square planar structure, although compounds have been found with another structure. Table 1 presents the results of X-ray diffraction studies on the square-planar nickel(II) complexes. The donor atoms in macrocyclic ligands can be oxygen and sulphur atoms, the nitrogen atom N_{am} in a secondary amino-group, the nitrogen atom N_{im} in an imino-group (–CH=N–), and the nitrogen atom N_{ion} coordinated to the metal ion with elimination of a

As was to be expected, the length of the nickel–nitrogen bond depends on the size of the macrocyclic ligand and is shortest in a 13-membered macrocycle (square-planar complexes with twelve-membered macrocycles have not been synthesised). In all cases the Ni–N_{am} bond length is greater than the Ni–N_{im} bond length for the same macrocyclic ligand. This is probably because the imino-group can be involved in the formation of π-bonds as well as a simple donor–acceptor bond, which should enhance the nickel–nitrogen interaction and should lead to the shortening of the distance between these atoms (see also Section IV).

The metal–donor atom bond length is greatly influenced by the structure of the macrocyclic ligand. Thus the Ni–N_{am} and Ni–N_{im} bond lengths in complex No.10 are shorter than in the complex No.9 (Table 1), although the ligands differ only by the relative positions of the imino-bonds and the methyl substituents. The presence of substituents in the ethylenediamine bridge between the donor atoms lengthens the metal–nitrogen bond (cf., for example, complexes No.7 and 8 or complexes No.10 and 12 in Table 1), although the introduction of substituents in the propylenediamine bridge hardly influences the distance (cf. compounds No.3 and 5). The flexibility of the macrocyclic ligand also determines the nickel–nitrogen bond length. Thus the Ni–N_{am} distance in complex No.6 is shorter than the analogous distance in complexes of other 14-membered ligands. The presence of the pyridine ring apparently increases the rigidity of the ligand, which leads to a decrease of the nickel–nitrogen bond length.

The shortest bond between the nickel ion and the nitrogen donor atom among the compounds listed in Table 1 is observed in complex No.20. The ligand forming this complex can be coordinated in two ways [(III) or (IV)]. In the nickel complex version (IV) obtains, so that two types of Ni–N bond are observed. The presence of six double bonds in the macrocyclic ligand molecule decreases the size of its plane, which is reflected in a decrease of the nickel–nitrogen bond length.

It follows from the data in Table 1 that the nickel–nitrogen distance varies consistently as a function of the nature of the donor atom. It increases in the sequence Ni–N_{cov} < Ni–N_{im} < Ni–N_{am}.

The nickel–sulphur distance is virtually constant regardless of which donor atoms, apart from those of sulphur, are coordinated to the nickel ion.

All the compounds in Table 1 are diamagnetic. Certain paramagnetic nickel(II) compounds having C.N. > 4, have now been ivestigated (Table 2). It follows from the data in Tables 1 and 2 that the nickel–nitrogen distance in high-spin complexes is greater than in diamagnetic complexes. The length of this bond increases with the size of the macrocyclic ligand. The Ni–O bond length depends on the charge on the oxygen atom. If it is negative ($acac^-$, CH_3COO^-), the nickel–oxygen distance is shorter than in complexes with neutral oxygen-containing ligands (H_2O), the Ni–$O_{(H_2O)}$ distance being almost independent of the nature of the macrocyclic ligand.

Only two iodide ions, out of the four present, are coordinated in complex No.23 [Table 2 (V)] and the nickel atom has been raised 0.30 Å above the plane of the four nitrogen atoms in the direction of the iodide ion[40]. A similar deviation of the nickel atom from the plane of the donor atoms in the direction of the axial ligand (by 0.33 Å) has been observed also in complex No.27.[44]

Table 2. The metal–donor atom distances (in Å) in high-spin macrocyclic nickel(II) complexes.

No.	Compound	Type of structure[a]	Ni–N_{am}	Ni–N_{im}	Ni–N_{ax}^b	Ni–O	Ni–Hal	Refs.
23	{[Ni(Me_2[13]dieneN$_4$)]I_2}I_2	D	1.92	1.87	—	—	2.96	40
24	[Ni([14]aneN$_4$)Cl$_2$]	F	2.06	—	—	—	2.49	41
25	[Ni(Me_6[14]dieneN$_4$)acac]ClO_4	G	2.11	—	—	2.06	—	42
26	[Ni(Me_6[14]aneN$_4$)CH_3COO]ClO_4	G	2.12	—	—	2.11	—	43
27	[Ni(N-Me_4[14]aneN$_4$)N_3]ClO	D	2.10	—	1.95	—	—	44
28	{Ni[$(CH_3OC_6H_4)_2$[14]dieneN$_2O_2$]I_2}	G	—	2.05	—	2.22	2.73	45
29	[Ni(Br_2[14]dieneN$_2O_2$)I_2]	G	—	1.92	—	2.07	2.88	46
30	[{Ni(N-Me_4[14]aneN$_4$)}$_2N_3$(N_3)2]I	F	2.15	—	2.13	—	—	47
31	[Ni(Me_2[16]dieneN$_4$)Cl, H_2O]Cl	F	2.14	2.10	—	2.22	2.43	48
32	[Ni(Bz_4[16]tetraeneN$_4$)I, H_2O]I	F	—	2.09	—	2.20	2.90	36

Remarks: [a] see Fig.2; [b] N_{ax} = donor nitrogen atom of the axial ligand; acac = acetylacetone.

The presence of the Ni–Ni bond has been demonstrated by X-ray diffraction in complexes with Me_4[14]4,6,11,13-tetraeneN$_4$ and Me_4[14]hexaeneN$_8$ ligands[49]. These diamagnetic coordination compounds have very similar structures and are dimeric both in the solid state and in solution with a nickel–nickel distance of approximately 3 Å. Nickel atoms are raised above the plane of the donor atoms towards one another.

2. Cobalt Complexes

The number of studies on the X-ray diffraction analysis of cobalt complexes of macrocyclic ligands is much smaller than for the nickel complexes. The results obtained are listed in Table 3. The general characteristics observed in the discussion of the stereochemistry of nickel complexes apply also to the cobalt complexes.

Table 3. The metal–donor atom distances (in Å) in certain macrocyclic cobalt complexes.

No.	Compound	Type of structure[a]	Co–N_{am}	Co–N_{im}	Co–N_{cov}	Co–N_{ax}	Co–other atoms	Refs.
33	[Co([12]aneN$_4$)$(NO_2)_2$]Cl	G	1.97	—	—	1.93 (NO_2)	—	16
34	[Co([12]aneN$_4$)CO_3]$ClO_4 \cdot H_2O$	G	1.97	—	—	—	1.92 (O_{CO_3})	50
35	[Co([14]aneN$_4$)en]$Cl_3 . 3H_2O$	G	1.99	—	—	1.98 (en)		51
36	[Co([14]aneN$_4O_2$)ser]$ZnCl_4 \cdot H_2O$	G	1.97	—	—	1.97 (ser)	1.90 (O_{ser})	52
37	[Co([14]aneN$_4$)CH_3, H_2O]$(ClO_4)_2$	F	1.97	—	—	—	2.01 (C_{CH_3}) 2.15 (O_{H_2O})	53
38	[Co(Me_2[14], 4,11dieneN$_4$)$(NCS)_2$]$SCN \cdot H_2O$	F	1.98	2.00	—	1.89 (NCS)		54
39	[Co(Me_6[14]dieneN$_4$)$(NH_3)_2$]$(ClO_4)_3$	F	1.99	1.95	—	1.95 (NH_3)		55
40	[Co(Me_6[14]4,14dieneN$_4$)$(CN)_2$]ClO_4	F	1.97	1.94	—	—	1.92 (C_{CN})	56
41	[Co(Me_2[14]5,7dieneN$_4$)H_2O]$(PF_6)_2$	C	1.99	—	1.92	—	2.28 (O_{H_2O})	57
42	[Co(Me_4[14]tetraeneN$_4$)$(NH_3)_2$]Br_3	F	—	1.90	—	1.97 (NH_3)		58
43	[Co(Me_4Bz_2[14]tetraeneN$_4$)I]$CHCl_3$	D	—	—	1.90	—	2.56 (I)	59
44	[Co([14]aneN$_4$)]$(ClO_4)_2$	A	1.98	—	—	—	—	60
45	[Co(Me_6[14]dieneN$_4$)$(H_2O)_2$]$(BF_4)_2$	F	1.97	1.94	—	—	2.48 (O_{H_2O})	55
46	[Co(Me_4[14]tetraeneN$_4$)$(H_2O)_2$]$(ClO_4)_2$	F	—	1.90	—	—	2.29 (O_{H_2O})	58
47	[Co(Me_4[14]hexaeneN$_8$)CO]	D	—	—	1.87	—	1.77 (C_{CO})	61

Remarks: [a] see Fig.2; en = ethylenediamine; ser = serine.

Table 4. The metal–donor atom distances (in Å) in the macrocyclic complexes of certain transition metals.

No.	Compound	Type of structure[a]	M–N	M–other atoms	M–4N plane	Refs.
48	[Fe(Me$_4$Bz$_2$[14]tetraeneN$_4$)]	B	1.92 (cov)	—	0.11	62
49	[Fe(Me$_4$Bz$_2$[14]tetraeneN$_4$)CO(NH$_2$NH$_2$)]	F	1.94 (cov)	1.75 (C_{CO}); 2.12 ($N_{NH_2NH_2}$)	0.11	63
50	[Fe(Me$_4$py$_2$[14]tetraeneN$_6$)(CH$_3$CN)$_2$](ClO$_4$)$_2$	F	1.89 (im); 190 (c)	1.94 (N_{CH_3CN})	—	64
51	[Fe(Oct$_2$Antr$_2$[14]hexaeneN$_8$)]	A	1.83 (im); 1.85 (ion)	—	—	65
52	[Fe(Me$_6$[14]dieneN$_4$)Cl]I	E	2.17 (am); 2.13 (im)	2.31 (Cl)	—	66
53	[Fe(Me$_4$Bz$_2$[14]tetraeneN$_4$)C$_6$H$_5$]	D	1.91 (cov)	1.93 ($C_{C_6H_5}$)	0.23	67
54	[Fe(Me$_4$Bz$_2$[14]tetraeneN$_4$)Cl]CH$_3$CN	D	2.00 (cov)	2.25 (Cl)	0.60	59
55	[Cu[14]aneN$_4$)](ClO$_4$)$_2$	A	1.95 (am)	—	—	14
56	[Cu([14]aneS$_4$)](ClO$_4$)$_2$	A	—	2.30 (S)	—	13,35
57	{[Cu(Me$_6$[14]dieneN$_4$)]$_2$CN}(ClO$_4$)$_3$	E	2.06 (am); 2.03 (im)	2.13 (N_{CN})	—	68
58	{[Cu(Me$_6$[14]dieneN$_4$)]$_2$Cl}(ClO$_4$)$_3$	E	2.06 (am)[b]; 2.00 (im)[c]	2.50 (Cl)	—	69
59	Mn(Me$_4$Bz$_2$[14]tetraeneN$_4$)NEt$_3$]	D	2.12 (cov)	2.25 (N_{NEt_3})	0.73	59
60	[Cr(Me$_6$[14]dieneN$_4$)NO$_2$, NO]	F	2.04 (am); 2.02 (im)	2.20 (N_{NO_2}); 1.70 (N_{NO})	—	70

Remarks: [a]see Fig. 2; [b]distance in trigonal plane; [c]distance to the vertex of the trigonal bipyramid.

Table 3 shows that the Co–N_{am} distance is almost independent of the degree of oxidation of the cobalt ion and remains virtually constant regardless of the mode of coordination of the macrocyclic ligands. Evidently the ability of ligands to form structures with a bent conformation of the macroring (i.e. structures where the donor atoms of the ligand do not occupy the equatorial plane in the coordination sphere of the metal) enables the nitrogen atoms to occupy the most convenient position in relation to the cobalt ion and to avoid strain in the macroring.

As a rule, the Co–N_{am} bond length is greater than the Co–N_{im} bond length. The only exception is complex No. 138 (Table 3), which may be accounted for by steric interactions, since in the ligand involved the imino-nitrogen is linked to a carbon atom which is itself joined to a methyl group, while the amino-nitrogen is linked to a carbon atom without alkyl substituents. The cobalt–oxygen distance is determined both by the nature of the macroring and by the characteristics of the axial ligands. The shortest distances are observed when a Co–O ionic bond is formed.

As for the nickel complexes, the equalisation of the Co–N_{im} and Co–N_{ion} bond lengths is observed in the presence of conjugation in the propylene bridge of the macrocyclic ligand. The shortest cobalt–nitrogen distance has been found in complex No. 47. The type of coordination of the macrocyclic ligand in the cobalt complexes differs from that in the nickel complex [the cobalt ion is coordinated to the nitrogen atoms of the α-di-imino-groups, as shown in stucture (III)].

3. Other Transition Metal Complexes

A number of iron(II) and iron(III) complexes have been investigated by X-ray diffraction. Some of the results of these investigations are presented in Table 4. The Fe–N distances are various and depend mainly on the type of coordination of the macrocylic ligand and the donor nature of the nitrogen atom. In trigonal-bipyramidal complexes the distance is somewhat greater than in tetragonal compounds.

Comparison of the carbonyl and alkyl derivatives of cobalt and iron shows that, whereas the M–C(CO) distances vary insignificantly [1.77 Å for Co(II) and 1.75 Å for Fe(II)], the M–C(R) distances differ to a greater extent. In complex No. 51 (Table 4) the distances between the nitrogen atoms and the iron atom are various, which indicates the absence of the delocalisation of the π-electrons in the propylene bridge (as in complex No. 20, Table 1).

The amount of X-ray diffraction data on other macrocyclic complexes is slight (Table 4). Only square-planar[13,14,35] and trigonal-bipyramidal[68,69] structures have been observed for the copper compounds. The structures of the macrocyclic manganese(II) [59] and chromium(I) [70] complexes have also been determined.

Inspection of the data in Tables 1–4 reveals a consistent variation of the metal–nitrogen donor atom distance in complexes of different metals with macrocyclic ligands. In terms of the decrease of the length of the bond, the metals can be arranged in the following sequence†:

$$Fe^{3+} > Fe^{2+} > Ni^{2+}\ (S=1) > Cu^{2+} > Co^{3+} \simeq Co^{2+} > Ni^{2+}\ (S=0)\ .$$

This series holds for any donor nitrogen atom (N_{am}, N_{im}, and N_{cov}). In the nickel complexes the metal–donor atom distance is greatly influenced by the spin state of the metal ion.

III. ABSORPTION SPECTRA OF IRON COMPLEXES

There are literature data on the absorption spectra of different macrocyclic iron(II) and iron(III) complexes which include both high-spin and low-spin compounds. The results of these studies will be considered below.

1. Iron(III) Complexes

In high-spin iron(III) complexes the ground state is ^6S and is not split in a crystal field of any symmetry. Complexes of this type are characterised by a low intensity of the *d*–*d* transitions, because they all spin-prohibited. In the spectra of the compounds investigated charge-transfer $L–Fe^{III}$ bands have been observed at ~30000 cm^{-1} for halide complexes[71,72] and at ~19000 cm^{-1} for thiocyanate[72] complexes.

The magnetic moments of all these compounds are in the range 5.7–6.1 μ_B. The lower magnetic moments of some of the complexes[72] have been explained by the admixture of the excited ^4E_g and $^2B_{2g}$ states to the $^6A_{1g}$ ground state.

Very few low-spin iron(III) complexes are known and their *d*–*d* spectra have in general been poorly characterised[73–75]. Their magnetic moments are in the range 2.1–2.3 μ_B. With increase of the number of double bonds in the macrocyclic ligand, a steady decrease of the magnetic moment has been

†Here *S* is the overall spin of the ion.

observed for isotypical complexes: $\mu_{eff} = 2.30$, 2.13, and 2.06 μ_B respectively for *trans*-$[FeLCl_2]^+$, where L = Me_6-[14]dieneN$_4$, Me_6[14]trieneN$_4$ and Me_4[14]tetraeneN$_4$.

It follows from the study of Chan and Poon[72] that the spin state of the iron ion is greatly influenced by the relative positions of the ligands: the complexes $[Fe([14]anN_4)X_2]^+$, where X = NCS^-, Cl^-, or Br^-, are high-spin for the *cis*-disposition of the monodentate ligand and low-spin in the case of the *trans*-coordination.

2. High-Spin Iron(II) Complexes

Among the high-spin complexes of bivalent ions, compounds with coordination numbers of 5 (C_{4v} symmetry) and 6 (D_{4h} symmetry) have been observed. The data on the magnetic moments and the electronic absorption spectra of these compounds are presented in Table 5. In the spectra of complexes of this type one may expect the presence of three bands of the spin-allowed transitions $^5B_1 \leftarrow {}^5B_2$, $^5A_1 \rightarrow {}^5B_2$, and $^5E \leftarrow {}^5B_2$. In practice usually two of these are observed (those with higher energies) as broad bands with a low intensity. The ground state in these complexes is $^5B_2$, as shown by Mössbauer spectroscopy[71]. The square-pyramidal complexes of the type under consideration are probably subject to some trigonal distortion[66].

The $^5B_1 \leftarrow {}^5B_2$ transition is determined in the first place by the very strong field of the macrocyclic ligand, since the energy of the $^5A_1 \leftarrow {}^5B_2$ transition is determined by the nature of the axial ligand. In square-pyramidal macrocyclic iron(II) complex a very marked splitting of the "octahedral" ^5E_g state (~7000 cm^{-1}) is observed, which has been explained by the presence of only one axial ligand and by the unusually strong field of the donor atoms of the macrocycle.

The energy of the $^5B_1 \leftarrow {}^5B_2$ transition in the complexes $[Fe(Me_2py[14]aneN_4)X]^+$, where $X^- = Cl^-$, Br^-, or I^-, increases with decrease of the strength of the field of the axial ligand[71], which may reflect the mutual influence of the ligands in the macrocyclic complexes (see Section VII). In terms of increasing strength of the equatorial field, the macrocyclic ligands can be arranged in the following sequence:

$$Me_2py[14]aneN_4 < Me_6[14]tetraeneN_4 < Me_6[14]dieneN_4.$$

Somewhat unexpectedly the di-imine ligand has a stronger field than the tetraimine ligand (see Section IV). Evidently the introduction of additional imine bonds decreases the size of the macroring and leads to the expulsion of the metal ion from the plane of the donor atoms, which weakens the metal–nitrogen interaction and decreases the strength of the field of the macrocyclic ligand.

The magnetic moments of compounds of this type are in the range 4.95–5.20 μ_B, which is somewhat less than in the hexacoordinate complexes (see below). In all probability the marked splitting of the $^5E_g(O_h)$ state reduces μ_{eff} as a result of the orbital contribution.

The magnetic and spectroscopic data on the iron(II) complexes with C.N. = 6 are listed in Table 5. The majority of these compounds have the *trans*-coordination of the axial ligands; the *cis*-coordination has been postulated for the complexes $[Fe(Me_2py[14]aneN_4)CH_3COO]PF_6$ and $[Fe(Me_6[14].$ $.tetraeneN_4)phen](ClO_4)_2$ due to the bidentate coordination of the additional ligands. The symmetry of the chromophore should be pseudo-octahedral in this case and the presence of a single broadened spin-allowed band due to the $^5E_g \leftarrow {}^5T_{2g}$ transition may be expected in the electronic spectrum. In the spectrum of $[Fe(Me_2py[14]aneN_4)(N_3)_2]$, which the authors[71] believe to have a *trans*-structure, no splitting was observed, because the azide ligand gives rise to a field whose strength is similar to that of the macrocyclic ligand. This hypothesis is supported also by the magnetic moment of the above compound.

Table 5. The magnetic moments and absorption bands of high-spin iron(II) complexes[a].

Compound	μ_{eff}, μ_B	Solvent	$^5A_1 \leftarrow {}^5B_2$	$^5B_1 \leftarrow {}^5B_2$	Refs.
$[Fe(Me_2py[14]aneN_4)Cl]PF_6$	4.95	CH_3NO_2	4.9 (4)	10.8 (4)	71
$[Fe(Me_2py[14]aneN_4)Br]PF_6$	5.11	CH_3NO_2	4.5 (5)	11.0 (5)	71
$[Fe(Me_2py[14]aneN_4)I]PF_6$	5.20	CH_3NO_2	4.2 (5)	11.4 (5)	71
$[Fe(Me_6[14]dieneN_4)Cl]ClO_4$	5.05	CH_3NO_2	4.7 (7)	12.2 (5)	9,76,77
$[Fe(Me_6[14]dieneN_4)Br]ClO_4$	5.11	CH_3NO_2	~5 (~5)	12.5 (5)	9,76,77
$[Fe(Me_6[14]dieneN_5)I]ClO_4$	5.15	CH_3NO_2	~5 (~4)	12.2 (4)	9,76,77
$[Fe(Me_6[14]tetraeneN_4)Cl]ClO_4$	5.00	CH_3NO_2	4.7 (3)	11.6 (3)	73
$[Fe(Me_6[14]tetraeneN_4)Br]ClO_4$	5.14	CH_3NO_2	4.8 (3)	11.7 (3)	73
$[Fe(Me_6[14]tetraeneN_4)I]ClO_4$	5.10	CH_3NO_2	~5	11.7 (3)	73
$[Fe(Me_6[14]aneN_4)Cl_2]$	5.58	$CHCl_3$	5.5 (1)	14.0 (2)	10
$[Fe(Me_6[14]aneN_4)Br_2]$	5.47	$CHCl_3$	5.0 (1)	14.1 (5)	10
$[Fe(Me_6[14]aneN_4)I_2]$	5.37	$CHCl_3$	5.0	14.2 (7)	10
$[Fe(Me_6[14]aneN_4)(CH_3COO)_2]$	5.70	$CHCl_3$	10.7 (1)	14.0 (2)	10
$[Fe(Me_2py[14]aneN_4)(N_3)_2]$	5.50	CH_3NO_2	11.7 (55) b		71
$[Fe(Me_2py[14]aneN_4)CH_3COO]PF_6$	5.11	CH_3OH	11.6 (10) b		71
$[Fe(Me_6[14]tetraeneN_4)phen](ClO_4)_2$	5.00	solid[c]	11.16)		73
$[Fe(13]aneN_4)(NCS)_2]$	5.42	solid[c]	8.8	11.5	78
$[Fe([15]aneN_4)(CH_3CN)_2](PF_6)_2$	5.52	CH_3CN	9.6 (4)	14.1 (4)	78
$[Fe([15]aneN_4)(NCS)_2]$	5.32	$CHCl_3$	10.4 (6)	12.6 (5)	78
$[Fe([16]aneN_4)(CH_3CN)_2](PF_6)_2$	5.55	CH_3CN	9.3 (3)	12.3 (4)	78
$[Fe([16]aneN_4)(NCS)_2]$	5.52	$CHCl_3$	9.1 (1)	11.1 (5)	78

Remarks: [a]here and henceforth the positions of the absorption bands are given in units of 10^3 cm^{-1}, the values of ε, expressed in litre cm^{-1} mol^{-1}, being given in brackets; [b] $^5E_g \leftarrow {}^5T_{2g}$ transition for octahedral symmetry; [c]spectra of compounds in the solid state; phen = phenanthroline.

The positions of the absorption bands in the spectra of these complexes depend, as for the compounds with C.N. = 5, on the strength of the field of the equatorial axial ligands. In the complexes $[Fe(Me_6[14]aneN_4)X_2]$ there is a correlation between the energy of the *d*–*d* transitions and the magnetic moments. With increase of the strength of the field due to the axial ligand, i.e. with increase of the energy of the $^5A_{1g} \leftarrow {}^5A_{2g}$ transition, the $^5B_{1g} \leftarrow {}^5B_{2g}$ band shifts to the low-energy region, which indicates a decrease of the macrocyclic ligand field strength. If the axial ligands are arranged in terms of the increasing splitting of the $^5E_g(O_h)$ state (the $CH_3COO^- < Cl^- < Br^- < I^-$ sequence), then it follows from the data in Table 5 that the magnetic moments of the complexes formed by them decrease in the same direction. This confirms the above hypothesis concerning the contribution of the orbital moment of the μ_{eff} of these compounds.

It follows from the spectra of the complexes $[Fe([X]aneN_4)Y_2]$, where X = 15, or 16 and Y = NCS^- or CH_3CN, that[78] the strength of the field of the macrocyclic ligand is greater in the acetonitrile complexes than in the thiocyanate complexes. Evidently the greater the axial ligand field strength the lower the macrocyclic ligand field strength and conversely. On passing from complexes of a 15-membered ligand to those of a 16-membered ligand the strength of the field due to the macrocycle diminishes by 180 cm^{-1} for the acetonitrile complexes and by 150 cm^{-1} for the thiocyanate complexes.

A series of square planar iron(II) complexes, having the triplet ground state $^3B_{2g}$, have been obtained recently[79]. Their effective magnetic moments are 3.2–4.3 μ_B and their electronic absorption spectra are characterised by the presence of two absorption bands in the ranges 4000–7000 and 12000–15000 cm^{-1}.

3. Low-Spin Iron(II) Complexes

The spin state of iron(II) is determined by both macrocyclic and axial ligands involved in coordination. For example, the complexes [Fe([14]aneN$_4$)X$_2$] are low-spin for X = CH_3CN, NCS^-, or CN^-, while among the complexes of the [15]aneN$_4$ ligand only the cyanide compounds are low-spin[78]. In many instances the absorption spectra of these complexes contain intense charge-transfer of intraligand transition bands, which mask the d–d bands. Such cases will not be considered. A diagram of the states of the low-spin hexacoordinate iron(II) complexes is presented in **Fig. 3***a*. Evidently at least four bands due to spin-allowed transitions can be expected in the absorption spectra of the tetragonal complexes of bivalent iron. However, if the splitting of the "octahedral" $^1T_{1g}$ and $^1T_{2g}$ states is not observed, then the absorption spectra of such compounds are interpreted from the standpoint of pseudo-octahedral symmetry. The spectroscopic data for the hexacoordinate low-spin iron(II) complexes are presented in Table 6.

The energy of the $^1T_{1g} \leftarrow {}^1A_{1g}$ transition is $10\,Dq - C$.[80] A method has been developed[81] for the calculation of the crystal field parameters for tetragonal low-spin complexes of ions with the d^6 configuration. According to the results of this study, the energies of the transitions are described by the following equations:

$$E(^1A_{2g} \leftarrow {}^1A_{1g}) = 10Dq^{xy} - C = \nu_2,$$
$$E(^1E_g \leftarrow {}^1A_{1g}) = 10\,Dq^{xy} - 35/4Dt - C = \nu_1,$$
$$Dt = 4/7\,(Dq^{xy} - Dq^z).$$

Hence we have

$$Dq^{xy} = \nu_2 + C,$$
$$Dq^z = Dq^{xy} - 7/4\,Dt,$$
$$Dt = 4/35\,(\nu_2 - \nu_1),$$

where Dq^{xy} (or Dq^E) is the strength of the field due to the equatorial macrocyclic ligand, Dq^z (or Dq^A) is the strength of the field due to the axial ligands, Dt is the tetragonal distortion parameter, and C is the Racah coefficient. If $Dq^{xy} > Dq^z$, then $Dt > 0$ and the sequence of levels corresponds to that illustrated in **Fig. 3***a*. If $Dq^{xy} < Dq^z$, then $Dt < 0$ and the ^1E_g level lies above the $^1A_{2g}$ level. This case obtains in the macrocyclic iron(II) complexes with cyanide axial ligands. Having adopted the Racah coefficient $C = 3300$ cm^{-1}, it is possible to calculate from the absorption bands Dq^{xy}, Dq^z, and Dt (Table 6).

Examination of the results shows that Dq^{xy} is influenced by the structure of the macrocyclic ligand. With increase of the number of imino-nitrogen atoms, the parameter increases. The number of methyl substituents in the macroring has a much weaker influence, although as a rule the greater the number of such substituents the smaller Dq^{xy} {cf., for example, the values of Dq^{xy} for [14]aneN$_4$ and Me$_6$[14]aneN$_4$ in the cyanide complexes}.

The strength of the field due to this macrocyclic ligand also diminishes with increase of Dq^z of the axial ligand and conversely. As will be shown subsequently, this phenomenon is characteristic also of the tetragonal cobalt(III) and nickel(II) complexes[83].

With increase of the size of the macrocyclic ligand, the strength of the field generated by it diminishes, which can be seen in relation to the complexes [Fe([X]aneN$_4$)(CN)$_2$], where X = 13, 14, and 15. On passing from a 13-membered to a 14-membered ligand, Dq^{xy} decreases by 180 cm^{-1}; on further increase of the number of members in the ring by unity, Dq^{xy} decreases by 190 cm^{-1}. These values are close to those for the high-spin iron(II) complexes (see above). Hence it follows that the change in the parameters Dq^{xy} with increase of the number of members in the macroring does not depend on the spin state of the iron(II) ion.

The magnetic moments of the tetragonal iron(II) complexes are in the range 0.4–0.8 μ_B, but, one should note that there is a tendency towards an increase of μ_{eff} with decrease of Dq^z.

IV. ABSORPTION SPECTRA OF COBALT COMPLEXES

Among the macrocyclic cobalt(II) complexes, compounds with C.N. = 4, 5, and 6 have been observed. The tetracoordinate complexes are of the low-spin type, while those with C.N. = 6 are of the high-spin type. The vast majority of cobalt(III) complexes are diamagnetic and have C.N. = 6.

1. High-Spin Cobalt(II) Complexes

The spectra of high-spin cobalt complexes show that the metal ion has a pseudo-octahedral environment[84,85]. The spectra are characterised by the presence of three absorption bands in the visible region at 8000, 16000, and 19000 cm^{-1}, which corresponds to the spin-allowed transitions

Table 6. Absorption bands and spectroscopic parameters of low-spin iron(II) complexes with C.N. = 6.

Compound	Solvent	$^1E_g \leftarrow {}^1A_{1g}$	$^1A_{2g} \leftarrow {}^1A_{1g}$	$^1B_{2g}$, $^1E_g \leftarrow {}^1A_{1g}$	Parameters, cm^{-1}			Refs.
					Dq^{xy}	Dq^z	Dt	
[Fe(Me$_6$[14]aneN$_4$)(CN)$_2$]	$CHCl_3$	20.2 (38)	16.1 (5)	26.4 (65) sh	1940	2760	−469	10
[Fe(Me$_2$py[14]aneN$_4$)(NCS)$_2$]	solid	15.6	20.4	—	2370	1410	549	71
[Fe(Me$_6$[14]aneN$_4$)Cl$_2$]	DMF	16.6 (77)	18.9 (88)	—	2220	1760	263	77
[Fe([13]aneN$_4$)(CN)$_2$]	CH_3OH	23.0 (78)	18.8 (65)	27.9 (71)	2210	3050	−480	78
[Fe([14]aneN$_4$)(CN)$_2$]	CH_3OH	21.1 (49)	17.0 (51)	27.3 (110)	2030	2850	−469	78
[Fe([15]aneN$_4$)(CN)$_2$]	CH_3OH	19.6 (27)	15.1 (62)	24.7 (64)	1840	2740	−514	78
[Fe(Me$_6$[14]tetraeneN$_4$)(NCS)$_2$]	solid	16.8	21.7	25.0	2500	1520	560	73,74
[Fe(Me$_6$[14]tetraeneN$_4$)(CH_3CN)$_2$](PF$_6$)$_2$	CH_3CN	15.4 (93)	21.3 sh	26.3 (400)	2460	1280	674	74
[Fe(Me$_4$[14]4,7,11,14tetraeneN$_4$)(py)$_2$](PF$_6$)$_2$	CH_3NO_2	12.1 (528)	19.3 (560)	—	2260	830	817	79
[Fe(Me$_2$[16]tetraeneN$_4$)(py)$_2$](PF$_6$)$_2$	CH_3NO_2	13.5 (20)	19.0 (133)	—	2230	1130	629	79
[Fe(Me$_2$[15]tetraeneN$_4$)(py)$_2$](PF$_6$)$_2$	CH_3NO_2	13.2 (23)	19.6 (320)	—	2290	1110	731	79
[Fe(Me$_2$[14]tetraeneN$_4$)(py)$_2$](PF$_6$)$_2$	CH_3NO_2	12.4 (580)	20.2 (493)	—	2350	780	903	82
[Fe(Me$_2$[14]tetraeneN$_4$)(NCS$_2$]	THF	15.9 (235)	20.2sh	—	2350	1490	491	82
[Fe(Me$_2$[14]tetraeneN$_4$)(CH_3CN)$_2$])PF$_6$)$_2$	CH_3CN	13.7 (46)	21.3 (105)	—	2460	940	868	82

Remarks: here and henceforth sh = shoulder.

$^4T_{2g} \leftarrow {}^4T_{1g}$, $^4A_{2g} \leftarrow {}^4T_{1g}$, and $^4T_{1g}(P) \leftarrow {}^4T_{1g}$ respectively. The majority of complexes of this type are formed by macrocyclic ligands having nitrogen and oxygen donor atoms. In these complexes the macrocycles have a distorted conformation and the monodentate ligands occupy the *cis*-positions in the octahedron.

The cobalt compounds with the N-$(CH_2C_6H_5)_4$[12]aneN$_4$ ligand are high-spin complexes with a trigonal-bipyramidal coordination[84]. This structure of the complexes is determined by the structure of the macrocyclic ligand, which consists of a 12-membered ring and contains four tertiary nitrogen atoms with bulky substituents. A number of bands have been observed in the absorption spectra of these compounds, but these have not been assigned.

The magnetic moments of both pseudo-octahedral and trigonal-bipyramidal cobalt(II) complexes have values of the order of 4.5–5.0 μ_B, which corresponds to the presence of three unpaired electrons.

2. Low-Spin Cobalt(II) Complexes

Among the low-spin complexes of bivalent cobalt, square-planar, square-pyramidal, and trigonal-bipyramidal compounds have been found.

The square-planar structure of cobalt(II) complexes is formed by virtue of the characteristics of the structures of the macrocyclic ligands. A series of bands due to spin-allowed transitions are observed in the spectra of these compounds. The bands are presented in Table 7.

Since the energy of the $^2A_{2g} \leftarrow {}^2A_{1g}$ transition depends on Dq^{xy}, the relative strength of the field due to the macrocyclic ligands can be inferred from it. It follows from Table 7 that Dq^{xy} increases in the sequence Me$_6$[14]aneN$_4$ < Me$_2$[14]4,7dieneN$_4$ < Me$_6$[14]dieneN$_4$ < Me$_6$[14]dieneN$_4$ < Me$_6$[14]tetraene N$_4$.

In square-pyramidal complexes the energy of the $^2E \leftarrow {}^2A_1$ transition is related to Dq^z. In terms of the decrease of the energy of this band, the axial ligands can be arranged in the sequence $H_2O \cong CH_3CN > Cl^- > Br^- > I^-$, which corresponds to the spectrochemical sequence.

Table 7. Magnetic moments and absorption bands of low-spin cobalt(II) complexes.

Compound	μ_{eff}, μ_B	Solvent	$^2E \leftarrow {}^2A_1$	$^2B_2 \leftarrow {}^2A_1$	Other bands	Refs.
[Co(Me$_6$[14]aneN$_4$)](ClO$_4$)$_2$		DMF	5.6 (6)	20.7 (70)	—	77,56
[Co(Me$_2$[14]4,7dieneN$_4$)](PF$_6$)$_2$	2.05	solid	7.0	21.7	—	57
[Co(Me$_6$[14]dieneN$_4$)](ClO$_4$)$_2$	—	DMF	6.2 (20)	21.8 (100)	28.7 (2500)	77
[Co(Me$_6$[14]dieneN$_4$)](ClO$_4$)$_2$	—	DMF	6.3 (44)	22.4 (130)	29.8 (2500)	77
[Co(Me$_6$[14]tetraeneN$_4$)](ClO$_4$)$_2$	2.12	CH_3NO_2	7.1 (39)	23.8 (257)	28.2 (1840)	87
[Co(Me$_2$[14]5,7dieneN$_4$)I]	1.94	solid	5.8	22.7	30.3	57
[Co(Me$_2$[14]4,7dieneN$_4$)I]I	1.88	solid	5.8	20.8	28.6	57
[Co(Me$_6$[14]tetraeneN$_4$)H$_2$O](ClO$_4$)$_2$	2.09	H_2O	7.9 (37)	23.8 (265)	28.5 (2850)	87
[Co(Me$_6$[14]tetraeneN$_4$)CH$_3$CN](ClO$_4$)$_2$	1.97	CH_3CN	7.8 (76)	24.4 (258)	29.6 (2820)	87
[Co(Me$_6$[14]tetraeneN$_4$)Cl]ClO$_4$	2.13	CH_3CN	7.1 (30)	22.2 (1265)	28.5 sh	87
[Co(Me$_6$[14]tetraeneN$_4$)Br]ClO$_4$	2.02	CH_3CN	6.8 (11)	19.6 sh	31.3 sh	87

Comparison of two cobalt complexes with ligands of identical structure (neutral and monoanionic) showed that the charged ligand has a higher value of Dq^{xy} (by 190 cm^{-1}) than the neutral ligand.

An absorption band at 30000 cm^{-1} is observed in almost all the spectra. It is associated with charge transfer from the metal to the π-antibonding orbital of the imino-group[82].

According to the results of long and Busch[88], the cobalt(II) complexes of Me$_2$py[14]dieneN$_4$ are low-spin and have a trigonal-bipyramidal coordination, but detailed studied on their absorption spectra have not been carried out.

3. Pseudo-Octahedral Cobalt(III) Complexes

According to their spectroscopic properties, all the cobalt(III) complexes can be divided into two large groups: pseudo-octahedral and tetragonal. The pseudo-octahedral complexes can be divided in their turn into compounds containing additional ligands, occupying two *cis*-positions in the octahedron (the macrocyclic ligand then assumes a bent conformation), and tetragonal compounds (with axial ligands in the *trans*-positions), in which the splitting of the "octahedral" absorption band is not observed.

Since the iron(II) and cobalt(II) ions have the same electronic configuration (d^6), the diagrams of their energy levels in octahedral and tetragonal fields are similar (Fig. 3*a*). The transition energies are as follows in the case of the pseudo-octahedral coordination[80]:

$$\nu_1 = E(^1T_{1g} \leftarrow {}^1A_{1g}) = 10\,Dq - C,$$
$$\nu_2 = E(^1T_{2g} \leftarrow {}^1A_{1g}) = 10\,Dq - C + 16\,B,$$

where C and B are Racah coefficients. Having adopted $C = 4B$, it is possible to calculate the parameters of the ligand field:

$$Dq = (3\nu_1 + \nu_2)/40 \quad B = (\nu_2 - \nu_1)/16\,.$$

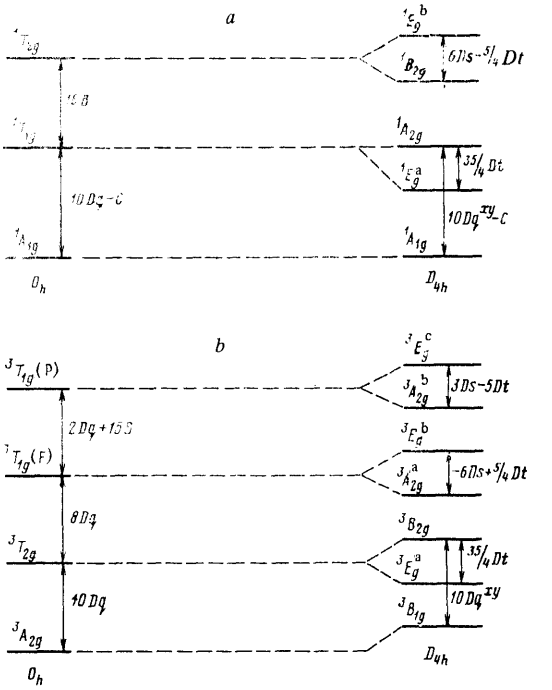


Figure 3. Diagrams and energies of the levels for the low-spin d^6 configuration (*a*) and the high-spin d^8 configuration (*b*) in octahedral (O_h) and tetragonal (D_{4h}) fields (the superscript a, b, and c are used to denote levels of identical symmetry and *Ds* and *Dt* are parameters of the tetragonal distortion).

The spectroscopic parameters of certain pseudo-octahedral complexes are listed in Table 8. They show that all the macrocyclic ligands can be arranged in the following sequence in terms of the decrease of Dq for a fixed bidentate ligand: $Me_6[14]dieneN_4 > 6,7,12,13Me_4[14]dieneN_4 > Me_2py[14]aneN_4 > [12]aneN_4 > Me_6[14]aneN_4 > 5,7,7,12,12,14Me_6[14]aneN_4$.

Comparison of the values of Dq for the oxalate and carbonate complexes shows that $Dq[CoLC_2O_4]^+ > Dq[CoLCO_3]^+$. The difference between them increases in the sequence of ligands $Me_2py[14]aneN_4 < Me_6[14]aneN_4 < [12]aneN_4$. The flexibility of the macroring increases in the same sequence: the pyridine ring in $Me_2py[14]aneN_4$ fixes the two ethylene bridges more rigidly than the six methyl groups in $Me_6[14]aneN_4$ and -[12]aneN$_4$, which have no substituents in the macroring.

The spectra of cobalt(III) complexes with monodentate ligands in the *cis*-positions[91,94,98] are very similar to the spectra of the compounds discussed above.

From the spectroscopic standpoint, the cobalt(III) ammines behave as octahedral compounds (Table 8). According to McClure[99], the splitting of the $^1T_{1g}$ and $^1T_{2g}$ levels in a field of D_{4h} symmetry arises owing to the difference between the σ- and π-antibonding properties of the equatorial and axial donor atoms. In the amine complexes this difference is too small to cause the splitting of the degenerate levels.

The value of Dq for the pseudo-octahedral complexes is determined by the rigidity of the ligand as well as the donor properties of all six atoms coordinated to cobalt. The more flexible the macrocyclic ligand, the much smaller the strain arising when it is coordinated to a cobalt ion, and the greater the overlap of the d orbitals of the latter with the orbitals of the donor ligand atoms.

Dq is also influenced by various other parameters: the number of substituents in the macroring and the number of double bonds and their relative positions. The influence of the latter factor is seen particularly clearly when the nephelauxetic coefficients β are compared. In terms of the increase of this parameter, the nitrogen donor atoms have been arranged in the sequence 4N(α-diim) < 2N(α-diim) + 2N(am) < 2N(im) + 2N(am) < 4N(am). This sequence reflects the decrease of the degree of covalence of the metal–nitrogen bond.

Table 8. Absorption bands and spectroscopic parameters of certain pseudo-octahedral cobalt(III) complexes.

Compound	Solvent	$^1T_{1g}\leftarrow{}^1A_{1g}$	$^1T_{2g}\leftarrow{}^1A_{1g}$	Parameters, cm^{-1}			Refs.
				Dq	B	β	
[Co(Me$_6$[14]aneN$_4$)C$_2$O$_4$]ClO$_4$	solid	18.4	25.5	2018	444	0.42	89
[Co(Me$_6$[14]aneN$_4$)CO$_3$]ClO$_4$	solid	18.2	25.4	2000	450	0.42	89
[Co(Me$_6$[14]aneN$_4$)acac](ClO$_4$)$_2$	solid	18.5	26.9	2060	525	0.49	89
[Co(Me$_6$[14]aneN$_4$)NO$_3$](NO$_3$)$_2$	solid	17.1	26.3	1940	575	0.54	89
[Co(Me$_6$[14]aneN$_4$)en]Cl$_3$	solid	18.0	25.8	1995	488	0.46	89
[Co(5,7,7,12,12,14Me$_6$[14]aneN$_4$) × C$_2$O$_4$]ClO$_4$	solid	17.9	26.6	2008	544	0.51	90
[Co(Me$_2$py[14]aneN$_4$)C$_2$O$_4$]ClO$_4$	CH$_3$OH	19.5 (271)	26.7 (329)	2130	450	0.42	91
[Co(Me$_2$py[14]aneN$_4$)CO$_3$]ClO$_4$	H$_2$O	19.3 (292)	27.0 (339)	2123	481	0.45	91
[Co(Me$_2$py[14]aneN$_4$)acac](ClO$_4$)$_2$	H$_2$O	19.7 (301)	26.4 (280)	2138	419	0.39	91
[Co(Me$_2$py[14]aneN$_4$)en](ClO$_4$)$_3$	H$_2$O	20.7 (250)	29.0 (256)	2248	519	0.49	91
[Co(Me$_6$[14]dieneN$_4$)CO$_3$]ClO$_4$	H$_2$O	20.0 (121)	28.6 (135)	2215	538	0.50	92
[Co(6,7,13,14Me$_4$[14]dieneN$_4$)CO$_3$]ClO$_4$	CH$_3$CN	19.8 (126)	26.0 (176)	2135	388	0.36	93
[Co([12]aneN$_4$)C$_2$O$_4$]ClO$_4$	H$_2$O	19.2 (245)	27.4 (205)	2120	513	0.48	94
[Co([12]aneN$_4$)CO$_3$]ClO$_4$	H$_2$O	18.8 (280)	27.2 (210)	2090	525	0.49	94
[Co(6,7,13,14Me$_4$[14]dieneN$_4$)(NH$_3$)$_2$]Cl$_3$	H$_2$O	22.4 (75)	30.0 (118)	2430	475	0.45	95
[Co([14]aneN$_4$)(NH$_3$)$_2$]Cl$_2$	H$_2$O	21.7 (60)	29.0 (70)	2353	456	0.43	95
[Co(Me$_6$[14]aneN$_4$)(NH$_3$)$_2$](ClO$_4$)$_3$	H$_2$O	20.6 (75)	28.1 sh	2248	469	0.44	96
[Co(Me$_3$[14]1,3dieneN$_4$)(NH$_3$)$_2$](ClO$_4$)$_3$	H$_2$O	22.0 (80)	29.0 (700)	2375	438	0.41	96
[Co(Me$_6$[14]dieneN$_4$)(NH$_3$)$_2$](ClO$_4$)$_3$	H$_2$O	22.0 (66)	29.6 (80)	2390	475	0.45	96
[Co(Me$_4$[14]tetraeneN$_4$)(NH$_3$)$_2$](ClO$_4$)$_3$	H$_2$O	23.1 (120)	28.6 sh	2448	344	0.32	96
[Co(5,7,12,14Me$_4$[14]dieneN$_4$) × (NH$_3$)$_2$]Cl$_2$ClO$_4$	H$_2$O	21.8 (74)	29.4 (92)	2370	475	0.45	97

Note: β = nephelauxetic coefficient.

4. Tetragonal Cobalt(III) Complexes

From the point of view of composition, complexes of this type can be divided into three large groups. The first group includes compounds formed by a macrocyclic ligand and two identical axial ligands. The composition of complexes of the second group includes two different axial ligands, while the complexes of the third group are characterised by the presence of an axial cobalt–carbon σ-bond and the second axial ligand can be both an anion (Cl^-, Br^-, I^-, NCS^-, or CN^-) and a neutral molecule (PPh_3, py, CH_3CN, or H_2O).

The splitting of the band due to the $^1T_{1g} \leftarrow {}^1A_{1g}$ transition is observed in the spectra of all these compounds. In certain cases the higher-energy "octahedral" band is also split. This makes it possible to calculate the parameters Dq^{xy}, Dq^z, and Dt by the method described in the discussion of iron(II) complexes[81]. The Racah coefficient C for the cobalt(III) ion was assumed to be 3800 cm^{-1}.

Table 9 presents data on the absorption spectra of complexes of the first group and their spectroscopic parameters are given below in Tables 13 and 14. The tetragonal cobalt complexes of this type are ideal objects for the investigation of the influence of various factors, particularly the structure of macrocyclic ligands, on the spectroscopic parameters. Busch and coworkers[101] investigated the dependence of Dq^{xy} on the degree of unsaturation of the macrocyclic ligand in relation to the bis(acetonitrile) complexes with 14-membered ligands. Their data show that Dq^{xy} increases with the

Table 9. Absorption bands of certain tetragonal cobalt(III) complexes of the type $[CoLX_2]^{n+}$.

L	X	Solvent	$^1E_g\leftarrow{}^1A_{1g}$	$^1A_{2g}\leftarrow{}^1A_{1g}$	$^1T_{2g}\leftarrow{}^1A_{1g}$	Refs.
Me$_6$[14]dieneN$_4$	H$_2$O	H$_2$O	17.3 (24)	24.2 sh	—	100
Me$_6$[14]dieneN$_4$	Cl$^-$	CH$_3$OH	16.0 (46)	22.4 sh	—	100
Me$_6$[14]dieneN$_4$	Br$^-$	CH$_3$OH	15.0 (65)	23.0 sh	31.6 sh	100
Me$_6$[14]tetraeneN$_4$	CH$_3$CN	CH$_3$CN	20.6 (47)	24.0 (72)	27.2 (31)	101
Me$_6$[14]tetraeneN$_4$	Cl$^-$	CH$_3$CN	16.7 (52)	—	—	73,87
Me$_4$[14]tetraeneN$_4$	Br$^-$	CH$_3$CN	15.8 (87)	25.6 (3470)	—	73,87
Me$_4$[14]tetraeneN$_4$	H$_2$O	solid	17.4	24.0	—	102,103
Me$_4$[14]tetraeneN$_4$	Cl$^-$	CH$_3$CN	17.4 (46)	23.3 (144)	—	104
Me$_4$[14]tetraeneN$_4$	CH$_3$CN	CH$_3$CN	20.8 (82)	25.5 (137)	30.4 (294)	101
Me$_4$[14]tetraeneN$_4$	Br$^-$	solid	16.7	22.2	—	102
Me$_2$[14]1,3dieneN$_4$	H$_2$O	H$_2$O	18.2 (35)	23.6 sh	—	102
Me$_2$[14]1,3dieneN$_4$	Cl$^-$	solid	16.2	23.5	—	104
Me$_2$[14]1,3dieneN$_4$	NCS$^-$	H$_2$O	19.2 (435)	21.9 (155)	—	105
Me$_2$[14]1,3dieneN$_4$	Br$^-$	solid	16.4	23.0	—	102
Me$_2$[14]1,3dieneN$_4$	CH$_3$CN	CH$_3$CN	20.6 (106)	24.1 (94)	28.1 (80)	101
[14]aneN$_4$	H$_2$O	H$_2$O	17.5 (67)	23.3 (84)	—	95,106
[14]aneN$_4$	OH$^-$	H$_2$O	18.9 (97)	21.3 (105)	—	95,106
[14]aneN$_4$	Cl$^-$	H$_2$O	15.7 (32)	22.7 (142)	—	107
2,3Me$_2$[14]aneN$_4$	Cl$^-$	CH$_3$OH	16.0 (112)	22.0 (112)	26.2 (135)	104
2,3Me$_2$[14]aneN$_4$	CH$_3$CN	CH$_3$CN	21.1 (129)	23.3 (41)	26.7 (102)	101
Me$_2$py[14]aneN$_4$	H$_2$O	H$_2$O	17.9 (29)	22.1 (245)	—	91
Me$_2$py[14]aneN$_4$	CN$^-$	H$_2$O	25.0 (84)	21.5 (151)	32.7 (315)	91
Me$_2$py[14]aneN$_4$	Cl$^-$	CH$_3$OH	16.2 (44)	21.2 (181)	25.9 (148)	91
Me$_2$py[14]aneN$_4$	NCS$^-$	H$_2$O	19.3 (393)	21.0 (364)	—	91
Me$_2$py[14]aneN$_4$	Br$^-$	CH$_3$OH	15.2 (60)	20.8 (183)	—	91
Me$_2$py[14]aneN$_4$	OH$^-$	H$_2$O	17.0 (29)	20.1 (152)	—	91
Me$_2$py[14]aneN$_4$	CH$_3$CN	CH$_3$CN	21.8 (331)	—	27.3 (266)	101
Bz$_4$[16]tetraeneN$_4$	Cl$^-$	solid	15.6	20.2	26.3; 28,2	108
Bz$_4$[16]tetraeneN$_4$	NCS$^-$	solid	16.6	19.7	29.0	108
Bz$_4$[16]tetraeneN$_4$	Br$^-$	solid	14.4	20.0	27.0	108
Bz$_4$[16]tetraeneN$_4$	N_3^-	solid	15.6	18.5	26.3	108
Me$_6$[14]aneN$_4$	H$_2$O	solid	16.6	21.6	27.5	107
Me$_6$[14]aneN$_4$	CN$^-$	solid	23.2	20.9	28.7	107
Me$_6$[14]aneN$_4$	Cl$^-$	H$_2$O	15.6 (31)	20.7 (35)	24.6 (50)	100
Me$_6$[14]aneN$_4$	NCS$^-$	solid	18.7	20.0	24.0; 26,7	107
Me$_6$[14]aneN$_4$	Br$^-$	H$_2$O	14.7 (45)	20.0 sh	25.1; 28,0	107
Me$_6$[14]aneN$_4$	OH$^-$	solid	16.6	18.9	24.9; 26,6	109
Me$_6$[14]aneN$_4$	CH$_3$CN	CH$_3$CN	20.3 (64)	22.2 (74)	25.8 (66)	101

number of double bonds in the macroring, which confirms the hypothesis that the amino-nitrogen is a more effective donor than the imino-nitrogen. This can be explained by the strong π-electronic interaction between the metal ion and the nitrogen donor atom: the rehybridisation of the unshared electron pair of the nitrogen, accompanying the conversion of the amine into the imine, should have a significant influence on Dq^{xy}. The fact that this parameter is virtually the same for the conjugated and non-conjugated tetraimines {cf., for example, the complexes with Me_4[14]tetraeneN$_4$ and Me_0[14]tetraeneN$_4$ or the di-imines Me_2[14]1,3dieneN$_4$ and Me_6[14]dieneN$_4$} shows that the reverse π-bond is not the main cause of the increase of Dq^{xy} when an amine is replaced by an imine. In all probability, the increase is caused by changes in the nature of the metal–nitrogen σ-bond. The decrease in ring size owing to the larger number of double bonds also makes a definite contribution to the increase of Dq^{xy} for imine ligands compared with amine ligands. Evidently the strengthening of the metal–nitrogen bond due to the π-electronic interaction and the decrease of the size of the macroring make the Co–N_{im} distance shorter than the Co–N_{am} distance (see Section II).

Regardless of the nature of the axial ligands, Dq^{xy} for macrocyclic ligands diminishes in the following sequence as a function of the nature of the nitrogen donor atoms: 4N(α-diimine) ≥ 4N(isolated imine) > 2N(α-diimine) + 2N(amine) ≅ *trans*-2N(imine, 6-membered ring) + 2N(amine) > *trans*-2N-(imine, five-membered ring) + 2N(amine) ≅ *cis*-2N(imine, six-membered ring) + 2N(amine) ≅ N(imine) + 3N(amine) > 4N(amine). In all probability this sequence of donor atoms is characteristic of all transition metals. The increase of Dq^{xy} in the sequence an < diene < tetraene for tetragonal iron(II) complexes had been noted previously and the same sequence is characteristic of nickel(II) complexes (see below).

Me_2py[14]dieneN$_4$ and Me_2py[14]aneN$_4$ are somewhat isolated in this series of macrocyclic ligands. Dq^{xy} for [Co(Me_2py[14]dieneN$_4$)($CH_3CN)_2$]($ClO_4)_3$ is greater than for the analogous complex with Me_4[14]tetraeneN$_4$. This effect cannot be explained exclusively by the donor properties of the pyridine nitrogen atom, because the values of Dq^{xy} for the cobalt(III) complexes of Me_2py[14]aneN$_4$ are close to those of the 2,3Me_2[14]aneN$_4$ complexes, while in the case of the nickel(II) complexes they resemble those for the complexes of saturated 14-membered ligands. In this instance a considerable increase of Dq^{xy} for the complexes of the Me_2py[14]dieneN$_4$ ligand can be explained by the conjugation between the pyridine ring and the α-di-imine groups of the macroring, which probably greatly increases the strength of the field due to this ligand.

The study of the influence of the size of the macroring on the spectroscopic properties of cobalt(III) complexes of the type [Co([X]aneN$_4$)Cl_2]ClO_4, where X = 13, 14, 15, and 16, showed[110] that Dq^{xy} increases with decrease of the size of the macroring. The authors of this study calculated the strain energy arising on coordination of the metal ion to the macrocyclic ligand. It is of interest to note that the Dq^{xy} are not correlated with the strain energy: Dq^{xy} increases in the sequence [16] < [15] < [14] < [13], while the sequence based on the decrease of the strain energy is [16] > [15] > [14] > [13]. Two important conclusions follow from this: (a) Dq^{xy} is related to the ratio of the sizes of the metal ion and the cavity within the macrocycle to a greater extent than to the overall strain energy of the ligand caused by coordination; (b) a 14-membered macrocycle is most suitable as regards size for the cobalt(III) ion.

The absorption spectra of cobalt complexes with two different axial ligands[90,91,95,105,107,108,111] resemble the spectra of the compounds discussed above.

Complexes with an axial cobalt–carbon σ-bond represent an interesting class of coordination compounds. They model vitamin B_{12} and their spectra are typical for tetragonal cobalt complexes and are presented in Table 10 together with certain calculated parameters. The large extinction coefficients of the absorption bands of these compounds can be explained by the high degree of covalence of their bonds. The parameters Dq^z(R) were calculated from the spectra in accordance with the additive rule $Dq^z(X+R) = \frac{1}{2}[Dq^z(X) + Dq^z(R)]$ subject to the condition that the values of Dq^z for CH_3CN, NCS^-, H_2O, Cl^-, Br^-, and I^- are 2180, 2000, 1720, 1460, 1300, and 1000 cm^{-1} respectively.

Table 10. Absorption bands and spectroscopic parameters of cobalt complexes of the type $[CoLRX]^{n+}$.

R	X	Solvent	$^1E_g \leftarrow {}^1A_g$	$^1A_{2g} \leftarrow {}^1A_{1g}$	Parameters, cm^{-1}				Refs.
					Dq^{xy}	Dt	$Dq^z(X+R)$	$Dq^z(R)$	
L = Me_4[14]tetraeneN$_4$									
CH_3^-	CH_3CN	CH_3OH	20.5 (2000)	23.8 (1450)	2760	377	2100	2020	112
CH_3^-	H_2O	H_2O	20.6 (2200)	23.8 (1400)	2760	366	2120	2780	103
CH_3^-	NCS^-	H_2O	20.6 (1570)	23.8 (1620)	2760	366	2120	2240	103
CH_3^-	Cl^-	$(CH_3)_2CO$	20.0 (2300)	24.2 (4600)	2800	480	1960	2570	112
CH_3^-	Br^-	$(CH_3)_2CO$	20.3 (2900)	24.8пл	2860	514	1960	2740	112
CH_3^-	I^-	$(CH_3)_2CO$	20.0 (4300)	25.0 (8500)	2880	571	1880	2860	112
$CH_2C_6H_5^-$	Cl^-	$(CH_3)_2CO$	19.9 (1700)	24.1 (4500)	2790	480	1950	2550	112
$CH_2C_6H_5^-$	Br^-	$(CH_3)_2CO$	19.6 (1600)	24.4 (4500)	2820	549	1860	2540	112
$CH_2C_6H_5^-$	I^-	$(CH_3)_2CO$	20.2 (2400)	23.8 (6000)	2760	411	2040	3180	112
$CH_2C_6H_5^-$	CH_2CN	CH_3OH	19.3 (2600)	23.7 (6000)	2750	503	1870	1560	112
L = Me_2py[14]dieneN4									
CH_3^-	—	CH_3OH	16.1 (525)	20.6 (1200)	2440	514	1540	3080	113
CH_3^-	Br^-	CH_3OH	20.4 (1050)	21.4 sh	2520	114	2350	3400	113
CH_3^-	H_2O	CH_3OH	20.6 (980)	21.8 sh	2560	137	2330	2940	113
$C_2H_5^-$	—	CH_3OH	15.7	20.5	2430	549	1470	2940	113

Compared with truly tetragonal complexes (i.e. complexes with identical axial ligands), in these compounds there is an additional factor which determines the value of Dq^z(R). Together with the influence of the macrocyclic ligand on Dq^z(R), the nature of the *trans*-axial ligand has also an effect. The maximum values of Dq^z have been obtained for compounds in which a second axial ligand is absent. In the presence of any *trans*-axial ligand Dq^z(R) is less than the maximum value. The values of this parameter can therefore be used as characteristics of the *trans*-influence of the ligands in macrocyclic complexes.

In compounds of the same macrocyclic ligand the *trans*-influence series of axial ligands in relation to the alkyl group is as follows {for example, for Me_4[14]tetraeneN$_4$ complexes}:

$$CH_3CN > NCS^- > Cl^- > Br^- > H_2O > I^-.$$

Some complexes do not show a splitting of the low-energy band and they can therefore be regarded as pseudo-octahedral. The values of β for these compounds are in the range 0.31–0.39, which confirms the high degree of covalence of their bonds.

V. SPECTRA OF NICKEL(II) COMPLEXES

Among nickel complexes with macrocyclic ligands, both high-spin and low-spin compounds have been found. All the low-spin complexes have a square-planar structure. The coordination number in the high-spin complexes is 5 or 6. From the standpoint of the symmetry of the chromophore, the pentacoordinate compounds can be classified as square-pyramidal (C_{4v}) or trigonal-bipyramidal (D_{3h}) complexes, while complexes with C.N. = 6 are pseudo-octahedral (O_h) or tetragonal-bipyramidal (D_{4h}).

1. Low-Spin Complexes

Depending on the relative strength of the field due to the axial and equatorial ligands, the ground state in the nickel(II) complexes (configuration d^8) can be both $^3B_{1g}$ (tetragonal high-spin complexes) and $^1A_{1g}$ (square-planar low-spin complexes). In the classical phthalocyanine and porphyrin compounds[114] the axial ligands are unable to compete with the strong field generated by the macroring and the triplet ground state of the nickel(II) ion does not occur. Synthetic macrocyclic ligands have Dq^{xy} smaller than for porphyrins but sufficiently large to form mainly low-spin complexes.

In nickel complexes of this type there is a possibility, in principle, of three spin-allowed transitions[80]. All the low-spin complexes which have been discovered have an absorption band in the range 18500–24000 cm^{-1} with an intensity of 20–500 litre cm^{-1} mol^{-1}, which the majority of investigators assign to the $^1A_{2g} \leftarrow {}^1A_{1g}(b_{1g} \leftarrow b_{2g})$ transition[92,93,97,115–153]. In a number of instances a band due to a second d–d transition has been observed in the range 25000–28000 cm^{-1}.[115–118] However, one should note that, if the assignment of the first band is correct, then its energy should correspond to $10Dq^{xy}$, but it has been found that the position of this band depends greatly on many factors—the non-coordinated anion, the ligand conformation, the solvent, the conditions used in the recording of the spectra, etc.

2. High-Spin Complexes

As already mentioned, square-pyramidal and trigonal-bipyramidal high-spin nickel(II) complexes with C.N. = 5 have been found. The absorption spectra of compounds of this type are characterised by the presence of four (rarely five) low-intensity absorption bands[119,154,155] due to transitions between split "octahedral" levels in a field of C_{4v} symmetry[80]. The magnetic moments of these complexes are in the range 2.80–3.20 μ_B.

The trigonal-bipyramidal nickel complexes have been obtained only with the alkylated macrocyclic ligands N-$(CH_2C_6H_5)_4$[12]aneN$_4$ [156] and N-Me_4[14]aneN$_4$.[120,157] The spectra of these complexes have at least five bands due to d–d transitions in the range 6000–25000 cm^{-1}, but the bands have not been assigned.

Nickel(II) complexes with C.N. = 6 can be divided, like the cobalt(III) complexes, into two large groups: pseudo-octahedral and tetragonal. The energy level diagrams for complexes of these types are presented in Fig. 3*b*. In terms of the one-electron approximation, the transition energies in the field of octahedral symmetry are as follows:

$$\nu_1 = E(^3T_{2g} \leftarrow {}^3A_{2g}) = 10\,Dq,$$
$$\nu_2 = E(^3T_{1g} \leftarrow {}^3A_{2g}) = 18\,Dq,$$
$$\nu_3 = E(^3T_{1g}(P) \leftarrow {}^3A_{2g}) = 12\,Dq + 15\,B.$$

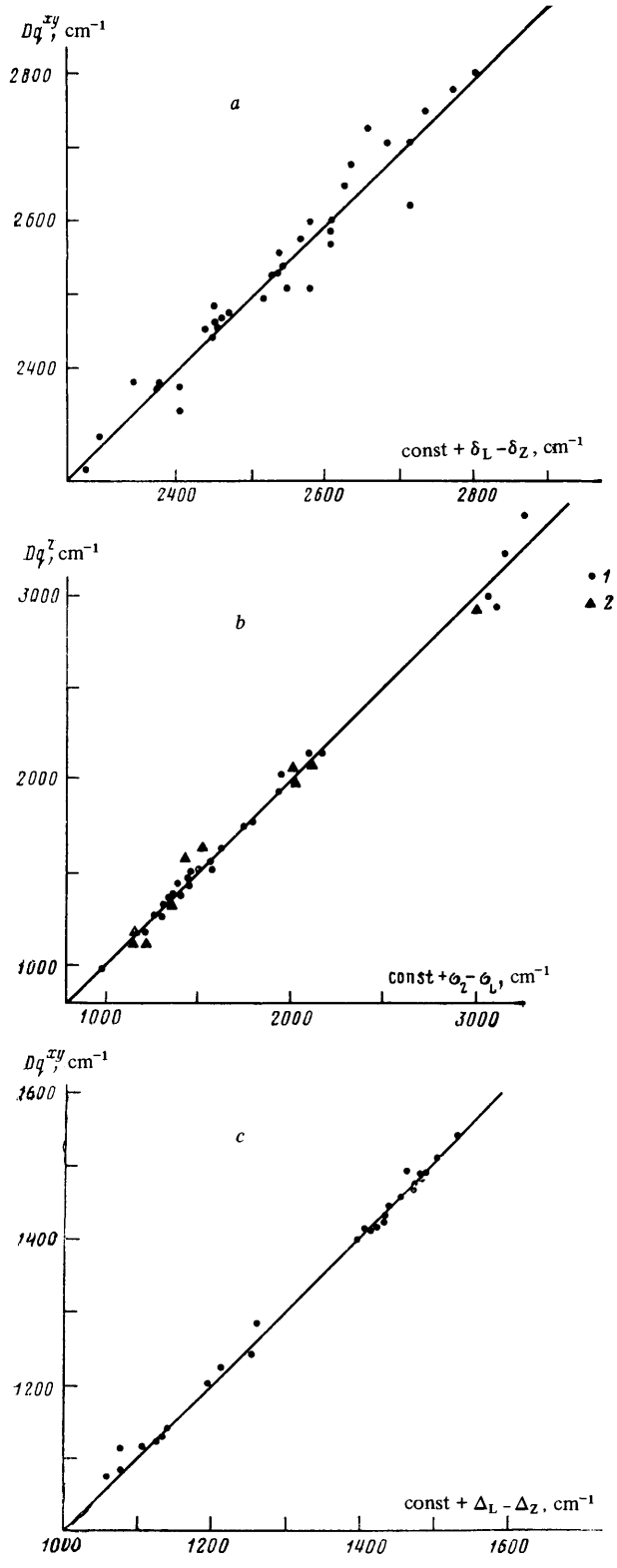


Figure 4. Correlation between Dq_{calc} and Dq_{exp}: *a*) for the values of Dq^{xy} in cobalt(III) complexes; *b*) for the values of Dq^z in cobalt(III) complexes [1) experimental points; 2) points obtained with the aid of Dq^{xy}_{calc}]; *c*) for the values of Dq^{xy} in nickel(II) complexes.

Numerous pseudo-octahedral nickel(II) complexes with macrocyclic ligands have been obtained and characterised[121-126,156-164]. Two or three bands due to *d*–*d* transitions have been observed in the spectra of these compounds in the ranges 10000–12000 (ν_1), 17000–19000 (ν_2), and 27000–29000 cm^{-1} (ν_3) with low extinction coefficients (10–40 litre cm^{-1} mol^{-1}). The values of *Dq* for compounds of this type are in the range 1000–1200 cm^{-1} and are independent of the macrocyclic ligand; they are typical for the amine complexes of nickel(II) and this also applies to the parameters β.

Among the complexes of the same macrocyclic ligand with different bidentate ligands, the highest value of *Dq* and the lowest of μ_{eff} have been found for the oxalate complexes[121], which are dinuclear compounds. Their magnetic moment is reduced owing to the Ni–Ni interaction via the $C_2O_4^{2-}$ bridge group.

A series of hexacoordinate complexes containing *cis*- and *trans*-monodentate ligands have also been isolated[122,123,157,161-163]. It is noteworthy that macrocyclic ligands containing nitrogen and sulphur donor atoms apparently have a low value of Dq^{xy}, since their complexes with Br^- and I^- ligands in the *trans*-positions do not show a splitting of the low-energy band[161,162].

Tetragonal distortion of the complexes entails the splitting of the degenerate levels (Fig. 3b), which permits the calculation of the parameters of the tetragonal field from the following formulae:

$$Dq^{xy} = 1/10E(^3B_{2g} \leftarrow {}^3B_{1g}),$$

$$Dt = {}^4/_{35}[E(^3B_{2g} \leftarrow {}^3B_{1g}) - E(^3E_g^a \leftarrow {}^3B_{1g})],$$

$$Dq^z = {}^1/_{10}[2E(^3E_g^a \leftarrow {}^3B_{1g}) - E(^3B_{2g} \leftarrow {}^3B_{1g})].$$

Table 11. Absorption bands of certain tetragonal nickel(II) complexes of the type $[NiLX_2]$ (in the solid state).

L	X	$^3E_g^a \leftarrow {}^3B_{1g}$	$^3B_{2g} \leftarrow {}^3B_{1g}$	$^3A_{2g}^a$, $^3E_g^b \leftarrow {}^3B_{1g}$	$^3A_{2g}^b$, $^3E_g^c \leftarrow {}^3B_{1g}$	Refs.
Me_2Ph_2[14]dieneN$_4$	NO_3^-	9.4	15.6	20.1	—	125
Me_2Ph_2[14]dieneN$_4$	Cl^-	9.3	15.4	19.8	—	125
Me_2Ph_2[14]dieneN$_4$	CH_3COO^-	10.1	15.1	19.9	—	125
Me_2Ph_2[14]dieneN$_4$	NCS^-	10.5	14.7	19.8	—	125
Me_6[14]aneN$_4$	CH_3COO	9.8	16.3	18.4	27.4	158
Me_6[14]aneN$_4$	Br^-	7.4	15.0	12.9; 19.0	26.2; 28.3	167
Me_6[14]aneN$_4$	Cl^-	8.4	14.7	15.1; 19.0	26.7; 28.7	167
Me_6[14]aneN$_4$	N_3^-	9.4	14.1	15.6; 19.5	29.8	167
Me_6[14]aneN$_4$	NCS^-	11.0	14.0	17.3; 20.0	29.8; 30.5	167
Bz$_4$[16]tetraeneN$_4$	N_3^-	10.0	14.7	17.0; 20.0	—	167
Bz$_4$[16]tetraeneN$_4$	NCS^-	10.9	14.7	17.4; 20.0	—	167
[14]aneN$_4$	Br^-	7.9	14.9	13.7; 19.3	27.1; 29.3	167
[14]aneN$_4$	Cl^-	8.6	14.8	15.2; 19.4	27.3; 29.2	167
[14]aneN$_4$	N_3^-	10.1	14.5	16.3; 19.8	—	167
[14]aneN$_4$	NCS^-	11.1	14.2	17.8; 20.2	—	167
2,3Me_2[14]aneN$_4$	Br^-	7.8	14.9	13.7; 19.3	27.0; 29.2	167
2,3Me_2[14]aneN$_4$	Cl^-	8.4	14.7	15.0; 19.2	27.1; 29.0	167
2,3Me_2[14]aneN$_4$	N_3^-	10.1	14.3	16.6; 19.6	—	167
2,3Me_2[14]aneN$_4$	NCS^-	11.2	14.1	18.0; 20.2	—	167
[15]aneN$_4$	Br^-	8.1	12.8	13.9; 17.5	25.5; 27.1	167
[15]aneN$_4$	Cl^-	8.7	12.4	14.4; 17.6	26.1; 27.3	167
[15]aneN$_4$	N_3^-	9.7	12.3	15.5; 17.8	27.5	167
[15]aneN$_4$	NCS^-	10.3	12.0	15.8; 18.4	28.5	167
[16]aneN$_4$	Br^-	7.3	11.3	13.1; 15.6	25.6	167
[16]aneN$_4$	Cl^-	7.8	11.2	13.5; 15.8	25.6	167
[16]aneN$_4$	N_3^-	9.0	10.9	14.7; 16.5	26.8	167
[16]aneN$_4$	NCS^-	9.6	10.7	15.4; 16.8	27.1	167
Bz$_4$[16]aneN$_4$	NCS^-	10.1	11.3	15.8; 17.4	28.0	167
Bz$_4$[16]aneN$_4$	Br^-	9.4	11.4	16.4	—	168
Bz$_4$[16]aneN$_4$	Cl^-	9.6	11.3	15.8	—	168

Remarks: for the designation of the energy levels, see Fig. 3b.

The absorption bands of tetragonal complexes of this type are presented in Table 11 (the parameters obtained from these spectra are compiled in Table 15). A series of tetragonal complexes, not listed in Table 11, have been obtained also for other macrocyclic ligands[119,122,123,127-130,161,165,166].

As for cobalt(III) complexes, the Me_2py[14]dieneN$_4$ ligand gives rise to the highest value of Dq^{xy} (1866 cm^{-1}) [167] among all the ligands investigated.

Dq^{xy} depends on the size of the macroring: [14]aneN$_4$ (1460 cm^{-1}) > [15]aneN$_4$ (1240 cm^{-1}) > [16]aneN$_4$ (1100 cm^{-1}) (the average values of Dq^{xy} were used, see Table 15). According to the data of Busch and coworkers[167], Dq^{xy} for the "ideal" Ni–N distance is 1213 cm^{-1}. The [15]aneN$_4$ ligand has a value of Dq^{xy} closest to the above (Table 15), which confirms the earlier hypothesis[11] that a 15-membered macroring is optimal for the high-spin nickel(II) ion.

As already mentioned, the introduction of electron-donating imino-groups instead of the amino-groups increases Dq^{xy}. Increments have been proposed[167] for the calculation of the values of Dq^{xy} from a specific value of this parameter—in the given instance from Dq^{xy}{[15]aneN$_4$}, as the most suitable for the high-spin nickel(II) ion. These increments are +210 cm^{-1} when a 15-membered ring is replaced by a 14-membered ring and −130 cm^{-1} when a 15-membered ring is replaced by a 16-membered ring; the replacement of the amino-group by an imino-group increases Dq^{xy} by 75 cm^{-1} for the first and second amino-groups, while the replacement of the third and fourth amino-nitrogen atoms by imino-nitrogen atoms increases Dq^{xy} by 155 cm^{-1}. The latter is due to the more marked decrease of the size of the macroring after the introduction of the third and fourth imino-groups compared with the introduction of the first and (or) the second.

The influence of the axial ligands on the Dq^{xy} parameters is examined below (see Section VII).

V. SPECTRA OF OTHER TRANSITION METAL COMPLEXES

Among the complexes of other transition metals, those of copper(II) have been most fully investigated. Unfortunately, the spectra of these compounds are characterised by a small number of broad absorption bands, which greatly diminishes the possibility of deriving information about them.

The absorption spectra of the majority of compounds investigated contain one broad band in the range 16000–20000 cm^{-1} with extinction coefficients of 50–200 litre cm^{-1} mol^{-1}.[92,93,97,125,130-133,169-176] There is apparently no direct correlation between the strength of the field due to the macrocyclic ligand and the position of this band, although an interesting relation has been observed[77] between the position of the above absorption band and the heat of formation of amine complexes of copper.

In a number of instances two[120,134,135,178] or even three[140] absorption bands have been observed in the spectra, but the amount of data is too small to make a correct assignment of these bands.

A square-pyramidal[171,179-181] or trigonal-bipyramidal[155] structure has been proposed for certain pentacoordinate copper compounds, the latter structure having been confirmed by X-ray diffraction[69]; however, the absorption bands were not assigned in the above studies.

Data on the absorption spectra of compounds of other transition metals are presented in Table 12. It is noteworthy that the energies of the $^4B_{2g} \leftarrow {}^4B_{1g}$ (for the d^3 configuration) and $^5B_{2g} \leftarrow {}^5B_{1g}$ (for the d^4 configuration) transitions correspond to values of $10Dq^{xy}$, which makes it possible to follow the variation of this parameter along the series

of transition metals. For compounds of the type $[M(Me_6[14]aneN_4)Cl_2]^{n+}$, the values of Dq^{xy} are as follows: 1700 cm^{-1} (V^{2+}), 1460 cm^{-1} (Cr^{3+}), 1940 cm^{-1} (Cr^{2+}), ~2410 cm^{-1} (Mn^{3+}), 2220 cm^{-1} (Fe^{2+}), 2450 cm^{-1} (Co^{3+}), and 1470 cm^{-1} (Ni^{2+}). It follows from this series that the values of Dq^{xy} for triply charged cations are greater than for doubly charged cations and are constant (~2450 cm^{-1}) within the limits of experimental error, while the values for M^{2+} increase markedly in the sequence Ni < V–Cr < Fe.

Table 12. Absorption bands and magnetic moments of tetragonal transition metal complexes.

Compound	μ_{eff}, μ_B	Solvent	ν_1	ν_2	ν_3	ν_4	Refs
$[V(Me_6[14]aneN_4)Cl_2]$	3.71	solid	12.5	17.0 sh	22.0	24.5	182
$[V(Me_6[14]aneN_4)Br_2]$	3.86	solid	10.3	16.0	21.0	23.8	182
$[V(Me_6[14]aneN_4)I_2]$	3.74	solid	8.5	15.5sh	20.0	24.4	182
$[V(5,12Me_2[14]aneN_4)Cl_2]$	3.73	solid	12.9	—	19.2 sh	23.8sh	182
$[Cr([14]aneN_4)Cl_2]Cl$	—	H_2O	17.5 (20)	24.6 (35)	27.4 (41)		183
$[Cr([14]aneN_4)(H_2O)_2](ClO_4)_3$	—	H_2O	19.6 (24)	24.7 (39)	25.6 (38)	28.6 (38)	183
$[Cr(Me_6[14]aneN_4)Cl_2]$	4.80	solid	14.7sh	19.4	—	—	184
$[Cr(Me_6[14]aneN_4)Br_2]$	4.82	solid	15.0sh	20.4	—	—	184
$[Cr(5,12Me_2[14]aneN_4)Cl_2]$	4.87	solid	14.3	19.7	—	—	184
$[Cr(5,12Me_2[14]aneN_4)Br_2]$	4.90	solid	15.4	19.6	—	—	184
$[Mn(Me_6[14]aneN_4)Cl_2]PF_6$	4.90	CH_3CN	10.9 (9)	24.1 sh	26.5 sh	—	135, 185
$[Mn(Me_6[14]aneN_4)Br_2]PF_6$	4.90	CH_3CN	11.7 (17)	23.2 sh	27.0 sh	—	135, 185

Remarks: the assignments for the d^3 configuration (V^{2+} and Cr^{3+}) are as follows: ν_1—$^4E_g \leftarrow {}^4B_{1g}$ transition; ν_2—$^4B_{2g} \leftarrow {}^4B_{1g}$ transition; ν_3 and ν_4—transitions to the components of the split $^4T_{1g}$ level (A_{2g} and ^4E_g); the assignments for the d^4 configuration (Cr^{2+} and Mn^{3+}) are as follows: ν_1—$^5A_{1g} \leftarrow {}^5B_{1g}$ transition; ν_2—$^5B_{2g} \leftarrow {}^5B_{1g}$ transition; ν_3—$^5E_g \leftarrow {}^5B_{1g}$ transition.

It is of interest to note that, in contrast to the cobalt(III) complexes, in the macrocyclic rhodium(III) complexes no splitting of the octahedral band is observed even for compounds in which the *trans*-disposition of the axial ligands has been demonstrated[130 186–188].

Apart from the tetragonal complexes, trigonal-bipyramidal vanadium(II) complexes[182] and pseudo-octahedral chromium(III) [183] and ruthenium(III) [189] complexes have also been obtained.

VII. THE MUTUAL INFLUENCE OF THE LIGANDS IN MACROCYCLIC COMPLEXES

In the studies of the tetragonal complexes of iron(II), cobalt(III), and nickel(II) it has been shown that Dq^{xy} for macrocyclic ligands varies as a function of the nature of the axial ligands and conversely that Dq^z for a specific axial ligand depends greatly on the nature of the coordinated macrocyclic compound. Similar findings were also made for natural macrocyclic complexes[190]. This phenomenon reflects the mutual influence of the ligands and, since the axial ligand is in the *cis*-position with respect to the macrocyclic ligand, reflects the *cis*-influence in complexes of this type.

It has been shown for cobalt(III) [83] and nickel(II) [167] complexes that the dependence of the quantities Dq^{xy} and Dq^z on the nature of the ligands and their mutual influence can be represented by the following simple equations:

$$(\text{for } Dq^{xy} \text{ in the cobalt complexes}), \quad (1)$$

$$(\text{for } Dq^{z} \text{ in the cobalt complexes}), \quad (2)$$

$$(\text{for } Dq^{xy} \text{ in the nickel complexes})\dagger, \quad (3)$$

where δ_L, σ_Z, and Δ_L are increments taking into account the nature of the ligand, for which the value of Dq is determined by the equation, and δ_Z, σ_L, and Δ_Z are increments taking into account the nature of the ligand in the *cis*-position with respect to the ligand whose parameter is calculated by the equation.

The spectroscopic parameters of the macrocyclic complexes, calculated from the data in Tables 9 and 11, as well as the increments in Eqns.(1), (2), and (3) are listed in Tables 13, 14, and 15. The constants in these equations were selected on the basis of the most reliable data and are as follows: $Dq^{xy} = 2450$ cm^{-1} for $[Co(Me_6[14]aneN_4)(H_2O)_2]^{3+}$ in Eqn.(1); $Dq^z = 1500$ cm^{-1} for $[Co(Me_2py[14]aneN_4)Cl_2]^+$ in Eqn.(2), and $Dq^{xy} = 1399$ cm^{-1} for $[Ni(Me_6[14]aneN_4)(NCS)_2]$ in Eqn.(3). The graphical relations between Dq_{exp} and Dq_{calc} are presented in Fig.4. All the straight lines have a slope of unity and the correlation coefficients are 0.975, 0.994, and 0.997 for Eqns.(1), (2), and (3) respectively.

The increments σ_L and Δ_L are determined by the structure of the macrocyclic ligands and the donor properties of the nitrogen atom, the nature of which has already been discussed in connection with the consideration of the tetragonal cobalt(III) and nickel(II) complexes. The values of σ_Z reflect the spectroscopic properties of the axial ligands and increase in parallel with the spectrochemical series for these ligands $Br^- < Cl^- < H_2O < OH^- < N_3^- < NCS^- < CH_3CN < CN^-$ in the case of the cobalt(III) ion. The *cis*-influence of the axial ligands is expressed by the parameters δ_Z and Δ_Z and in the case of cobalt the ligands can be arranged in the following sequence in terms of the parameter δ_Z: $CH_3CN < H_2O < CN^- \leq Cl^- < NCS^- < Br^- < N_3^- < OH^-$.

The influence of the axial ligands on Dq^{xy} can be explained as follows. The part of the electron density orbital d_{z^2} associated mainly with the axial ligands is located in the equatorial plane XY and the mutual influence of the ligands can be transmitted via this orbital, because the maximum overlap of the atomic orbitals of the metal with the orbitals of the donor nitrogen atoms occurs in the XY plane. The influence of the macrocyclic ligand on Dq^z, expressed by the parameter σ_L, can be explained by the steric interactions between the alkyl or benzyl substituents in the macroring and the axial ligands, apart from the cause indicated above. This interaction has been observed in the ^1H NMR spectra of a series of macrocyclic complexes[191] and has also been characterised as the *cis*-influence.

The available data are as yet insufficient to construct a relation similar to Eqn.(2) for the Dq^z of the nickel complexes, although it has been shown for a limited number of ligands (Cl^-, Br^-, N_3^-, and NCS^-) [167] that there is a definite relation between the parameters Dq^{xy} and Dq^z, and that the susceptibility of the axial ligands to changes in Dq^{xy} increases in the sequence $Br^-(-0.54) = Cl^-(-0.54) < N_3^-(-0.39) < NCS(-0.33)$ (the slopes of the linear relations between Dq^z and Dq^{xy} are given in brackets).

It follows from the foregoing that Dq^{xy} and Dq^z are not constants and vary as a function of the properties of the ligands in the *cis*-positions. In the presence of various axial

#This equation is not quoted by Martin et al., [167] but follows from the results obtained.

ligands in the macrocyclic complex the situation is complicated still further, because in calculations of the parameters Dq^{xy} and Dq^{z} it is necessary to take into account the mutual influence of the *trans*-ligands as well as the influence of two different axial ligands on the macrocyclic ligand.

Table 13. The parameters Dq^{xy} and the increments in Eqn.(1) for cobalt(III) complexes of the type $[CoLX_2]^{n+}$ (in cm^{-1}).

L	X								δ_L
	CH_3CN	H_2O	CN^-	Cl^-	NCS^-	Br^-	N_3^-	OH^-	
$Me_6[14]dieneN_4$	2780	2800 sh	—	2620 sh	—	2680 sh	—	—	270
$Me_4[14]tetraeneN_4$	2930	2780	—	2710	—	2600	—	—	240
$Me_2[14]1,3dieneN_4$	2790	2740 sh	—	2730	2570	2510	—	—	210
$[14]aneN_4$	—	2710	—	2650	2600	2510	—	2490 sh	180
$2,3Me_2[14]aneN_4$	2710	—	—	2580	—	—	—	—	120
$Me_2py[14]aneN_4$	—	2590	2530	2500	2480	2460	—	2390	70
$Bz_4[16]tetraeneN_4$	—	—	—	2460	2350	2380	2230	—	0
$Me_6[14]aneN_4$	2600	2540	2470	2450	2380	2380 sh	—	2270	0
δ_Z	−80	0	80	90	140	170	250	270	—

Remark: sh = calculated from the shoulder.

Table 14. The parameters Dq^{z} and the increments in Eqn.(2) for cobalt(III) complexes of the type $[CoLX_2]^{n+}$ (in cm^{-1}).

X	L						σ_Z
	$Me_2py[14]aneN_4$	$Me_4[14]ane$	$2,3Me_2[14]aneN_4$	$Me_4[14]tetraeneN_4$	$Me_6[14]dieneN_4$	$Me_2[14]1,3dieneN_4$	
CN^-	3230	2930	—	—	2910*	—	1680
CH_3CN	—	2220	2270	1990	2100	2090	780
NCS^-	2140	2120	—	—	1990*	2030	550
N_3^-	2060*	—	—	—	1840*	—	520
OH^-	1770	1750	—	—	—	—	300
H_2O	1630	1540	—	1460	1500пл	1580*	130
Cl^-	1590	1430	1380	1350	1340пл	1270	0
Br^-	1340	1320	1270	1180	1120*	1160	−130
σ_L	0	50	100	160	160	220	—

Remark: sh = calculated from the shoulder; *calculated from the value of Dq^{xy} by Eqn.(1).

Table 15. The parameters Dq^{xy} and the increments in Eqn.(3) for nickel complexes of the type $[NiLX_2]$ (in cm^{-1}).

L	X					Δ_L
	Br^-	Cl^-	CH_3COO^-	N_3^-	NCS^-	
$Me_2Ph_2[14]dieneN_4$	—	1540	1510	—	1470	74
$Bz_4[16]tetraeneN_4$	—	—	—	1473	1465	63
$[14]aneN_4$	1487	1480	—	1445	1418	24
$2,3Me_2[14]aneN_4$	1487	1471	—	1426	1414	16
$Me_6[14]aneN_4$	1492	1469	1430	1413	1399	0
$[15]aneN_4$	1283	1242	—	1227	1202	−205
$Bz_4[16]aneN_4$	1140	1130	—	—	1115	−325
$[16]aneN_4$	1128	1116	—	1087	1074	−342
Δ_Z	−66	−59	−36	−17	0	

It follows from Table 12 that the position of the absorption band associated with Dq^{xy} depends on the nature of the axial ligands in the case of vanadium(II), chromium(II), chromium(III), and manganese(III) complexes. In all probability this phenomenon is general for all transition metals.

As shown in the present review, macrocyclic ligands constitute an interesting class of compounds forming complexes with metal ions. The wide variety of the structures of these complexes is determined both by the structure of the macrocyclic ligands and the properties of their donor atoms, on the one hand, and by the characteristics of the electronic structure of the metal ions, on the other.

Apparently, as for alkali and alkali earth metal complexes with macrocyclic polyethers[8], the relative dimensions of the cavity within the macrocyclic ligand and of the transition metal ion play an important role in determining various properties (kinetic, thermodynamic, spectrochemical, electrochemical, etc.) of their complexes. If the size of the macrocyclic ligand is insufficient for it to be coordinated to the metal in a planar conformation, then complexes of a different structure with a bent macrocyclic ligand are formed. Complexes of this type are formed also when a macrocyclic ligand of sufficient size contains bulky substituents in its ring (particularly at the nitrogen atoms) or when an additional bidentate ligand is involved in the coordination.

Complexes with macrocyclic ligands occupying the equatorial plane in the coordination sphere of the metal are subject to marked tetragonal distortion, which gives rise to a unique possibility for the investigation of the influence of various factors on the spectrochemical parameters of the complexes. It has been shown that the parameters obtained reflect the mutual influence of the ligands in these complexes.

From the spectrochemical point of view, macrocyclic compounds are as a rule some of the most powerful ligands for which the values of Dq have been determined and are inferior, as regards field strength, only to ligands of the type of cyanide ions or nitro-groups.

REFERENCES

1. B.D.Berezin, "Koordinatsionnye Soedineniya Porfirinov i Ftalotsianina" (Coordination Compounds of Porphyrins and Phthalocyanine), Izd.Nauka, Moscow, 1978.
2. R.B.Woodward, Pure Appl.Chem., **33**, 145 (1973).
3. F.Hembright, Pure Appl.Chem., **46**, 1207 (1977).
4. G.P.Gurinovich, A.N.Sevchenko, and K.N.Solovev "Spektroskopiya Khlorofilla i Rodstvennykh Soedinenii" (The Spectroscopy of Chlorophyll and Related Compounds), Izd.Nauka i Tekhnika, Minsk, 1968.
5. D.H.Busch, Helv.Chim.Acta, Fasc.Extraord., Alfred Werner (1866–1919), 174 (1967).
6. M.W.Witman and J.H.Weber, Inorg.Chim.Acta, **25**, 263 (1977).
7. D.H.Busch, in "Coordination Chemistry". Vol.2. (Edited by A.Martell), ACS Monograph 174. Washington, 1978, p.260.
8. J.J.Christensen, D.J.Eatough, and R.M.Izatt, Chem.Rev., **74**, 351 (1974).
9. V.L.Goedken, P.H.Merrel, and D.H.Busch, J.Amer. Chem.Soc., **94**, 3397 (1972).
10. J.C.Dabrowiak, P.H.Merrel, and D.H.Busch, Inorg. Chem., **11**, 1979 (1972).
11. L.Y.Martin, L.J.DeHayes, L.J.Zompa, and D.H.Busch, J.Amer.Chem.Soc., **96**, 4046 (1974).
12. M.F.Richardson and R.E.Sievers, J.Amer.Chem.Soc., **94**, 4134 (1972).
13. M.D.Glick, D.P.Gavel, L.L.Diaddario, and D.B.Rorabacher, Inorg.Chem., **15**, 1190 (1976).
14. T.E.Jones, L.L.Zimmer, L.L.Diaddario, D.B.Rorabacher, and L.A.Ochrymovicz, J.Amer. Chem.Soc., **97**, 7163 (1975).

15. E.N.Maslen, L.M.Engelhardt, and A.H.White, J.Chem.Soc., Dalton Trans., 1799 (1974).
16. Y.Itaka, M.Shina, and E.Kimura, Inorg.Chem., **13**, 3886 (1974).
17. J.M.Waters and K.R.Whittle, J.Inorg.Nuclear Chem., **34**, 155 (1972).
18. J.Kraewski, Z.Urbanczyk-Lipkowska, and P.Glzinski, Bull.Acad.Sci.Polon., Ser.Sci.Chim., **25**, 853 (1977).
19. J.Kraewski, Z.Urbanczuk-Lipkowska, and P.Gluzinski, Bull.Acad.Sci.Polon., Ser.Sci.Chim., **25**, 939 (1977).
20. N.F.Curtis, D.A.Swann, and T.N.Waters, J.Chem. Soc., Dalton Trans., 1963 (1973).
21. R.Dewar and E.Fleischer, Nature, **222**, 372 (1969).
22. A.I.Gusiev, J.W.Kraewski, and Z.Urbanczyk-Lipkowska, Bull.Acad.Sci.Polon., Ser.Sci.Chim., **22**, 385 (1974).
23. J.Kraewski, Z.Urbanczyk-Lipkowska, and P.Gluzinski, Bull.Acad.Sci.Polon., Ser.Sci.Chim., **22**, 955 (1974).
24. J.Kraewski, Z.Urbanczyk-Lipkowska, and P.Gluzinski, Roczniki Chemii, **51**, 2385 (1977).
25. B.T.Kilbourn, R.R.Ryan, and J.D.Dunitz, J.Chem. Soc.A, 2407 (1969).
26. M.F.Bayley and I.E.Maxwell, J.Chem.Soc., Dalton Trans., 938 (1972).
27. F.Hanic and D.Mikloes, J.Cryst.Mol.Struct., **2**, 107 (1972).
28. D.A.Swann, T.N.Waters, and N.F.Curtis, J.Chem. Soc., Dalton Trans., 1115 (1972).
29. P.B.Donaldson, P.A.Tasker, and N.W.Alcock, J.Chem.Soc., Dalton Trans., 2262 (1976).
30. P.B.Donaldson, P.Haria, and P.A.Tasker, J.Chem. Soc., Dalton Trans., 2382 (1976).
31. I.E.Maxwell and M.F.Bayley, J.Chem.Soc., Dalton Trans., 935 (1972).
32. M.C.Weiss, G.Gordon, and V.L.Goedken, Inorg. Chem., 16, 305 (1977).
33. F.Hanic, M.Handlovič, and O.Lindgren, Coll. Czech.Chem.Comm., **37**, 2119 (1972).
34. V.L.Goedken and S.M.Peng, J.Amer.Chem.Soc., **95**, 5773 (1973).
35. P.D.Davis, L.K.White, and R.L.Beleford, Inorg. Chem., **14**, 1753 (1975).
36. S.W.Hawkinson and E.B.Fleischer, Inorg.Chem., **8**, 2402 (1969).
37. M.Seno, S.Tuchiya, and S.Ogawa, J.Amer.Chem. Soc., 99, 3014 (1977).
38. E.B.Fleischer, J.Amer.Chem.Soc., **85**, 1353 (1963).
39. F.Cariati, G.Mattongo, F.Morazzoni, and A.Sgamellotti, "Proceedings of the XIIIth International Conference on Coordination Chemistry, Sao Paulo, Brazil, 1977", p.143.
40. J.A.Cunningham and R.E.Sievers, J.Amer.Chem. Soc., **95**, 7183 (1973).
41. B.Bosnich, R.Mason, P.J.Pauling, G.B.Robertson, and M.L.Tobe, J.Chem.Soc.Chem.Comm., 97 (1965).
42. N.F.Curtis, D.A.Swann, and T.N.Waters, J.Chem. Soc., Dalton Trans., 1408 (1973).
43. P.O.Whimp, M.F.Bayley, N.F.Curtis, J.Chem. Soc.A, 1956 (1970).
44. M.J.D'Aniello, M.F.Mocella, F.Wagner, E.K.Barefield, and T.C.Paul, J.Amer.Chem.Soc., **97**, 192 (1975).
45. R.A.Lalancette, D.J.Maechia, and W.F.Furrey, Inorg.Chem., **15**, 584 (1976).
46. D.L.Johnston and W.DeW.Horrocks, Jr., Inorg. Chem., **10**, 687 (1971).
47. F.Wagner, M.T.Mocella, M.J.D'Aniello, A.H.J.Wang, and E.K.Barefield, J.Amer.Chem.Soc., **96**, 2625 (1974).
48. J.F.Myers and H.L.Kennard, Chem.Comm., 77 (1972).
49. S.M.Peng, J.A.Ibers, M.Millar, and R.H.Holm, J.Amer.Chem.Soc., **98**, 8037 (1976).
50. J.H.Loehlin and E.B.Fleischer, Acta Cryst., **B32**, 3063 (1976).
51. T.F.Lai and C.K.Poon, Inorg.Chem., **15**, 1562 (1976).
52. R.J.Geue, M.R.Snow, J.Spingborg, A.J.Herlt, A.N.Sargeson, and D.Taylor, Chem.Comm., 285 (1976).
53. J.E.Endicott, D.Halko, Th.S.Roche, M.D.Glick, and W.Butler, "Proceedings of the XVIth International Conference on Coordination Chemistry, Dublin, 1974", p.3, 43.
54. R.J.Restivo, J.Horney, and G.Ferguson, J.Chem. Soc., Dalton Trans., 514 (1976).
55. M.D.Glick, J.M.Kuczaj, and J.F.Endicott, J.Amer. Chem.Soc., **95**, 5097 (1973).
56. P.R.Ireland and W.T.Robinson, J.Chem.Soc.A, 663 (1970).
57. G.W.Roberts, S.C.Cummings, and J.A.Cunningham, Inorg.Chem., **15**, 2503 (1976).
58. M.D.Glick, W.G.Schmonsees, and J.F.Endicott, J.Amer.Chem.Soc., **96**, 5661 (1974).
59. M.C.Weiss, B.Bursten, S.M.Peng, and V.I.Goedken, J.Amer.Chem.Soc., **98**, 8021 (1976).
60. J.F.Endicott, J.Lilie, J.M.Kuczaj, B.S.Ramaswamy, W.C.Schmonsees, M.G.Simic, M.D.Glick, and D.P.Rillema, J.Amer.Chem.Soc., **99**, 429 (1977).
61. V.L.Goedken and S.M.Peng, Chem.Comm., 914 (1974).
62. V.L.Goedken, J.P.Pluth, S.M.Peng, and B.Bursten, J.Amer.Chem.Soc., **98**, 8014 (1976).
63. V.L.Goedken, J.Molin-Case, and Y.Whang, Chem. Comm., 337 (1973).
64. V.L.Goedken et al., J.Amer.Chem.Soc., **96**, 7693 (1974).
65. R.G.Little, J.A.Ibers, and J.E.Baldwin, J.Amer. Chem.Soc., **97**, 7049 (1975).
66. V.L.Goedken, J.Molin-Case, and G.G.Christoph, Inorg.Chem., **12**, 2894 (1973).
67. V.L.Goedken, S.M.Peng, and Y.Park, J.Amer. Chem.Soc., **96**, 284 (1974).
68. R.Jungst and G.Stucky, Inorg.Chem., **13**, 2404 (1974).
69. R.A.Bauer, W.R.Robinson, and D.W.Margerum, Chem.Comm., 289 (1973).
70. D.Wester, R.C.Edwards, and D.H.Busch, Inorg. Chem., **16**, 1055 (1977).
71. D.P.Riley, P.H.Merrel, J.A.Stone, and D.H.Busch, Inorg.Chem., **14**, 490 (1975).
72. P.K.Chan and C.K.Poon, J.Chem.Soc., Dalton Trans., 858 (1976).
73. V.L.Goedken and D.H.Busch, J.Amer.Chem.Soc., **94**, 7355 (1972).
74. J.C.Dabrowiak and D.H.Busch, Inorg.Chem., **14**, 1881 (1975).
75. D.C.Olson and J.Vasilevskis, Inorg.Chem., **11**, 980 (1972).
76. P.H.Merrel, V.L.Goedken, and D.H.Busch, J.Amer. Chem.Soc., **92**, 7590 (1970).
77. D.P.Rillema, J.F.Endicott, and E.Papaconstantiou, Inorg.Chem., **10**, 1739 (1971).
78. D.D.Watkins, D.P.Riley, J.A.Stone, and D.H.Busch, Inorg.Chem., **15**, 387 (1976).
79. D.P.Riley, J.A.Stone, and D.H.Busch, J.Amer. Chem.Soc., **99**, 767 (1977).

80. A.B.P.Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdan–London–New York, 1968.
81. R.A.D.Wentworth and T.S.Piper, Inorg.Chem., **4**, 709 (1965).
82. D.P.Riley, J.A.Stone, and D.H.Busch, J.Amer. Chem.Soc., **98**, 1752 (1976).
83. K.B.Yatsimirskii and Ya.D.Lampeka, Teor.Eksper. Khim., **13**, 786 (1977).
84. C.M.Sarther and E.L.Blinn, Inorg.Chem., **15**, 3083 (1976).
85. L.G.Amstrong et al., Inorg.Chem., **16**, 1665 (1977).
86. J.Vasilevskis and D.C.Olson, Inorg.Chem., **10**, 1228 (1971).
87. A.M.Tait and D.H.Busch, Inorg.Chem., **15**, 197 (1976).
88. K.M.Long and D.H.Busch, Inorg.Chem., **9**, 505 (1970).
89. P.O.Whimp and N.F.Curtis, J.Chem.Soc.A, 1827 (1966).
90. P.O.Whimp and N.F.Curtis, J.Chem.Soc.A, 188 (1968).
91. E.Ochiai and D.H.Busch, Inorg.Chem., **8**, 1474 (1969).
92. N.Sadasivan and J.F.Endicott, J.Amer.Chem.Soc., **88**, 5468 (1966).
93. R.W.Hay, D.P.Piplani, and B.Jeragh, J.Chem.Soc., Dalton Trans., 1951 (1977).
94. J.P.Collman and P.W.Schneider, Inorg.Chem., **5**, 1380 (1966).
95. B.Bosnich, C.K.Poon, and M.L.Tobe, Inorg.Chem., **4**, 1102 (1965).
96. D.P.Rillema and J.F.Endicott, Inorg.Chem., **11**, 2361 (1972).
97. R.W.Hay and B.Jeragh, J.Chem.Soc., Dalton Trans., 1261 (1977).
98. C.K.Poon and M.L.Tobe, J.Chem.Soc.A, 1549 (1968).
99. D.S.McClure, in "Advances in the Chemistry of Coordination Compounds" (Edited by S.Kirschner), The Macmillan Co., New York, 1961, p.498.
100. J.A.Kernohan and J.F.Endicott, Inorg.Chem., **9**, 1504 (1970).
101. A.M.Tait, F.V.Lovecchio, and D.H.Busch, Inorg. Chem., **16**, 2206 (1977).
102. D.P.Rillema, J.F.Endicott, and J.R.Barber, J.Amer. Chem.Soc., **95**, 6987 (1973).
103. T.S.Roche and J.F.Endicott, Inorg.Chem., **13**, 1575 (1974).
104. S.C.Jackels, K.Farmery, E.K.Barefield, N.J.Rose, and D.H.Busch, Inorg.Chem., **11**, 2893 (1972).
105. C.K.Poon and C.L.Wong, Inorg.Chem., **15**, 1573 (1976).
106. T.P.Dasgupta and G.M.Harris, J.Amer.Chem.Soc., **99**, 2490 (1977).
107. P.O.Whimp and N.F.Curtis, J.Chem.Soc.A, 867 (1966).
108. S.C.Cummings and D.H.Busch, Inorg.Chem., **10**, 1220 (1971).
109. N.Sadasivan, J.A.Kernohan, and J.F.Endicott, Inorg.Chem., **6**, 770 (1967).
110. Y.Hung, L.Y.Martin, S.C.Jackels, A.M.Tait, and D.H.Busch, J.Amer.Chem.Soc., **99**, 4029 (1977).
111. C.K.Poon, C.L.Wong, and P.W.Mak, J.Chem.Soc., Dalton Trans., 1931 (1977).
112. K.Farmery and D.H.Busch, Inorg.Chem., **11**, 1901 (1972).
113. E.Ochiai et al., J.Amer.Chem.Soc., **91**, 3201 (1969).
114. J.H.Weber and D.H.Busch, Inorg.Chem., **4**, 472 (1965).
115. V.L.Goedken and D.H.Busch, Inorg.Chem., **10**, 2679 (1971).
116. E.K.Barefield, F.V.Lovecchio, N.E.Tokel, E.Ochiai, and D.H.Busch, Inorg.Chem., **11**, 283 (1972).
117. C.M.Kerwin and G.A.Melson, Inorg.Chem., **12**, 2410 (1973).
118. W.Rosen and D.H.Busch, J.Amer.Chem.Soc., **91**, 4694 (1969).
119. F.L.Urbach and D.H.Busch, Inorg.Chem., **12**, 408 (1973).
120. R.Bustorf and T.A.Kaden, Helv.Chim.Acta, **57**, 1035 (1974).
121. N.F.Curtis and G.A.Reader, J.Chem.Soc.A, 1771 (1971).
122. M.S.Holtman and S.C.Cummings, Inorg.Chem., **15**, 660 (1976).
123. J.F.Myers and N.J.Rose, Inorg.Chem., **12**, 1238 (1973).
124. L.G.Warner and D.H.Busch, J.Amer.Chem.Soc., **91**, 4092 (1969).
125. D.F.Cook, N.F.Curtis, and R.W.Hay, J.Chem.Soc., Dalton Trans., 1160 (1973).
126. N.F.Curtis and T.N.Milestone, Austral.J.Chem., **28**, 275 (1975).
127. N.F.Curtis, J.Chem.Soc.A, 2834 (1971).
128. L.G.Warner, N.J.Rose, and D.H.Busch, J.Amer. Chem.Soc., 90, 6938 (1968).
129. F.Wagner and E.K.Barefield, Inorg.Chem., **15**, 408 (1976).
130. R.W.Hay and D.P.Piplani, J.Chem.Soc., Dalton Trans., 1956 (1977).
131. N.F.Curtis, J.Chem.Soc., 2644 (1964).
132. J.M.Palmer, E.Papaconstantinou, and J.F.Endicott, Inorg.Chem., **8**, 1516 (1969).
133. N.F.Curtis, J.Chem.Soc., Dalton Trans., 347 (1974).
134. J.G.Martin and S.C.Cummings, Inorg.Chem., **12**, 1477 (1973).
135. P.S.Bryan and J.C.Cabrowiak, Inorg.Chem., **14**, 299 (1975).
136. D.A.House and N.F.Curtis, J.Amer.Chem.Soc., **86**, 1331 (1964).
137. G.A.Melson and D.H.Busch, J.Amer.Chem.Soc., **86**, 4834 (1964).
138. L.T.Taylor, F.L.Urbach, and D.H.Busch, J.Amer. Chem.Soc., **91**, 1072 (1970).
139. S.C.Cummings and R.E.Sievers, J.Amer.Chem.Soc., **92**, 215 (1970).
140. T.J.Truex and R.H.Holm, J.Amer.Chem.Soc., **94**, 4529 (1972).
141. B.Bosnich, M.L.Tobe, and G.A.Webb, Inorg.Chem., **4**, 1109 (1965).
142. J.L.Karn and D.H.Busch, Inorg.Chem., **8**, 1149 (1969).
143. S.C.Cummings and R.E.Sievers, Inorg.Chem., **9**, 1131 (1970).
144. E.K.Barefield and D.H.Busch, Inorg.Chem., **10**, 108 (1971).
145. L.Rusnak and R.B.Jordan, Inorg.Chem., **10**, 2199 (1971).
146. N.F.Curtis, Y.M.Curtis, and H.K.J.Powell, J.Chem.Soc.A, 1015 (1966).
147. N.F.Curtis and Y.M.Curtis, J.Chem.Soc.A, 1653 (1966).
148. J.Riker-Nappier and D.W.Meek, Chem.Comm., 442 (1974).
149. T.L.Lotz and T.A.Kaden, Chem.Comm., 15 (1977).
150. E.G.Jäger, Z.Chem., **4**, 437 (1964).
151. E.G.Jäger, Z.Chem., **8**, 30 (1968).

152. H.Kobayashi and B.Korybut-Daszkiewicz, Bull. Chem.Soc.Japan, **45**, 2485 (1972).
153. P.A.Koliński et al., Bull.Acad.Sci.Polon., Ser.Sci. Chim., **17**, 13 (1969).
154. N.F.Curtis, J.Chem.Soc., 924 (1965).
155. Y.M.Curtis and N.F.Curtis, Austral.J.Chem., **19**, 609 (1966).
156. G.A.Kalligeros and E.L.Blinn, Inorg.Chem., **11**, 1145 (1972).
157. M.J.D'Aniello and E.K.Barefield, J.Amer.Chem. Soc., **98**, 1610 (1976).
158. N.F.Curtis, J.Chem.Soc.A, 1579 (1968).
159. N.F.Curtis, J.Chem.Soc.A, 1584 (1968).
160. N.F.Curtis and Y.M.Curtis, Inorg.Chem., **4**, 804 (1965).
161. R.W.Hay, G.A.Lawrance, and U.R.Stone, J.Chem. Soc., Dalton Trans., 924 (1976).
162. R.W.Hay, A.L.Galyer, and G.A.Lawrance, J.Chem. Soc., Dalton Trans., 939 (1976).
163. N.F.Curtis and D.A.House, J.Chem.Soc.A, 537 (1967).
164. L.G.Armstrong and L.F.Lindoy, Inorg.Chem., **14**, 1322 (1975).
165. G.R.Brubacker and D.H.Busch, Inorg.Chem., 5, 2114 (1966).
166. M.S.Elder, G.M.Prinz, P.Thornton, and D.H.Busch, Inorg.Chem., 7, 2426 (1968).
167. L.Y.Martin, C.R.Sperati, and D.H.Busch, J.Amer. Chem.Soc., **99**, 2968 (1977).
168. V.Katović et al., Inorg.Chem., **11**, 479 (1972).
169. M.M.Blight and N.F.Curtis, J.Chem.Soc., 3016 (1962).
170. D.C.Olson and J.Vasilevskis, Inorg.Chem., **10**, 463 (1971).
171. B.E.Barefield and F.Wagner, Inorg.Chem., **12**, 2435 (1973).
172. D.A.House and N.F.Curtis, J.Amer.Chem.Soc., **86**, 223 (1964).
173. B.Jezowska-Trzebiatowska, R.Kolinski, B.Korybut-Daszkiewicz, J.Mrozinski, and W.Wojciechowski, Bull. Acad.Sci.Polon., Ser.Sci.Chim., **17**, 411 (1969).
174. E.Sledziewska, Bull.Acad.Sci.Polon., Ser.Sci.Chim., **20**, 123 (1972).
175. N.F.Curtis, J.Chem.Soc., Dalton Trans., 863 (1973).
176. D.A.House and N.F.Curtis, J.Amer.Chem.Soc., **84**, 3248 (1962).
177. L.Fabrizzi, P.Paoletti, and A.B.P.Lever, Inorg. Chem., **15**, 1502 (1976).
178. J.G.Martin, R.M.C.Wei, and S.C.Cummings, Inorg. Chem., 11, 475 (1972).
179. V.Katović, L.T.Taylor, and D.H.Busch, Inorg. Chem., **10**, 458 (1971).
180. L.F.Lindoy, H.C.Lip, L.F.Power, and J.H.Rea, Inorg.Chem., **15**, 1724 (1976).
181. A.R.Amundsen, J.Whelan, and B.Bosnich, J.Amer. Chem.Soc., **99**, 6730 (1977).
182. A.Dey and F.Mani, Inorg.Chim.Acta, **19**, L39 (1976).
183. J.Ferguson and M.L.Tobe, Inorg.Chim.Acta, 4, 109 (1970).
184. A.Dey and F.Mani, Inorg.Chem., **15**, 2574 (1976).
185. P.S.Bryan and J.C.Dabrowiak, Inorg.Chem., **14**, 296 (1975).
186. E.J.Bounsall and S.R.Koprich, Canad.J.Chem., **48**, 1481 (1970).
187. K.Travis and D.H.Busch, Inorg.Chem., **13**, 2591 (1974).
188. N.F.Curtis and D.F.Cook, J.Chem.Soc., Dalton Trans., 691 (1972).
189. P.K.Chan, D.A.Isabirye, and C.K.Poon, Inorg. Chem., **14**, 2579 (1975).
190. H.A.O.Hill, in "Inorganic Biochemistry" (Edited by G.L.Eichhorn)(Translated into Russian), Izd.Mir, Moscow, 1978, p.538.
191. E.S.Gore, J.C.Dabrowiak, and D.H.Busch, Chem. Comm., 923 (1972).

Institute of Physical Chemistry,
Academy of Sciences of Ukrainian SSR,
Kiev

RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

November 1980

Translated from *Uspekhi Khimii*, **49**, 2065 - 2085 (1980)

U.D.C. 547.02 : 541.122 : 541.8

The Influence of Solvation on the Acid-Base Properties of Organic Compounds in Various Media

K.M.Dyumaev and B.A.Korolev

The influence of non-specific (electrostatic) and specific (with formation of a hydrogen bond) solvation of ions in water on the strength of different organic acids is considered by comparing their deprotonation constants (pK_d) in water, nitromethane (a solvent which serves as a model for electrostatic solvation), and in the gas phase. The decisive role of the electrostatic solvation of ions in the variation of pK_d and in the weakening of the influence of substituents on the pK_d for ammonium, anilinium, and pyridinium cations, benzoic acids, and phenols on passing from the gas phase to water and also in the differentiation of the basicities of primary, secondary, and tertiary amines in water is demonstrated. The pK_d for organic OH-, $\dot{O}H$-, NH-, $\dot{N}H$-, $\dot{P}H$-, and CH-acids in water, dimethyl sulphoxide, and nitromethane are compared, which permits the determination of the relation between the localisation of the charge in organic ions and dipolar species, on the one hand, and their solvation via hydrogen bonding and dispersion interaction in solution, on the other. The relation between the capacity of bridge groups to transmit electrons and the medium is considered.
The bibliography includes 122 references.

CONTENTS

I.	Introduction	1021
II.	Comparison of the abilities of aprotic polar solvents to form hydrogen bonds	1022
III.	Contribution of electrostatic solvation to the changes in the relative strengths of $\dot{N}H$- and OH-acids on passing from the gas phase to aprotic polar solvents and water	1024
IV.	The influence of solvation via hydrogen bonding on the relative strengths of organic acids in aprotic polar solvents and water	1027
V.	The influence of the medium on the transmission of electronic effects via bridge groups	1030

I. INTRODUCTION

The considerable influence of solvation on the rate and direction of chemical reactions in solutions is generally known[1-5]. One of the reactions most convenient for the quantitative study and interpretation of the influence of solvation effects is the reversible acid–base interaction which consists of a very simple reversible system, whose equilibrium constant can be measured for a wide range of compounds in many different media:

$$HA \rightleftharpoons A^- + H^+, \quad K_d\ (\Delta G_d^\circ) \qquad (1)$$

$$BH^+ \rightleftharpoons B + H^+, \quad K_d\ (\Delta G_d^\circ) \qquad (2)$$

The standard free energy of the deprotonation reactions (1) and (2) in a solvent S ($\Delta G_d^{\circ S}$) is determined by the "internal" and "external" components of the free energy[1,4]:

$$\Delta G_d^{\circ S} = \Delta G_{d,\,int}^{\circ S} + \Delta G_{d,\,ext}^{\circ S} = \Delta G_d^{\circ g} + \Sigma \Delta G_s^{\circ S}. \qquad (3)$$

The internal component depends only on the structure of the acid and the conjugate base and is determined by the free energy of the process in the gas phase (g): $\Delta G^{S}_{d,int} = \Delta G^{g}_{d}$.

The external component is determined by the influence of the medium on the deprotonation process, i.e. by the free energy of solvation (ΔG^{S}_{s}) of all the species; for example, for reaction (1) we have

$$\Delta G^{S}_{d,ext} = \Sigma \Delta G^{S}_{s} = \Delta G^{S}_{s}(H^{+}) + \Delta G^{S}_{s}(A^{-}) - \Delta G^{S}_{s}(HA). \quad (3)$$

It follows from Eqn.(3) that, in order to elucidate the solvation effects in the solvent S, it is necessary to know the acid–base properties not only in this solvent but also in the gas phase. In the course of many decades chemists investigating protolytic equilibria in solutions (mainly in water) were unable to do this. However, during the last ten years the position changed radically: with the aid of methods developed recently, it has been possible to measure the acidities in the gas phase of a large number of organic compounds[6], for example, substituted aliphatic[7] and aromatic carboxylic acids[8], alcohols[9], phenols[10], and aliphatic and aromatic ammonium cations[11–15].

It is noteworthy that the characteristics of water—high dielectric constant ε, high capacity for the formation of hydrogen bonds (HB), and a highly developed structure—lead to very complex solvation interactions in an aqueous medium[16]. Since any type of solvation can influence the deprotonation constant pK_d and the transmission of the effects of substituents, an unambiguous interpretation of the results for the aqueous medium is difficult[1] even when data are available for the gas phase: thus the same experimental data for substituted $\overset{+}{N}H$-acids have been explained[17–20] by the effect of specific solvation (with formation of the $\overset{+}{N}H\ldots OH_2$ hydrogen bond), while in other studies[11,12] they have been accounted for by the non-specific (electrostatic) solvation of ammonium cations. The subdivision of the solvation effects under consideration into reactions (1) and (2) involves considerable fundamental difficulties[19]: for example, both effects are intensified with increase of the charge on the $\overset{+}{N}H$ group of the substituted ammonium cations; furthermore, the hydrogen bond with the ions (at any rate $\overset{+}{N}H\ldots OH_2$) is largely electrostatic[11,19,21] and is determined by the charge of the ions.

Despite the above difficulties[3], problems of this kind can be solved. One of the possible ways involves the consideration of the influence of solvation on the pK_d in a medium which serves as a model of only the electrostatic solvation of the ions A^- and BH^+, i.e. in a solvent with a fairly high dielectric constant and a greatly weakened capacity for the formation of hydrogen bonds with different hydrogen donors and acceptors. A comparative study of data for the gas phase, the model solvent, and water would make it possible to elucidate the influence of electrostatic solvation and solvation via hydrogen bonding on the acid–base properties in an aqueous medium. There is no doubt that the model solvent must be sought among aprotic polar solvents (APS) incapable of forming the $A^-\ldots HS$ bond. During the last 10 years, the acid–base properties of a large number of organic compounds have been determined quantitatively in a series of APS (see, for example, Refs.22–29), which permits an approach to the solution of the problem under consideration.

II. COMPARISON OF THE ABILITIES OF APROTIC POLAR SOLVENTS TO FORM HYDROGEN BONDS

Examination of numerous literature data shows that the model solvent which satisfies the conditions specified above most satisfactorily is nitromethane. Since its dielectric constant ($\varepsilon = 38.6$) is fairly high, the free energies of the electrostatic solvation $\Delta G_S(I^{\pm})_{el}$ of the ions $I^{\pm}$ in water ($\varepsilon = 80.1$) and nitromethane, calculated from the Born equation[1,30,31]

$$\Delta G_S(I^{\pm})_{el} = -\frac{e^2}{2r}\left(1 - \frac{1}{\varepsilon}\right) \quad (4)$$

(here e is the charge and r the radius of the ion), are similar and differ only by ~1%.

Table 1. The dielectric constants ε and indices of the capacity of the solvents S for electron-donating solvation.

Solvent	ε[35,38]	DN[36,37]	$\delta^{23}Na^{+}$[48]	$10^3\Delta g$[39]	$\Delta\nu_{PhOH\ldots S}$[40]	$\Delta\nu_{MeOD\ldots S}$[41]	$10^3(\Delta\nu/\nu)_{HOH\ldots S}$[42,43]	$K_{MeOH\ldots S}$[44]	$-\Delta H_{PhOH\ldots S}$[45]	$\lg W^{S}_{H^+}$
Dimethyl sulphoxide (DMSO)	48.9	29.8	0.9	43	362	192	—	7.6	6.5	−3.3[46]
Dimethylformamide (DMF)	36.7	26.6	5.8	42	291	166	—	4.24	6.1	−2.7[46]
Diethyl ether	4.3	19.2	—	—	280	130	40.0	1.16	5.0	—
Methanol	32.7	19.0	4.4	39	218	—	—	—	—	1.9[46]
Water (W)	80.1	18.0	0.0	46	156	—	74.6	—	—	0.0
Acetone	20.7	17.0	—	33	224	123	35.1	1.60	4.7	7[32]
Propylene carbonate	69.0	15.1	—	26	—	—	—	—	—	—
Sulpholane	42.0	14.8	—	—	157	—	—	—	4.9	10.3*
Acetonitrile	37.5	14.1	7.8	31	160	103	31.8	1.22	4.3	8.1[46]
Nitrobenzene	34.8	4.4	7.6	—	67	53	20.5	—	2.0*	—
Nitromethane (NM)	38.6	2.7	15.4	3	65	59	21.1	0.20	1.9*	15[47]
Benzene	2.3	0.1	—	0**	48	52	18.6	0.80	1.5	—
Carbon tetrachloride	2.2	(0)	—	—	0	31	11.9	0	0	—
Cyclohexane	2.0	(0)	—	—	(0)	25	—	(0)	(0)	—
Gas phase (g)	1.0	—	—	—	—	0	0	—	—	

* From data in Ref.48; **toluene.

Notation: DN is the Gutmann donor number, $-\Delta H$ the heat of formation of the complexes $SbCl_5\ldots S$ in $C_2H_4Cl_2$ (kcal mol^{-1}), $\delta^{23}Na^{+}$ the shift of the $^{23}Na^{+}$ peak in the NMR spectrum of the $NaBPh_4$ solution in S (p.p.m), Δg the change in the parameter of the EPR spectrum of the copper complex in S, $\Delta\nu_{PhOH\ldots S}$ the shift of the vibration frequency of the OH group of phenol following the PhOH...S interaction in CCl_4 (cm^{-1}), $\Delta\nu_{MeOD\ldots S}$ the shift of the vibration frequency of the OD group in MeOD on passing from the gas phase to the solvent S (cm^{-1}), $(\Delta\nu/\nu)_{HOH\ldots S}$ the ratio of the vibration frequency shift of the OH group of water on passing from the gas phase to the solvent S to the frequency in the gas phase, $K_{MeOH\ldots S}$ the formation constant of the complex MeOH...S in CCl_4, $-\Delta H_{PhOH\ldots S}$ the enthalpy of formation of the complex PhOH...S in CCl_4 (kcal mol^{-1}), and $\lg W^{S}_{H^+}$ the coefficient of proton solvation (transition from water to the polar solvent S).

Nitromethane[32] belongs to the class of APS containing hydrogen atoms linked only to carbon atoms and exhibiting a very weak capacity for the specific solvation of anions via hydrogen bonds[2,16,33,34]. On the other hand, the molecules of the majority of APS contain electronegative O, N, and S atoms and are capable of relatively intense specific solvation of acid and cationic centres[16]. However, numerous experimental data (Table 1) have shown that nitromethane is in fact less capable, compared with all other APS, of specific electron-donating solvation of electrophilic and cationic centres, particularly solvation involving the formation of the $XH\ldots O_2N$Me bond.

Inspection of the data in Table 1 and also the values of *DN*, $\Delta\nu_{PhOH...S}$, $\Delta\nu_{MeOD...S}$, and other indices of the electron-donating capacity[48-53] for a wider range of solvents shows that, among the known (~15) APS, nitromethane exhibits the weakest capacity for specific electron-donating solvation, particularly with formation of hydrogen bonds with uncharged acids. In conformity with this conclusion, measurements of the dissociation constants of the salts BH^+Cl^- (BH^+ = quinuclidinium or tributylammonium)[37] have shown that nitromethane solvates ammonium cations much more weakly than, for example, propylene carbonate, dimethylformamide (DMF), and dimethyl sulphoxide (DMSO).

It also follows from the data in Table 1 that nitromethane resembles more closely alkanes and CCl_4, which are incapable of forming hydrogen bonds with hydrogen donors, than water†, DMF, or DMSO, i.e., compared with these solvents, the capacity of nitromethane to behave as a hydrogen acceptor in the formation of hydrogen bonds is very low. This has also been confirmed by studies of the dependence of ν for the OH groups of water[43] and phenol[54] and the NH group of pyrrole[42,55,56] in solutions on the dielectric constant of the solvent, where the point of nitromethane fits satisfactorily on the linear plot of $\Delta\nu/\nu$ against $(\varepsilon-1)/(2\varepsilon+1)$ for the gas phase, alkanes, and chloroalkanes, while the points for solvents forming the hydrogen bonds XH...S with water, phenol, and pyrrole, namely water, DMSO, acetonitrile, ketones, ethers, and amines, deviate from this relation. The weak# capacity of nitromethane for the formation of the XH...,O_2NMe bond is apparently due to the distribution of the partial negative charge in the nitro group between the two oxygen atoms, which sharply weakens its tendency towards interaction with hydrogen donors[32,57-59] compared with other APS.

Thus the capacity of nitromethane for specific donor and acceptor solvation and particularly for the formation of hydrogen bonds with the ions A^- and BH^+ is very low and constitutes an insignificant fraction of the corresponding property of water. Consequently nitromethane can be regarded as a model solvent suitable for the elucidation of the influence of hydrogen bonding on the pK_d of various acids in water.

The availability of data for a large series of neutral and cationic organic acids in nitromethane, in which the proton is attached to oxygen, nitrogen, phosphorus, and carbon atoms (see Tables 3, 4, and 6)§ also permits an approach to the problem of the relation between the structure and solvation of these compounds.

Table 2. The standard free energies of deprotonation (ΔG_d, kcal mol^{-1}) of organic acids in various media[a].

Medium	$\overset{+}{N}H_4$	$MeN\overset{+}{H}_3$	$Me_2\overset{+}{N}H_2$	$Me_3\overset{+}{N}H$	$PhN\overset{+}{H}_3$	$C_5H_5\overset{+}{N}H$	$Me_4\overset{+}{P}H$	*N*-Methyl-2-hydroxypyridinium	MeCOOH	PhCOOH	PhOH	Fluorene
Gas phase[b]	193[11]	203[11]	210[11]	214[11]	200[11]	210[11]	215[18]	209[64]	342[6]	332[6]	343[6]	346[6]
Nitromethane[c]	24.2[27]	27.1[27]	28.0[27]	26.9[65]	15.9[27]	19.8[66]	25[d,67]	14.1[66,68]	31.5[28]	30.1[28]	38.5[29]	48[e]
Acetonitrile	22.4[69]	25.0[69]	25.6[69]	24.0[69]	14.4[70]	16.8[70]	—	—	30.5[70]	28.3[71]	37[72]	—
DMF	12.9[73]	—	—	11[f,73]	6.0[74]	7[9]	—	—	18.5[74]	16.8[74]	25[72]	—
DMSO	14.3[70]	15[f,70]	14[f,70]	11[f,26]	5.0[26]	4.6[75]	7.0[75]	—	17[26]	15[26]	23[26]	31[26]
Water[27,76,77]	12.6	14.5	14.7	13.4	6.3	7.1	11.8[75]	0.4[64]	6.5	5.7	13.6	28.7[26]

[a] The values of ΔG_d in the solutions were calculated from the literature values of $pK_d^{25°}$ by the equation $\Delta G_d(\text{kcal mol}^{-1}) = 1.365pK_d^{25°}$.

[b] The values for $\overset{+}{N}H$-acids have been adjusted to $\Delta G_d^g(Me\overset{+}{N}H_3) = 203$ kcal mol^{-1}.[64]

[c] Quoted in accordance with the scale of Bauer and Foucqult[47] (see Korolev and Kashkovskaya[28]).

[d] $Et_3\overset{+}{P}H$; the values of pK_d for $Me_3\overset{+}{P}H$ and $Et_3\overset{+}{P}H$ in water and DMSO are virtually equal[75].

[e] Estimated from the $pK_d^{NM}-pK_d^W$ correlation for CH-acids (Table 6, series 5).

[f] Calculated from data for ethylamines (the difference between the basicities of the corresponding ethyl- and methyl-amines in water, $MeNO_2$,[27] and MeCN [69] agree to within 0.2 of a pK unit and have the following values: ~0 between $EtNH_2$ and $MeNH_2$ and between Et_2NH and Me_2NH; ~1.0 p*K* unit between Et_3N and Me_3N).

† In contrast to other solvents, the tendency of water to form hydrogen bonds is much greater (by a factor of 1.5 to 2)[17,53] than that[48] of isolated water molecules; in order to characterise water as a medium, the values of *DN* and $\Delta\nu_{PhOH...S}$, describing the properties of water molecules in dilute solutions in chloroalkanes, must be increased by a factor of 1.5–2. For example, for an aqueous medium *DN* ≅ 33.[48]

Contradictory views on this problem are still being expressed in the review literature (see, for example, Bell[34] and Yanovskaya[60]).

§ In the case of other APS data are available for a much more restricted range of compounds (4–6 series, see Tables 3 and 4) compared with nitromethane. The solvation-induced weakening of the sensitivity of the pK_d of three series of organic acids to the influence of substituents on passing from the gas phase to DMSO and water was examined in a recent study by J.E.Bartmess, J.A.Scott, and R.T.McIver, J.Amer. Chem.Soc., **101**, 6056 (1979).

III. CONTRIBUTION OF ELECTROSTATIC SOLVATION TO THE CHANGES IN THE RELATIVE STRENGTHS OF $\overset{+}{N}H$- AND OH-ACIDS ON PASSING FROM THE GAS PHASE TO APROTIC POLAR SOLVENTS AND WATER

It is known that the changes in the deprotonation constants [pK_d; Eqns.(1) and (2)] on passing from one medium to another are determined mainly by the solvation of the charged species[2,11,61,62]. More than 80% of the solvation energy of ions in polar solvents is determined by the non-specific electrostatic solvation[16], which depends on the dielectric constant ε; the specific solvation, which is to a large extent determined by the formation of hydrogen bonds[35], makes a smaller contribution. On passing from the gas phase ($\varepsilon = 1$) to polar solvents ($\varepsilon \geq 30$), the change in acid strength should therefore depend mainly on the electrostatic solvation. In other words, the values of pK_d should vary markedly on passing from the gas phase to water, nitromethane, and other APS and should vary comparatively little on passing from one polar solvent to another.

Table 3. Transmission of the electronic effects of substituents in $\overset{+}{N}H$-acids in different media.

No. of series	Acid[a] X–M–$\overset{+}{N}H$	Bridge group	ρ^g	ρ^{NM}	ρ^W	α^{NM}	$R^{NM,g}$	$R^{W,g}$	$R^{W,NM}$
1	X (X′) (X″) $\overset{+}{N}H$	—	6.5[b9]	4.1[b,c27]	3.2[b79–81]	0.73	1.6	2.0	1.3
2	$XC_5H_4\overset{+}{N}H$	C_5H_4	13.8[d]	7.6[88]	6.0[82]	0.80	1.8	2.3[12]	1.3
3	$XC_6H_4\overset{+}{N}H_3$	C_6H_4	7.5[d]	4.2[e65]	2.9[83]	0.72	1.8	2.6[13]	1.45

[a] X = substituent and M = bridge group; [b] the value of ρ^* is quoted; [c] the value of ρ^* in MeCN is 4.2;[24] [d] calculated from the values of $R^{W,g}$ and ρ^W; [e] the value of ρ in MeCN and MeOH is 4.1 [65] and that in DMSO is 3.8.[65]

Notation: $\alpha^{NM} = (\rho^g - \rho^{NM})/(\rho^g - \rho^W)$; $R^{NM,g} = \rho^g/\rho^{NM}$; $R^{W,g} = \rho^g/\rho^W$; $R^{W,NM} = \rho^{NM}/\rho^W$.

Table 4. Transmission of the electronic effects of substituents in OH-acids in different media.

No. of series	Acid[a] X-M-OH	Bridge group	ρ^g	ρ^{NM}	ρ^W	α^{NM}	$R^{NM,g}$	$R^{W,g}$	$R^{W,NM}$
4	XOH	—	7.0[b9]	4.6[c98]	2.7[b9]	0.6	1.5	2.6	1.7
5	XC_6H_4OH	C_6H_4	15.0[d]	4.5[e29]	2.2[83]	0.82	3.3	6.8[10]	2.0
6	XCOOH	CO	5.5[b9]	3.6[b,f28]	1.8[b99]	0.51	1.5	3.0	2.0
7	XC_6H_4COOH	C_6H_4CO	10.6[1e]	2.55[g65]	1.00	0.84	4.2	10.6	2.55

[a] X = substituent and M = bridge group; [b] the value of ρ^* is quoted; [c] the value of ρ^{*DMSO} is quoted instead of ρ^{*NM}, which is permissible, since the values of $\rho(\rho^*)$ for OH-acids in $MeNO_2$, DMSO, and DMF are similar (see Ref.33 and footnotes *e*, *f*, and *g*); [d] calculated from the values of $R^{W,g}$ and ρ^W; [e] $\rho^{MeCN} = 4.5$, $\rho^{DMF} = 4.5$, and $\rho^{DMSO} = 4.3$ [72]; [f] the values of ρ^* for MeCN, DMF, and DMSO are 3.5 [24]; [g] $\rho^{MeCN} = 2.4$ [100] and 2.6,[9] $\rho^{DMF} = 2.35$,[9,100] and $\rho^{DMSO} = 2.5$ [100] and 2.6.[9] For the significance of the notation, see Table 3.

This conclusion is fully confirmed by the experimental data in Table 2 and Fig.1: the change in ΔG_d for OH-, $\overset{+}{O}H$-, $\overset{+}{N}H$-, $\overset{+}{P}H$-, and CH-acids on passing from water to nitromethane and other APS (10–25 kcal mol^{-1}) amounts to a very small fraction (5–8%) of the decrease of ΔG_d in the transition gas phase → polar solvent (170–320 kcal mol^{-1}).¶ The solvation energy of the proton $\Delta G_s^S(H^+)$, which amounts to ~260.5 kcal mol^{-1} for water[11] and ~240 kcal mol^{-1} for nitromethane (calculated from $\lg {}^W\gamma_{H^+}^{NN}$; Table 1) plays a decisive role in the enormous increase of acidity in solutions. The energy of solvation of organic ions $\Delta G_s^S(I^\pm)$ (50–80 kcal mol^{-1}; [15,25] see Table 5) likewise plays an important role; the solvation of uncharged species is several times weaker[2,15].

Table 5. The solvation energies of organic ions determined by the charge [$-\Delta G_s^S(I^\pm)_{el+hb}$, kcal mole^{-1}*].

Ion $I^\pm$	Water	Nitromethane	Dimethyl sulphoxide
$\overset{+}{N}H_4$	80	71	86
$Me\overset{+}{N}H_3$	72 (8)	64 (7)	77 (9)
$Me_2\overset{+}{N}H_2$	65 (7)	58 (6)	69 (8)
$Me_3\overset{+}{N}H$	60 (5)	53 (5)	63 (6)
$C_5H_5\overset{+}{N}H$	58	50	60
$Ph\overset{+}{N}H_3$	67	56	70
$Me_3\overset{+}{P}H$	52	44	51
$MeCOO^-$	83	74	70
$PhCOO^-$	76	67	64
PhO^-	78	69	66

* The solvation energies were calculated from the equations[11,38] $\Delta G_s^S(BH^+)_{el+hb} = \Delta G_d^g - \Delta G_d^S + \Delta G_s^S(H^+)$ and $\Delta G_s^S(A^-)_{el+hb} = -\Delta G_d^g + \Delta G_d^S - \Delta G_s^S(H^+) + \Delta G_s^S(HA)_{hb}$. The values of ΔG_d^g and ΔG_d^S are listed in Table 2; $\Delta G_s^W(H^+) = -260.5$ kcal mole^{-1},[11] $\Delta G_s^{NM}(H^+) = -240$ kcal mole^{-1} (see above), and $\Delta G_s^{DMSO}(H^+) = -265$ kcal mol^{-1} (calculated from $\lg {}^W\gamma_{H^+}^{DMSO}$,[46] Table 1). Using Kolthoff's data[33] and assuming that the $\Delta G_s^S(HA)_{hb}$ for $PhNO_2$ and $MeNO_2$ are close to zero (see above), we have $\Delta G_s^W(HA)_{hb} \cong -5$ kcal mol^{-1} and $\Delta G_s^{DMSO}(HA)_{hb} \cong -7$ kcal mol^{-1}. The accuracy of the absolute values of $\Delta G_s^S(I^\pm)_{el+hb}$ is to within several kcal mol^{-1}, while the relative values are correct to within 1 kcal mol^{-1}. The effect of each methyl group in the ammonium cations is indicated in brackets.

When the pK_d are compared in a single medium, the proton solvation factor cancels out and the differences in the solvation of the ions BH^+ and A^- become of primary importance. Bearing in mind the foregoing, it is logical to assume that the change (weakening) of the influence of substituents on pK_d in the gas phase → water transition is caused mainly by the non-specific electrostatic solvation of ions. However, the literature data on this problem are contradictory. Thus the weakening (compared with the gas phase) of the influence of substituents on the basicity of amines and pyridines ($\overset{+}{N}H$-acids) and the differences in basicity between different classes of amines in water have been explained[17–20], in conformity with the most widely held view, by the specific hydration of ammonium cations via the hydrogen bonds $\overset{+}{N}H\ldots OH_2$,

¶ These figures correspond to the increase of K_d in solutions by a factor of 10^{125}–10^{230}. Fig.1 also shows that the effect of solvation on pK_d is much greater than that of the structure[1,63].

while other workers[11,12] explain it by the non-specific electrostatic hydration of cations due to the high dielectric constant. For neutral acids HA, the weakening of the influence of substituents on the pK_d in water can also be caused by both types of solvation of the anions A^- indicated above[78], but in many investigations only the formation of the $A^-...HOH$ hydrogen bond has been discussed[7,10,62].

Table 6. Parameters of the relations between the pK_d for acids in nitromethane[27-29,65-68,107-112] and water[22,73,77,113]: $pK_d^{NM} = R^{W,NM}\, pK_d^W + b$.

No.	Series	$R^{W,NM}$	b	r	s	n	pK_d^W for $pK_d^{NM} = 16$
			Neutral acids				
1	$XCOOH$[107]	2.04±0.11	11.23	0.994	0.42	6	2.3
2	XC_6H_4COOH[107]	2.61±0.11	8.44	0.993	0.20	9	2.9
3	XC_6H_4OH[107]	1.94±0.09	6.24	0.997	0.24	5	5.0
4	X_2NH[a]	1.1[b]	7.4[b]	—	—	2	8.1[b]
5	X_3CH[c]	1.2[b]	4.8[b]	—	—	2	7.8[b]
			Cationic acids				
6	$X_3\overset{+}{P}OH$[d]	2.3	10.9	—	—	2	2.2
7	$X_3\overset{+}{A}sOH$[112]	1.96	8.31	0.980	0.37	5	3.9
8	$X_2C{=}\overset{+}{O}H$[e]	1.85±0.06	6.39	0.996	0.39	9	5.2
9	$XC_6H_4\overset{+}{N}OH$[107]	1.64±0.18	7.61	0.982	0.45	5	5.1
10	$X(NH_2)_2C_3N_3H^+$[f]	1.39±0.05	5.67	0.995	0.14	9	7.4
11	XC_6H_4NH[107]	1.22±0.03	5.77	0.996	0.25	13	8.4
12	$X_3\overset{+}{P}H$[107]	1.22±0.12	4.76	0.991	0.53	4	9.2
13	$X_3\overset{+}{N}H$[g]	1.35±0.04	3.85	0.995	0.30	13	9.0
14	$X_2\overset{+}{N}H_2$[g]	1.30±0.03	3.56	0.997	0.27	12	9.6
15	$X\overset{+}{N}H_3$[g]	1.26±0.01	3.50	0.999	0.26	27	9.9

[a] Polynitroarylamines[107]; [b] approximate data; [c] 9-substituted fluorenes[107]; [d] Et_3PO,[110,113], $PhCH{=}CHP(O)Alk_2$;[111,113] the parameters of line 6 are close to those of the relation calculated[107] on the basis of the correlation between $pK_d^W(6)$ and $pK_d^{NM}(6)$ with $\Sigma\sigma^P$; [e] pyridones, $(H_2N)_2CO$, DMF, $MeCONH_2$, phenalenone[107]; [f] 6-substituted 2,4-diamino-*sym*-triazines[109]; [g] aliphatic and aromatic amines[27,65].

The results of the study of the relative roles of the above solvation factors with the aid of nitromethane as a model solvent[65] are presented in Tables 3 and 4. Before discussing the data in these two Tables, we shall consider the relations between the constants of equilibria (1) and (2) and ion solvation. It has been shown[11,33] that the change in the influence of substituents X on the pK_d for reactions (1) and (2) on passing from the gas phase to a polar solvent S is determined to a first approximation by the change in the free energy of solvation of the ions A^- and BH^+, which is due to the presence of the charge† and includes both the contribution ΔG_s^S.

† This quantity represents the solvation energy of ions A^- and BH^+, from which the neutral component, assumed equal to the solvation energy of the neutral species HA or B, has been subtracted[11,33]. It has been called[11,33] the "electrostatic" [11] or "electrical" [33] component, having in view solvation caused by the charge of the ion, i.e. solvation due to the purely electrostatic interaction and the formation of a hydrogen bond; we believe that this component is best referred to as the "solvation energy determined by the charge" and that it should be designated by $\Delta G_s^S(I^\pm)_{el+hb} = \Delta G_s^S(I^\pm)_{el} + \Delta G_s^S(I^\pm)_{hb}$.

$.(I^\pm)_{el}$ due to electrostatic solvation and the contribution $\Delta G_s^S(I^\pm)_{hb}$ due to the formation of the hydrogen bonds $A^-...HS$ and $BH^+...S$:

$$1.36(\delta p K_d^g - \delta p K_d^S) = \delta \Delta G_d^S (I^\pm)_{el} + \delta \Delta G_d^S (I^\pm)_{hb},$$

where the operator δ [4,17,18] denotes a change in the substituent, for example, $\delta pK_d(BH^+) = pK_d(XBH^+) - pK_d(BH^+)$. In order to elucidate the contribution of each of these components, the changes in δpK_d on passing from the gas phase to nitromethane (incapable of forming a hydrogen bond) and from the gas phase to water (forming strong hydrogen bonds) are considered in Tables 3 and 4:

$$\alpha^{NM} = (\delta p K_d^g - \delta p K_d^{NM})/(\delta p K_d^g - \delta p K_d^W).$$

Bearing in mind the limited number of known values of δpK_d for the same X in different media (for example, for aliphatic amines in the gas phase and in solutions), the quantities δpK_d can be conveniently expressed in terms of the values of ρ in the Hammett and Taft equations ($\delta pK_d^S = -\rho^S\sigma_X$):

$$\alpha^{NM} = (\rho^g - \rho^{NM})/(\rho^g - \rho^W).$$

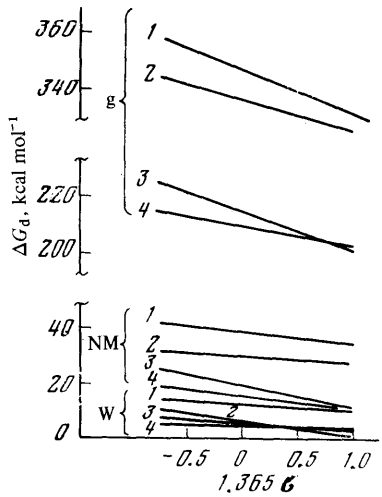


Figure 1. Schematic representation of the Hammett relations between the ΔG_d for the acids XC_6H_4OH (line *1*), XC_6H_4COOH (line *2*), $XC_5H_4\overset{+}{N}H$ (line *3*), and $XC_6H_4\overset{+}{N}H_3$ (line *4*) in the gas phase (g), nitromethane (NM), and water (W) and the σ constants of the substituents (according to the data in Tables 2, 3, and 4).

The data for ammonium cations of different structure in the gas phase, nitromethane, and water are compared in Table 3. For series 1–3, the values of ρ in nitromethane are much closer to those in water than in the gas phase; the values of α^{NM} show that the decrease of ρ on passing from the gas phase to nitromethane is 73–80% of the corresponding change in ρ on passing from the gas phase to water. Consequently the specific solvation of ammonium cations with formation of the $\overset{+}{N}H...OH_2$ hydrogen bond is responsible for only a small proportion (1/5–1/4) of the weakening of the influence of substituents in the gas phase → water transition and a major proportion of this effect is caused by the purely electrostatic hydration of the ammonium cations.

An interesting feature of amines is that, when $pK_d - \Sigma\sigma^*$ plots based on the variables of the Taft equation are constructed, the points for primary, secondary, and tertiary amines in the gas phase fit on a single straight line to a first approximation[9] #, while the points for the amines in water give rise to different straight lines[79,80]; the values of pK_d increase in the sequence $X_3\overset{+}{N}H < X_2\overset{+}{N}H_2 < X\overset{+}{N}H_3 < \overset{+}{N}H_4$, which is usually explained[9,79-81] by the formation of hydrogen bonds with different numbers of hydrogen atoms in the ammonium cations. According to the results already examined, the change in the degree of hydration of substituted ammonium cations must be determined not by hydrogen bonding but by electrostatic solvation and the relations between pK_d and $\Sigma\sigma^*$ for water and nitromethane should be similar. This conclusion has been confirmed by the data of Korolev et al.[27]: the distances between the $pK_d - \Sigma\sigma^*$ straight lines for $X_3\overset{+}{N}H$, $X_2\overset{+}{N}H_2$, and $X\overset{+}{N}H_3$ are similar for both solvents. Comparison of the basicities of the amines in the two solvents leads to the same results (see Section IV).

Consequently, a major proportion of the differences between the $pK_d - \Sigma\sigma^*$ straight lines for the conjugate acids of primary, secondary, and tertiary amines is caused by the electrostatic solvation of the ammonium cations in water and not by the number of $\overset{+}{N}H\ldots OH_2$ hydrogen bonds formed; it has been shown[11] that the increase in the degree of electrostatic solvation in the sequence $X_3\overset{+}{N}H < X_2\overset{+}{N}H_2 < X\overset{+}{N}H_3 < \overset{+}{N}H_4$ can be explained by the decrease of the effective radius of the cations, which is determined by the size of the cations and the degree of asymmetry of their charges.

These results show that the weakening of the influence of substituents on the pK_d and the differentiation of the basicities of the series of X_3N, X_2NH, and XNH_2 amines on passing from the gas phase to water are determined mainly by the change in the degree of non-specific electrostatic hydration of the ammonium cations. This conclusion is unexpected, because in most studies (specially devoted to this subject) it has been claimed up to the present time (see, for example, Refs.17–20, 81, and 96) that the above characteristics of the behaviour of amines in water are caused by the formation of the $\overset{+}{N}H\ldots OH_2$ hydrogen bonds§. However, the data presented above agree with those of Aue et al.[11], who concluded that the additional (compared with the metal cations or $X_4\overset{+}{N}$) interaction of the $\overset{+}{N}H_4$ ion with water is small and amounts to ~2 kcal mol^{-1} per hydrogen atom, while the decrease of the hydration energy in the successive transitions from $\overset{+}{N}H_4$ to $Me_4\overset{+}{N}$ is ~6–8 kcal mol^{-1} per hydrogen atom.

The data presented below (Table 5) confirm these conclusions. Indeed, the differences between the solvation energies of the $\overset{+}{N}H_4$, $Me\overset{+}{N}H_3$, $Me_2\overset{+}{N}H_2$, and $Me_3\overset{+}{N}H$ ions in solvents differing very greatly in their capacity for the formation of $\overset{+}{N}H\ldots S$ hydrogen bonds vary in the range 1–2 kcal mol^{-1} and, as might have been expected, they increase only slightly as the $\overset{+}{N}H\ldots S$ hydrogen bonds are strengthened in the sequence nitromethane, water, DMSO.

Inspection of the data in Table 4 for neutral OH-acids shows that their values of α^{NM} are in the range 0.5–0.8, i.e. that a considerable proportion of the weakening of the influence of substituents on the pK_d of the acids HA on passing from the gas phase to water is caused by the electrostatic solvation of the ions A^- in the aqueous medium. For benzoic acids and phenols, this proportion is 80%. Consequently, contrary to the widely held view[10,62], the $XC_6H_4COO^-\ldots HOH$ and $XC_6H_4O^-\ldots HOH$ hydrogen bonds are responsible for only 1/5 of the decrease of ρ in the gas phase → water transition¶.

We may note that McMagon and Kebarle[10] infer the degree of solvation of anions in water and APS from the factor by which ρ^g is greater than ρ^W and ρ^{APS}. However ρ^S is none other than ρ^g decreased as a result of the solvation of the ions; therefore in elucidating the solvation effects, one must consider not the factor by which ρ^W and ρ^{APS} have been reduced compared with ρ^g but the actual amount of the reduction. For example, for the XC_6H_4COOH series ($\rho^g = 10.6$, $\rho^{NM} = 2.55$, and $\rho^W = 1.00$), one must compare the differences $\rho^g - \rho^W = 10.6 - 1.00 = 9.6$ and $\rho^g - \rho^{NM} = 10.6 - 2.55 = 8.00$, which are fairly close, and not the ratios $\rho^g/\rho^W = 10.6/1 = 10.6$ and $\rho^g/\rho^{NM} = 10.6/2.55 = 4.2$, which differ considerably.

The possibility of a marked change in the degree of electrostatic solvation of the anions in APS follows from the results of studies[102-104] where the solvation of the halide, XO^-, $XC_6H_4O^-$, and $XC_6H_4COO^-$ ions was considered in DMSO, which is incapable of behaving as a hydrogen donor on formation of a hydrogen bond.

The significant role of the electrostatic solvation of the ions A^- and BH^+ in the decrease δpK_d on passing from the gas phase to water is due to the fact that ~80% of the entire solvation energy of ions in polar solvents (particularly in water) is determined by their electrostatic solvation[16]. The substituents X, which intensify (or weaken) the localisation of the charge in the organic ion, increase (or diminish) both the degree of electrostatic solvation[31] and the degree of ion solvation via hydrogen bonding[19]. Both these effects decrease δpK_d, but the much greater energy of the electrostatic solvation of ions explains its considerable role in the weakening of the influence of the substituent X on the pK_d in water. The

---

It has been observed[15] that the points of alkyl substituents on this approximate straight line, common to alkyl and polar (electronegative) substituents, form linear groups with an increased slope, which has also been observed for other series for both the gas phase[9,84] and for solutions[35,85-88]. It has now been established that the effects of alkyl substituents are of a different type compared with the inductive influence of polar substituents[1] and that the effects of all groups cannot be described by a single Taft equation[21,35,89-94], i.e. in plotting pK_d against $\Sigma\sigma^*$ polar substituents should be used[21,35,93,94]. Bearing in mind that the points for amines with polar substituents in the gas phase do not exhibit a tendency towards the formation of individual straight lines, we think it most reasonable to consider the $\Delta G_d^g - \Sigma\sigma^*$ correlation for ammonium cations as an approximately single straight line[9] distorted by the specific effects of hydrocarbon substituents (for example, the effect of the polarisability of alkyl substituents[9,14,85,95]). Despite these distortions, the values of ρ^* obtained in this way[9] for amines (6.5) and alcohols (7.0) in the gas phase are apparently correct, since an approximate estimate of the transmission of only the inductive effect in the gas phase leads to similar values of ρ^* for these series (increased by ~15–20%; calculated from the data of Taft et al.[85]).

§ The view has been expressed[15,97] that the role of solvation in the changes of the relative basicities of amines in water is small.

¶ It has been shown recently[101] that the interaction of substituted pyridinium ions and phenoxides with a single water molecule in the gas phase (with formation of the $XC_5H_4\overset{+}{N}H\ldots OH_2$ and $XC_6H_4O^-\ldots HOH$ hydrogen bonds) leads to a much smaller (by a factor of ~5) weakening of the influence of substituents than the solvation of these ions in aqueous solution.

cause of the change in the degree of electrostatic solvation becomes clear[31,105] from an examination of the Born equation [Eqn.(4)]: the introduction of a substituent capable of delocalising the charge (for example, of an electron acceptor into the anion A^-) increases the effective ionic radius and leads to a corresponding decrease of the degree of electrostatic solvation of the ion. This effect is always directed towards the compensation of the influence of the substituent on pK_d.[105]

IV. THE INFLUENCE OF SOLVATION VIA HYDROGEN BONDING ON THE RELATIVE STRENGTHS OF ORGANIC ACIDS IN APROTIC POLAR SOLVENTS AND WATER

Examination of the data of the previous section shows that the change in the strength of acids and of their sensitivity to the influence of substituents on passing from the gas phase to polar solvents is determined mainly by the non-specific electrostatic solvation of ions. However, on passing from one polar solvent to another, the degree of electrostatic solvation of ions changes very little[16,106] and the difference in the specific solvation of ions, which is to a large extent caused by the formation of hydrogen bonds, may become of primary importance. In order to elucidate the role of hydrogen bonds, it was of interest to compare different types of acids in polar solvents with markedly different capacities for the formation of hydrogen bonds, for example, in water, DMSO, and nitromethane:

HB	A^-...HS	BH^+...S
Water	s.	s.
Dimethyl sulphoxide	v.w.	v.s.
Nitromethane	v.w.	v.w.

Notation: s., v.w., and v.s. denote strong, very weak, and very strong hydrogen bonds.

The experimental data obtained in the last ten years for DMSO and nitromethane (Tables 6 and 7) permit such a comparison[107]. We may note that if the specific solvation of the ions A^- and BH^+ [Eqns.(1) and (2)] were absent from all the solvents or were the same, then the points for all types of acids on the plot of pK_d^S against $pK_d^{S_1}$ should fall on a single straight line to a first approximation. The results of a comparison of the pK_d for 15 series of neutral and cationic oxygen, nitrogen, phosphorus, and carbon acids in these solvents, presented in Figs.2–4 and Tables 6–8, show that each structural series gives rise to an individual straight line displaced relative to the other series and having a slope different from unity. Consequently, each class of acids in the given solvent has a characteristic solvation energy, different from those of the other classes and depending on the substituents, the differences in the positions of the straight lines for different types of acids being fairly large (up to 10 pK units; see Fig.3).

Examination of the data in Fig.2 and Table 6 for the neutral acids HA (series 1–5) shows that the acids can be arranged in the following sequence in terms of the displacement relative to the pK_d^W axis (for example, for $pK_d^{NM} = 16$):

$$pK_d^W: XCOOH \ll XC_6H_4COOH < XC_6H_4OH < X_2NH \simeq X_3CH.$$

For $pK_d^{DMSO} = 10$, the acids HA give rise to a similar sequence of the plots of pK_d^{DMSO} against pK_d^W (Fig.3 and Table 7):

$$pK_d^W: XCOOH \ll XC_6H_4COOH < XC_6H_4OH < X_2NH < X_3CH.$$

This behaviour is explained by the fact that, in contrast to nitromethane and DMSO, water is a fairly powerful hydrogen donor in the formation of the A^-... HOH hydrogen bonds. This leads to additional stabilisation in water of anions with a localised charge and to a decrease of the pK_d of their conjugate acids in water. Thus the lowest values of pK_d in water are those of carboxylic acids in the conjugate bases of which (carboxylates) the charge is localised on the carboxylate group; on passing to phenoxides, where the degree of delocalisation of the charge is greater[10,29], and A^-...HOH hydrogen bond is weakened, and the pK_d for phenols are higher. The A^-...HOH hydrogen bond is weaker still for NH-acids (polynitroarylamines) and CH-acids (9-substituted fluorenes), where the charge on the anions is even more localised owing to the smaller electronegativity of the nitrogen and carbon atoms and the "electron withdrawing" influence of the nitrogroups.

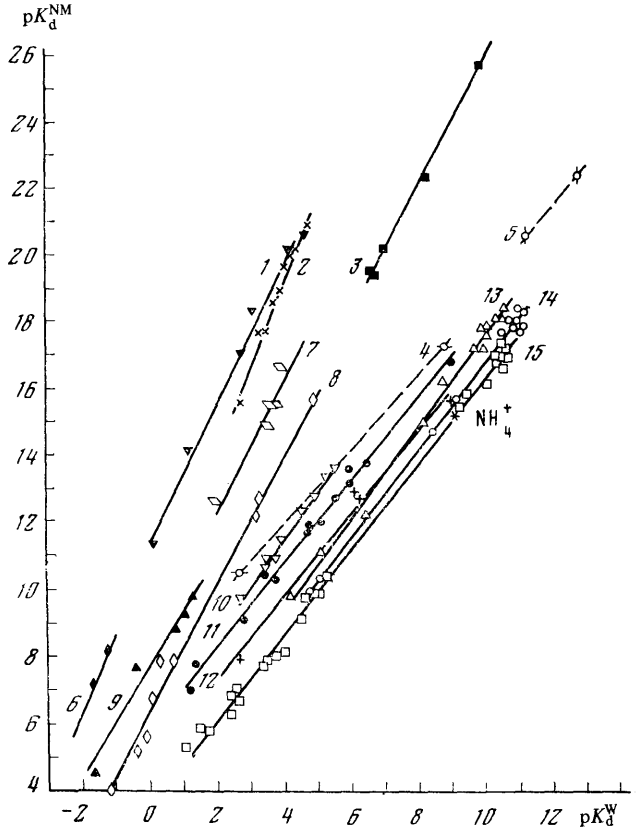


Figure 2. Relations between pK_d in nitromethane and water[65,107,109,112]: *1*)–*15*) see Table 6.

The intensification of ion solvation with formation of hydrogen bonds is known to weaken the influence of substituents of the pK_d,[3,61] which should lead to an increase of the slope R of the plots of pK_d^{NM} and pK_d^{DMSO} against pK_d^W. The data in Tables 6 and 7 show that the values of $R^{W,NM}$ and $R^{W,DMSO}$ to

a first approximation obey this rule for all the series (except XCOOH)#:

$$R^{W,NM}: XC_6H_4COOH\ (2.6) > XC_6H_4OH\ (1.95) > X_2NH\ (\sim 1.1) \sim X_3CH\ (\sim 1.2);$$
$$R^{W,DMSO}: XC_6H_4COOH\ (2.45) > XC_6H_4OH\ (2.15) > X_2NH\ (1.55) \geqslant X_3CH\ (1.45).$$

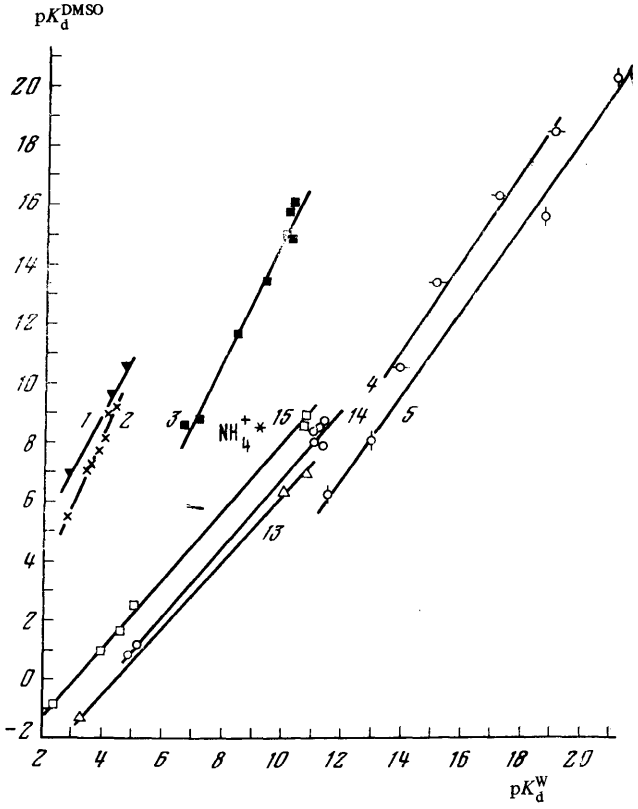


Figure 3. Relations between pK_d in dimethyl sulphoxide and water[65,107]: *1*)–*5*) and *13*)–*15*) see Table 7.

Taking into account the very weak ability of nitromethane and DMSO to function as hydrogen donors in the formation of hydrogen bonds, one may expect that the points for all neutral acids on the plot of pK_d in these solvents (Fig.4) should lie on a single straight line with a slope close to unity. Examination of Fig.4 shows that this prediction holds only for oxygen acids: the XCOOH, XC_6H_4COOH, and XC_6H_4OH series give rise to closely spaced straight lines with a slope of approximately unity. As regards NH- and CH-acids, their pK_d in DMSO are greatly reduced compared with OH-acids. The NH- and CH-acids investigated, forming anions with a highly delocalised charge, are apparently additionally stabilised in DMSO as a result of a disperson interaction[3], which is determined by the increased polarisability of DMSO compared with nitromethane[2]. This hypothesis is consistent with available data showing that the dispersion stabilisation of the carbanions in DMSO can lead to a decrease of the pK_d for CH-acids in DMSO by several pK units[61]. This factor must operate also in the correlation between pK_d in DMSO and water (Fig.3), where, together with the factor associated with the formation of the $A^-...HOH$ hydrogen bond, it leads to a decrease of pK_d for NH- and CH-acids in DMSO by up to 12 pK units compared with OH-acids.

Table 7. Parameters of the relations[107] between the pK_d for acids in DMSO [22,26,70,72,73,100] and water[22,73,77]: $pK_d^{DMSO} = R^{W,\,DMSO} pK_d^W + b$.

No.	Series	$R^{W,DMSO}$	$-b$	r	s	n	pK_d^W for $pK_d^{DMSO} = 10$
			Neutral acids				
1	XCOOH	1.94±0.07	−3.32	0.999	0.09	3	3.4
2	XC_6H_4COOH	2.43±0.13	−0.61	0.993	0.17	7	3.9
3	XC_6H_4OH	2.14±0.10	4.14	0.993	0.39	8	6.6
4	X_2NH *	1.55±0.15	8.17	0.990	0.60	4	11.7
5	X_3CH *	1.46±0.09	8.52	0.997	0.67	4	12.7
			Cationic acids				
13	$X_3\overset{+}{N}H$ *	1.14±0.04	3.03	0.999	0.21	3	11.4
14	$X_2\overset{+}{N}H_2$ *	1.19±0.04	2.94	0.997	0.30	7	10.9
15	$X\overset{+}{N}H_3$ *	1.18±0.02	1.67	0.999	0.14	6	9.9

* See footnote *a*, *b*, and *g* to Table 6.

Table 8. Parameters of the relations[107] between the pK_d for acids in nitromethane[28,29,65,107] and DMSO [22,26,70,72,73,100,107]: $pK_d^{NM} = R^{DMSO,\,NM} pK_d^{DMSO} + b$.

No.	Series	$R^{DMSO,NM}$	b	r	s	n	pK_d^{DMSO} for $pK_d^{NM} = 16$
			Neutral acids				
1	XCOOH	0.99±0.16	8.30	0.987	0.43	3	7.8
2	XC_6H_4COOH	1.13±0.06	7.23	0.994	0.18	7	7.8
3	XC_6H_4OH	0.94±0.05	9.54	0.997	0.26	4	6.9
4	X_2NH *	0.8**	13.6**	—	—	2	3.0**
5	X_3CH *	1.0**	13.0**	—	—	2	3.3**
			Cationic acids				
13	$X_3\overset{+}{N}H$ *	1.08±0.05	8.47	0.994	0.38	7	7.0
14	$X_2\overset{+}{N}H_2$ *	1.08±0.01	6.73	1.000	0.11	7	8.6
15	$X\overset{+}{N}H_3$ *	1.12±0.01	4.81	1.000	0.13	6	10.0

*See footnotes *a*, *c*, and *g* to Table 6.

**Approximate data.

Proceeding now to the consideration of cationic acids BH^+, we may note that, according to the results of the previous Section, the $\overset{+}{N}H...OH_2$ hydrogen bonds should not play a major role in increasing the values of pK_d^W in the sequence $X_3\overset{+}{N}H < X_2\overset{+}{N}H_2 < X\overset{+}{N}H_3 < \overset{+}{N}H_4$. Examination of the relation between pK_d^{NM} and pK_d^W for $\overset{+}{N}H$-acids (Fig.2, series 13–15) confirms this conclusion, since primary, secondary, and tertiary amines form comparatively closely spaced straight lines (the distances between them are 0.3–0.5 of a pK unit, while the distance between the $pK_d^W - \Sigma\sigma^*$ straight lines is 1.1–2.5

The cause of the lower slope for the XCOOH series compared with XC_6H_4COOH was examined in Section V.

pK units). For DMSO, which is a much weaker hydrogen acceptor in the formation of a hydrogen bond than water, the influence of the number of $\overset{+}{N}H...OSMe_2$ hydrogen bonds is more appreciable: when pK_d^{NM} is plotted against pK_d^{DMSO} and pK_d^{DMSO} is plotted against pK_d^{W}, the straight lines of amines are displaced along the pK_d^{DMSO} axis in such a way that the values of pK_d^{DMSO} decrease in the sequence $\overset{+}{N}H_4 > X\overset{+}{N}H_3 > X_2\overset{+}{N}H_2 > X_3\overset{+}{N}H$ (Figs. 3 and 4).

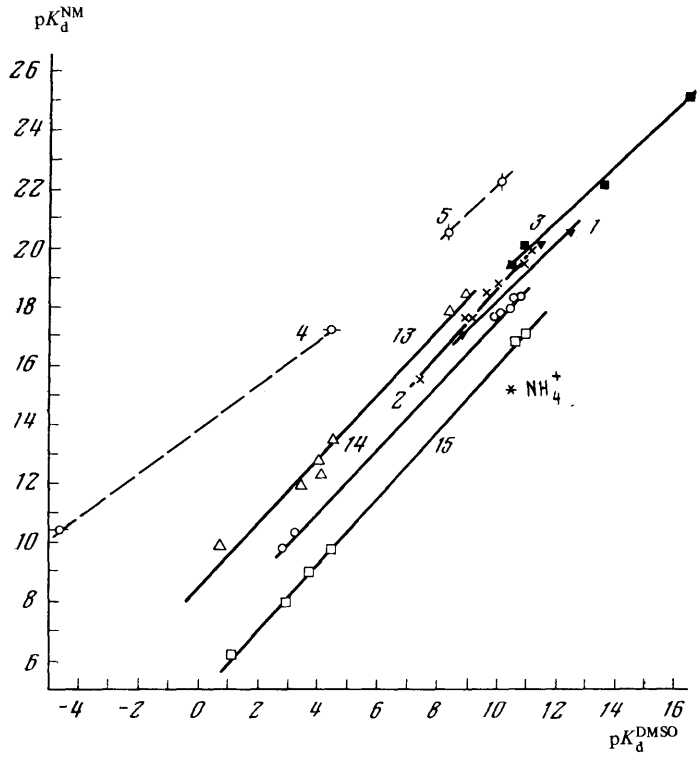


Figure 4. Relations between pK_d in nitromethane and dimethyl sulphoxide[65,107]: *1*)–**5**) and *13*)–*15*) see Table 8.

In contrast to OH-acids, where a significant increase in sensitivity to the influence of substituents is observed on passing from water, forming $A^-...HOH$ hydrogen bonds, to APS incapable of such solvation [$R^{W,S} = 2.0–2.6$ for S = nitromethane, DMSO, acetonitrile, or DMF (Table 4)[72,100]], for $\overset{+}{N}H$-acids the difference between water and nitromethane, which differ very markedly as regards their capacity for the formation of the $\overset{+}{N}H...S$ hydrogen bond, is small [$R^{W,NM} = 1.3–1.4$ (Table 3)]. Furthermore, the decrease of $R^{W,S}$ for $\overset{+}{N}H$-acids in the sequence acetonitrile (1.3-calculated from Korolev's data[65]) ≅ nitromethane (1.3) > DMSO(1.17) > water (1.0) agrees satisfactorily with the slight increase of the dielectric constants of the solvents in this sequence (Table 1). The data obtained confirm the conclusion that the $\overset{+}{N}H...OH_2$ hydrogen bonds play a very insignificant role in the decrease δpK_d for $\overset{+}{N}H$-acids in an aqueous medium. The increased energy of the hydrogen bonds formed by the anions of OH-acids ($XO^-...HOH$, $XCOO^-...HOH$) compared with the energy of the $\overset{+}{N}H...OH_2$ bond can apparently be explained by the considerable localisation of the negative charge on one or two electronegative oxygen atoms in these anions, while in $\overset{+}{N}H$-acids the positive charge is either distributed between the four hydrogen atoms in $\overset{+}{N}H_4$ or is delocalised by virtue of the substituent in $X_n\overset{+}{N}H_{4-n}$ (for example, the charge on the $\overset{+}{N}H$ group in $Me_3\overset{+}{N}H$ is only 0.3).[114]

The fact that the relative values of pK_d for pyridinium cations in water are lower by 0.6–1.0 of a pK unit than for tertiary ammonium cations (Fig. 2, series 11 and 13) is probably due to the difference between the capacities for the formation of hydrogen bonds: the $\rangle N...HOH$ bond is more favourable than $X_3N...HOH$. This conclusion is consistent with the results of a study[115] of the formation of complexes of pyridines and tertiary amines with *p*-fluorophenol. The basicity of 2,4-diamino-*sym*-triazines in water (Fig. 2, series 10; the proton adds to the ring nitrogen atom[109]) is lower by a further 0.4–0.7 of a pK unit, which can apparently be explained by the increased stabilisation of the bases in water via the formation of an N...HOH bond with several nitrogen atoms of the heterocycle and the amino-groups; the energy of these hydrogen bonds should diminish greatly after protonation. The results obtained show that, within the limits of the same type of acids, the positions of the straight lines for acids of different structure can be determined by the differences between the solvation of species without a formal charge.

Examination of the relations between pK_d^{NM} and pK_d^{W} for the cationic acids BH^+ of different types (Fig. 2, series 6–13) shows that they are displaced along the pK_d^{W} axis, forming the series

$$pK_d^W: X_3\overset{+}{P}OH < X_3\overset{+}{A}sOH < X_2C{=}\overset{+}{O}H \simeq XC_5H_4\overset{+}{N}OH < X_3\overset{+}{N}H \simeq X_3\overset{+}{P}H.$$

It is noteworthy that, in contrast to $\overset{+}{N}H$- and $\overset{+}{P}H$-acids, the conjugated bases of the $\overset{+}{O}H$-acids ($E{=}O - E^+{-}O^-$, where $E = \rangle P$, $\rangle As$, $\rangle N$, or $\rangle C$) carry a considerable partial negative charge localised on the electronegative oxygen atom, which cannot be stabilised by the formation of hydrogen bonds, with nitromethane, while in water they are very effectively solvated with formation of the $E^+{-}O^-...HOH$ bond. As a result of this, $\overset{+}{O}H$-acids exhibit an additional acidity in water compared with $\overset{+}{N}H$- and $\overset{+}{P}H$-acids. The increase of the acidity in water of the $\overset{+}{O}H$-acids in the series $\overset{+}{N}OH \cong \overset{+}{C}OH < \overset{+}{A}sOH < \overset{+}{P}OH$ can evidently be explained by the increased tendency towards the formation of $E^+{-}O^-...HOH$ hydrogen bonds in the series of bases $\overset{+}{N}{-}O^- \cong C{=}O < As{=}O < P{=}O$. This series is consistent with the relative increase of the strength of the hydrogen bonds between the above bases and *p*-fluorophenol; for example, for $pK_d^W \cong 0$, the enthalpies of formation of complexes with *p*-fluorophenol are $\overset{+}{N}{-}O^-$ (6.7 kcal mol^{-1}) ≦ C=O (7.0–7.1 kcal mol^{-1}) < P=O (8.7 kcal mole^{-1}).[116]

The slope of the plots of pK_d^{NM} against pK_d^{W} for the cationic acids BH^+ increases, as is to be expected, with increase in the degree of hydration of the conjugated bases via the formation of B...HOH hydrogen bonds (Table 6):

$$R^{W,NM}: X_3\overset{+}{P}H\,(1.2) \simeq X_3\overset{+}{N}H\,(1.2–1.3) < XC_5H_4\overset{+}{N}OH\,(1.65) \leqslant$$

$$\leqslant X_2C{=}\overset{+}{O}H\,(1.85) < X_3\overset{+}{A}sOH\,(1.95) < X_3\overset{+}{P}OH\,(2.4).$$

Thus, comparison of the strengths of the organic acids HA and BH^+ of different structure in water, DMSO, and nitromethane shows that the $A^-...HOH$ and B...HOH hydrogen bonds have an appreciable influence on their pK_d, increasing their acidity and weakening their sensitivity to the effects of substituents with increasing strength of the hydrogen bond,

which is associated with the increased localisation of the negative charge in the conjugate bases A^- and B; the influence exerted by the $BH^+...OH_2$ hydrogen bond is much smaller. The enhanced acidity of CH- and NH-acids in DMSO is consistent with additional dispersion stabilisation of the anions with a delocalised charge in this solvent.

V. THE INFLUENCE OF THE MEDIUM ON THE TRANSMISSION OF ELECTRONIC EFFECTS VIA BRIDGE GROUPS

Tables 3 and 4 present the values of $R^{W,g}$ characterising the weakening of the transmission of the electronic effects of substituents to the reaction centre on passing from the gas phase to water and also the values of $R^{NM,g}$ and $R^{W,\tilde{N}M}$. These data[65] show that the $R^{W,g}$ increase with increasing size of the bridge group M in series 1,2, and 3,4 and 5, and 6 and 7 (Tables 3 and 4). The values of R in the neutral acids HA increase to a particularly marked extent: the introduction of the phenylene bridge group entails an increase of $R^{W,g}$ by a factor of 2.6–3.5 ($R^{NM,g}$ increases by a factor of 2–3). If carboxylic acids are regarded as OH acids with a CO bridge group, then, despite the different reaction centres, the values of $R^{W,g}$ increase monotonically in the series X–M–OH, where M = –, CO, C_6H_4, or C_6H_4CO (Table 4). The increase of $\delta pK_d^g/\delta pK_d^W$ with increase of n has also been observed for the compounds $CF_3(CH_2)_n\overset{+}{N}H_3$ ($n = 1,2,3$).[14]

The above data show that the effect under discussion is probably general. It can be accounted for qualitatively[14] on the basis of the Kirkwood–Westheimer theory[21], which takes into account the effective dielectric constant of the medium between the substituent and the charged reaction centre: the greater the distance between the polar substituent and the charged centre, the greater proportion of its interaction with the charge takes place via the solvent and the effective dielectric constant of the space transmitting the influence of the substituent will approach the dielectric constant of the solvent. The greater increase of $R^{W,g}$ than that of $R^{NM,g}$ in the series 4 and 5 and 6 and 7 in Table 4 as well as the comparatively small but appreciable increase (by a factor of ~1.2) of the values of $R^{W,\tilde{N}M}$ in the same series can be understood from the standpoint of this theory.

The data presented have a direct bearing on the question of the dependence of the transmission coefficient π' (characterising the ability of the bridge group M to transmit electrons[117]) on the medium. According to the initial postulate, π' is determined by the structure of the bridge M and should be independent of the medium[118–120]. Many experimental data are consistent with this hypothesis[117,121], but there are some which conflict with it[35,122]. The results presented above§ show that in the general case the ability of the group M to transmit electrons cannot be independent of the medium in which its determined; it should remain unchanged only in media with comparatively similar dielectric constants.

§ The values of ρ_I for series 1,4, and 6 can be calculated from the relation $\rho_I = 6.23\,\rho^*$ (which follows from $\sigma^* = 6.23\,\sigma_I$),[117] taking into account the fact that the ρ_I for series 5 and 7 (Koppel' and Karel'son[9]) (and probably also series 3) are close to the values of ρ in Tables 3 and 4, which makes it possible to find the transmission coefficient π' characterising the transmission of the inductive effect via the phenylene group; for example, $\pi'(C_6H_4) = \rho_I(7)/\rho_I(6) \cong \rho(7)/6.23\rho^*(6)$. Hence it follows that the ratio of the values of π' in two series is equal to the ratio of the values of R for the two series in the same media.

---o0o---

The data presented in this review show that comparison of the pK_d of substituted organic acids in the gas phase and in water with the pK_d in aprotic polar solvents (particularly in nitromethane) can yield important information about the characteristics of the solvation of these compounds. Thus the results demonstrate the decisive role of the non-specific electrostatic hydration of the ions A^- and BH^+ in weakening the effect of the substituents on the pK_d for the ammonium, anilinium, and pyridinium cations, benzoic acids, and phenols on passing from the gas phase to water and in the differentiation of the basicities of primary, secondary, and tertiary amines in water. The influence of hydrogen bonds on the acid–base properties of organic compounds of various types in water has been elucidated; it has been found that, for identical protonation constants, the tendency of charged and dipolar species A^- and B towards the formation of the hydrogen bonds $A^-...HOH$ and B...HOH increases with the localisation of the charge: $X_3C^- \leqslant X_2N^- < XC_6H_4O^- < XC_6H_4COO^-$ and $X_3P \cong X_3N < XC_5H_4\overset{+}{N}O^- \cong X_2C{=}O < X_3As{=}O < X_3P{=}O$. The role of the dispersion solvation of anions with a delocalised charge (X_3C^-, X_2N^-) in solvents such as DMSO has been demonstrated. An appreciable increase of the ratio ρ^g/ρ^W with increase of the size of the bridge group has been observed for different $\overset{+}{N}H$- and OH-acids, which is qualitatively consistent with the Kirkwood–Westheimer theory and indicates the dependence of the ability of the bridge group to transmit electrons on the medium.

There is no doubt that the study of acid–base properties in the gas phase and in non-aqueous solvents, which is developing at a high rate, will make it possible to elucidate in the future new characteristics of the solvation of organic molecules, which are very important for the explanation and prediction of reactions which are not only of theoretical interest but also play an important role in industry.

REFERENCES

1. M.I.Kabachnik, Uspekhi Khim., **48**, 1523 (1979) [Russ.Chem.Rev., No.9 (1979)].
2. A.J.Parker, Chem.Rev., **69**, 1 (1969).
3. L.M.Epshtein, Uspekhi Khim., **48**, 1600 (1979) [Russ.Chem.Rev., No.9 (1979)].
4. J.E.Gordon, "The Organic Chemistry of Electrolyte Solutions" (Translated into Russian), Izd.Mir, Moscow, 1979, p.379.
5. M.I.Vinnik, Uspekhi Khim., **35**, 1922 (1966) [Russ. Chem.Rev., No.11 (1966)].
6. J.B.Cumming and P.Kebarle, Canad.J.Chem., **56**, 1 (1978).
7. K.Hiraoka, R.Yamdagni, and P.Kebarle, J.Amer. Chem.Soc., **95**, 6833 (1973).
8. R.Yamdagni, T.B.McMagon, and P.Kebarle, J.Amer. Chem.Soc., **96**, 4035 (1974).
9. I.A.Koppel' and M.M.Karel'son, Reakts.Sposobn. Org.Soed., **11**, 985 (1975).
10. T.B.McMagon and P.Kebarle, J.Amer.Chem.Soc., **99**, 2222 (1977).
11. D.H.Aue, H.M.Webb, and M.T.Bowers, J.Amer. Chem.Soc., **98**, 318 (1976).
12. D.H.Aue, H.M.Webb, M.T.Bowers, Ch.L.Liotta, C.J.Alexander, and H.P.Hopkins, J.Amer.Chem. Soc., **98**, 854 (1976).
13. K.D.Summerhaus, S.K.Pollack, R.W.Taft, and W.J.Hehre, J.Amer.Chem.Soc., **99**, 4585 (1977).

14. R.W.Taft, in "Proton-Transfer Reactions", (Edited by E.Caldin and V.Gold), Chapman, London, 1975, p.31.
15. A.F.Popov and Zh.P.Piskunova, Symposium, "Problemy Fiziko-Organicheskoi Khimii" (Problems of Physical Organic Chemistry), Izd.Naukova Dumka, Kiev, 1978, p.3.
16. A.J.Parker, Electrochim.Acta, 21, 671 (1976).
17. E.M.Arnett, B.Chawla, L.Bell, M.Taagepera, W.J.Hehre, and R.W.Taft. J.Amer.Chem.Soc., **99**, 5729 (1977); **101**, 7141 (1979).
18. R.W.Taft, J.F.Wolf, J.L.Beauchamp, G.Scorrano, and E.M.Arnett, J.Amer.Chem.Soc., **100**, 1240 (1978).
19. E.M.Arnett, in "Proton-Transfer Reactions" (Edited by E.Caldin and V.Gold), Chapman, London, 1975, p.79.
20. E.M.Arnett and G.Scorrano, Adv.Phys.Org.Chem., **13**, 83 (1976).
21. J.Hine, "Structural Effects on Equilibria in Organic Chemistry", Wiley, New York, 1975, pp.35, 94, 204.
22. V.Palm (Editor), "Tablitsy Konstant Skorosti i Ravnovesiya Geteroliticheskikh Organicheskikh Reaktsii" (Tables of Rate Constants and Equilibrium Constants for Heterolytic Organic Reactions), Moscow, 1975, Vol.1(1).
23. M.K.Chantooni and I.M.Kolthoff, J.Phys.Chem., **79**, 1176 (1975).
24. M.Peips, U.Koppel, U.Pihl, and I.Koppel, Reakts. Sposobn.Org.Soed., **12**, 207 (1976).
25. C.D.Ritchie, in "Solute-Solvent Interactions" (Edited by J.F.Coetzee and C.D.Ritchie), Dekker, New York, 1976, p.229.
26. B.A.Korolev, T.V.Levandovskaya, and M.V.Gorelik, Zhur.Obshch.Khim., **48**, 157 (1978).
27. B.A.Korolev, M.A.Mal'tseva, A.I.Tarasov, and V.A.Vasnev, Zhur.Obshch.Khim., **44**, 864 (1974).
28. B.A.Korolev and E.I.Kashkovskaya, Zhur.Obshch. Khim., **49**, 909 (1979).
29. B.A.Korolev and E.I.Kashkovskaya, Zhur.Obshch. Khim., **49**, 2360 (1979).
30. C.M.Criss and M.Salomon, in "Physical Chemistry of Organic Solvent Systems" (Edited by A.K.Covington and T.Dickinson), Plenum Press, New York, 1973, p.253.
31. T.B.McMagon and P.Kebarle, J.Amer.Chem.Soc., **98**, 3399 (1976).
32. J.Badoz-Lambling and J.C.Bardin, Electrochim. Acta, **19**, 715 (1974).
33. I.M.Kolthoff, Anal.Chem., **46**, 1992 (1974).
34. R.P.Bell, "The Proton in Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1977, p.81.
35. V.Palm, "Osnovy Kolichestvennoi Teorii Organicheskikh Reaktsii" (Fundamentals of a Quantitative Theory of Organic Reactions), Izd.Khimiya, Leningrad, 1977, pp.106, 133, 258, 332.
36. V.Gutmann, "Coordination Chemistry in Non-Aqueous Solutions" (Translated into Russian), Izd.Mir, Moscow, 1971, p.30.
37. U.Mayer, Coord.Chem.Rev., **21**, 159 (1976).
38. R.H.Erlich and A.I.Popov, J.Amer.Chem.Soc., **93**, 5620 (1971).
39. T.Ogata, T.Fujisawa, N.Tanaka, and H.Yokoi, Bull. Chem.Soc.Japan, **49**, 2759 (1976).
40. I.Koppel and A.Paju, Reakts.Sposobn.Org.Soed., **11**, 121 (1974).
41. A.G.Burden, G.Collier, and J.Shorter, J.Chem. Soc., Perkin Trans.II, 1627 (1976).
42. L.J.Bellamy, H.E.Hallam, and R.L.Williams, Trans. Faraday Soc., **54**, 1120 (1958).
43. E.Greinacher, W.Luttke, and R.Mecke, Z.Elektrochem., **59**, 23 (1955).
44. P.J.Krueger and H.D.Mettee, Canad.J.Chem., **42**, 288 (1964).
45. R.S.Drago, B.Wayland, and R.L.Carlson, J.Amer. Chem.Soc., **85**, 3125 (1963).
46. I.M.Kolthoff and M.K.Chantooni, J.Phys.Chem., **76**, 2024 (1972).
47. D.Bauer and A.Foucqult, J.Electroanal.Chem., **67**, 19 (1976).
48. R.L.Benoit and C.Louis, in "The Chemistry of Non-aqueous Solvents" (Edited by J.J.Lagowski), New York, 1978, Vol.VA, p.64.
49. W.J.De Witte, L.Liu, E.Mei, J.L.Dye, and A.I.Popov, J.Solution Chem., **6**, 337 (1977); Spectrochim.Acta, **31A**, 697 (1975).
50. A.A.Orr, J.Paint.Technol., **47**, 45 (1975).
51. E.A.Kanevskii, V.B.Rengevich, and G.R.Pavlovskaya, Dokl.Akad.Nauk SSSR, **238**, 619 (1978).
52. L.N.Balyatinskaya and T.V.Kurchenko, Zhur. Obshch.Khim., **46**, 1113 (1976).
53. A.V.Iogansen, Teor.Eksper.Khim., 7, 302, 312 (1971).
54. M.-L.Josien and N.Fuson, J.Chem.Phys., **22**, 1169 (1954).
55. M.D.Joesten and L.J.Shaad, "Hydrogen Bonding", Dekker, New York, 1974, p.197.
56. H.E.Hallam and T.C.Ray, Nature, **189**, 915 (1961).
57. M.A.Coplan and R.M.Fuoss, J.Phys.Chem., **68**, 1181 (1964).
58. P.Walden and E.J.Birr, Z.Phys.Chem., **A163**, 321 (1933).
59. W.F.Baitinger, P.von R.Schleyer, T.S.S.R.Murty, and L.Robinson, Tetrahedron, **20**, 1635 (1964).
60. L.A.Yanovskaya, "Sovremennye Teoreticheskie Osnovy Organicheskoi Khimii" (Modern Theoretical Foundations of Organic Chemistry), Izd.Khimiya, Moscow, 1978, p.207.
61. C.D.Ritchie, in "Solute-Solvent Interactions" (Edited by J.F.Coetzee and C.D.Ritchie), Dekker, New York, 1969, p.219.
62. J.B.Cumming, M.A.French, and P.Kebarle, J.Amer. Chem.Soc., **99**, 6999 (1977).
63. C.Agami, Bull.Soc.chim.France, 869 (1974).
64. D.H.Aue, L.D.Betowski, W.R.Davidson, M.T.Bowers, P.Beak, and J.Lee, J.Amer.Chem.Soc., **101**, 1361 (1979).
65. B.A.Korolev, Zhur.Obshch.Khim., **49**, 2366 (1979).
66. B.A.Korolev, L.A.Osmolovskaya, and K.M.Dyumaev, Zhur.Obshch.Khim., **48**, 2358 (1978).
67. B.A.Korolev and B.I.Stepanov, Izv.Vys.Ucheb. Zaved., Khim.i Khim.Tekhnol., **11**, 1193 (1968).
68. B.A.Korolev, L.A.Osmolovskaya, and K.M.Dyumaev, Zhur.Obshch.Khim., **49**, 898 (1979).
69. J.F.Coetzee, Progr.Phys.Org.Chem., **4**, 45 (1967).
70. I.M.Kolthoff, M.K.Chantooni, and S.Bhowmik, J. Amer.Chem.Soc., **90**, 23 (1968).
71. M.K.Chantooni and I.M.Kolthoff, J.Amer.Chem. Soc., **92**, 7025 (1970).
72. M.K.Chantooni and I.M.Kolthoff, J.Phys.Chem., **80**, 1306 (1976).
73. V.Palm (Editor), "Tablitsy Konstant Skorosti i Ravnovesiya Geteroliticheskikh Organicheskikh Reaktsii" (Tables of Rate Constants and Equilibrium Constants for Heterolytic Organic Reactions), Moscow, 1976, Vol.2(1).

74. I.M.Kolthoff, M.K.Chantooni, and H.Smagowskii, Anal.Chem., **42**, 1622 (1970).
75. J.-J.Delpuech and D.Nicole, J.Chem.Research (M), 2762 (1978).
76. F.M.Jones and E.M.Arnett, Progr.Phys.Org. Chem., **11**, 263 (1974).
77. A.Albert and E.P.Serjeant, "Ionisation Constants of Acids and Bases" (Translated into Russian), Izd. Khimiya, Moscow, 1964.
78. E.M.Arnett and L.E.Small, J.Amer.Chem.Soc., **99**, 808 (1977).
79. H.K.Hall, J.Amer.Chem.Soc., **79**, 5441 (1957).
80. E.Folkers and O.Runquist, J.Org.Chem., **29**, 830 (1964).
81. F.E.Condon, J.Amer.Chem.Soc., **87**, 4485 (1965).
82. A.Fisher, W.J.Galloway, and J.Vaughan, J.Chem. Soc., 3591 (1964).
83. A.I.Biggs and R.A.Robinson, J.Chem.Soc., 388 (1961).
84. J.F.Wolf, R.H.Staley, I.Koppel, M.Taagepera, R.T.McIver, J.C.Beauchamp, and R.W.Taft. J.Amer. Chem.Soc., **99**, 5417 (1977).
85. R.W.Taft, M.Taagepera, J.L.M.Abboud, J.F.Wolf, D.J.De Frees, W.J.Hehre, J.E.Bartmess, and R.T.McIver, J.Amer.Chem.Soc., **100**, 7765 (1978).
86. A.P.Grekov and V.V.Shevchenko, Reakts.Sposobn. Org.Soed., **5**, 47 (1968).
87. A.Pihl, V.Pihl, and A.Talvik, Reakts.Sposobn.Org. Soed., **2**, 173 (1965).
88. B.A.Trofimov and I.S.Emel'yanov, Reakts.Sposobn. Org.Soed., **7**, 564 (1970).
89. M.Charton, J.Amer.Chem.Soc., **99**, 5687 (1977).
90. F.G.Bordwell, J.E.Bartmess, and J.A.Hautala, J.Org.Chem., **43**, 3095 (1978).
91. F.G.Bordwell and H.E.Fried, Tetrahedron Letters, **13**, 1121 (1977).
92. C.A.Grob and M.G.Schlegeter, Helv.Chim.Acta, **59**, 264 (1976).
93. C.D.Ritchie, J.Phys.Chem., **65**, 2091 (1961).
94. C.D.Ritchie and W.F.Sager, Progr.Phys.Org.Chem., **2**, 323 (1964).
95. J.I.Brauman and L.K.Blair, J.Amer.Chem.Soc., **92**, 5986 (1970).
96. I.M.Koshkina, Symposium, "Sovremennye Problemy Organicheskoi Khimii" (Modern Problems of Organic Chemistry), Izd.Leningrad.Gos.Univ., Leningrad, 1971, No.2, p.92.
97. N.G.Korzhenevskaya, G.D.Titskii, and E.V.Titov, Ukrain.Khim.Zhur., **45**, 350 (1979).
98. I.Koppel, L.A.Maretskaya, U.Koppel, and V.Pihl, Reakts.Sposobn.Org.Soed., **14**, 86 (1977).
99. I.Koppel, M.Karelson, and V.Palm, Reakts.Sposobn. Org.Soed., **10**, 497 (1973).
100. I.M.Kolthoff and M.K.Chantooni, J.Amer.Chem.Soc., **93**, 3843 (1971).
101. W.R.Davidson, J.Sunner, and P.Kebarle, J.Amer. Chem.Soc., **101**, 1675 (1979).
102. E.M.Arnett, L.E.Small, D.Oancea, and D.Johnston, J.Amer.Chem.Soc., **98**, 7346 (1976).
103. E.M.Arnett, D.E.Johnston, L.E.Small, and D.Oancea, Faraday Symp.Chem.Soc., No.10, 20 (1975).
104. E.M.Arnett, L.E.Small, R.T.McIver, and J.S.Miller, J.Amer.Chem.Soc., **96**, 5638 (1974).
105. P.Kebarle, in "Environmental Effects on Molecular Structure and Properties" (Edited by B.Pullman), Reidel, Dordrecht, 1976, p.81.
106. I.M.Kolthoff and M.K.Chantooni, J.Phys.Chem., **77**, 527 (1973).
107. B.A.Korolev, Zhur.Obshch.Khim., **50**, 841 (1980).
108. B.A.Korolev and M.A.Mal'tseva, Zhur.Obshch.Khim., **46**, 1605 (1976).
109. B.A.Korolev and M.A.Mal'tseva, Zhur.Obshch.Khim., **43**, 1556 (1973).
110. B.I.Stepanov, B.A.Korolev, and A.I.Bokanov, Zhur.Obshch.Khim., **39**, 316 (1969).
111. V.V.Yakshin, M.I.Tymonyuk, L.I.Sokal'skaya, and B.N.Laskorin, Dokl.Akad.Nauk SSSR, **247**, 128 (1979).
112. B.N.Laskorin, V.V.Yakshin, N.A.Lyubosvetova, and B.D.Chernokal'skii, Zhur.Obshch.Khim., **47**, 1118 (1977).
113. N.K.Skvortsov, G.F.Tereshchenko, B.I.Ionin, and A.A.Petrov. Zhur.Obshch.Khim., **43**, 981 (1973).
114. D.H.Aue, H.M.Webb, and M.T.Bowers, J.Amer. Chem.Soc., **98**, 311 (1976).
115. H.B.Yang and R.W.Taft, J.Amer.Chem.Soc., **93**, 1310 (1971).
116. E.M.Arnett, E.Mitchell, and T.Murthy, J.Amer. Chem.Soc., **96**, 3875 (1974).
117. Yu.A.Zhdanov and V.I.Minkin, "Korrelyatsionnyi Analiz v Organicheskoi Khimii" (Correlation Analysis in Organic Chemistry), Izd.Rostov.Gos.Univ., Rostov, 1966, pp.56, 185.
118. H.H.Jaffe, J.Chem.Phys., 21, 415 (1953).
119. Si-Jung Yeh and H.H.Jaffe, J.Amer.Chem.Soc., **81**, 3287 (1959).
120. V.Palm, Uspekhi Khim., **30**, 1069 (1961) [Russ. Chem.Rev., No.9 (1961)].
121. L.M.Litvinenko, V.A.Dadali, and B.N.Bespalyi, Ukrain.Khim.Zhur., **39**, 1020 (1973).
122. R.S.Cheshko, L.M.Litvinenko, V.A.Dadali, and Nguyen Thi Thanh, Ukrain.Khim.Zhur., **39**, 184 (1973).

Institute of Organic Intermediates
and Dyes (NIOPiK), Moscow

Translated from *Uspekhi Khimii*, **49**, 2086-2117 (1980) U.D.C. 539.192 + 194 + 196

The Structure of the Electronic Excitation of Molecules in Quantum-chemical Models

A.V.Luzanov

Methods for the analysis of the excited states of molecules and their electronic distribution are examined. The advantages of using procedures based on transition density matrices are noted. The application of the delocalisation numbers of the transition, reflecting the multiconfiguration nature of the electronically excited state, the excitation localisation numbers, providing a quantitative measure of the localisation of the transition in a particular molecular fragment, the interfragment charge transfer numbers, the atomic excitation energy indices, indicating the fraction of the molecular excitation energy which can be assigned to a given atom, etc., all of which have been introduced recently, are discussed. The structural-chemical factors favouring the isolation of the excitation of a single fragment are considered.
The bibliography includes 99 references.

CONTENTS

I. Introduction 1033
II. The interaction of the configurations and the transition operators in the theory of electronic spectra 1033
III. The configurational-orbital analysis of excited states. The special role of natural orbitals 1035
IV. The method of excitation localisation numbers 1037
V. Isolation of transitions at individual fragments and molecular structure 1039
VI. Analysis of charge transfer in the method of transition operators 1041
VII. Distribution of excitation energy among the structural elements of the molecule 1044

I. INTRODUCTION

The theoretical and applied aspects of molecular spectroscopy have been closely related for a long time to quantum-chemical studies on the excited states of molecules. The role of theory in the interpretation of spectroscopic experiments, which are so common in modern physicochemical research techniques, still remains important. The experimental difficulties in the direct estimation of the parameters of the electronic structure, which determine the real behaviour of molecular systems, are not the only explanation. In this field many fundamental concepts follow naturally primarily from the theory which permits, in principle, the understanding of all the details of the behaviour of the electron shell in any of its states and sometimes even in states which are not observed.

Such claims do not imply in any way that all the fundamental problems of the theory of molecules have already been solved. The obstacles to the determination of detailed electronic-nuclear wave functions are generally known. However, intensive use of approximate quantum-chemical models has undoubtedly played a positive role in the understanding of the excited state by workers in the field of spectroscopy as a tangible feature with a specified internal structure, which can be inferred from the corresponding wave function. The latter is usually represented by a fairly complex set of the coefficient $c_{\mu i}$ of the expansion of the molecular orbitals, the coefficients d_{pi} of the configurational interaction, etc. Unfortunately, the abundance of numerical data frequently conceals from the investigator the very structure for the investigation of which the entire computation has been undertaken. Furthermore, the idea of the delocalisation of electrons, which is natural for quantum mechanics as a whole, at one time in the past made it impossible for chemists to see the familiar autonomy of the fragments of complex molecules. In this connection, many theoreticians attempted, while retaining the quantum-chemical rules of construction, to interpret excited and other electronic molecular states in terms of the more readily understood terms of localisation, charge transfer, etc.[1-6] However, in this field, which is so important for the understanding of the nature of the electronic spectra of complex molecules, rigorously proved criteria or quantitative characteristics had not been developed until recently. In the present review an attempt is made to consider the tendency, established in recent years, to carry out such analysis on the basis of a structural-chemical interpretation of the excited states of molecules.

II. THE INTERACTION OF THE CONFIGURATIONS AND THE TRANSITION OPERATORS IN THE THEORY OF ELECTRONIC SPECTRA

The methods used hitherto in calculations on large organic molecules and in the interpretation of their spectroscopic properties have been discussed in detail in monographs[7-12] and in a review[13]. Here we shall consider only comparatively new methods of calculation using the transition density matrix, which will prove to be the main instrument in the version of the analysis of the excited states to which we shall give preference.

The wave function $|\Phi>$ of the ground state of the molecule must be constructed with obligatory allowance for the electron–electron interaction. In the Hartree–Fock model, which has served as a standard hitherto, this is achieved by representing $|\Phi>$ in terms of a determinant of occupied molecular spin-orbitals $|\phi_1>, \ldots |\phi_i>, \ldots |\phi_N>$. Then, according to the Brillouin theorem[14], any determinant $|\Phi_{i\to p}>$, obtained from $|\Phi>$ by replacing a self-consistent spin-orbital $|\phi_i>$ by a vacant spin-orbital $|\phi_p>$, has zero matrix elements of the Hamiltonian H with the ground state $|\Phi>$:

$$\langle\Phi|H|\Phi_{i\to p}\rangle=0; \quad p=N+1, \ldots, M, \tag{1}$$

where M is the dimension of the spin-orbital basis set. Consequently the set of all the functions $|\Phi_{i\to p}>$ can be regarded as a basis set of N electronic functions on which the space of all possible excited states $|\Phi_*>$ has been superimposed

and, by virtue of Eqn.(1), the fulfilment of the natural condition of "excitation" is guaranteed for the latter:

$$\langle\Phi|H|\Phi_*\rangle=0. \quad (2)$$

After finding the self-consistent orbitals of the ground state, it is easy to achieve a configurational mixing of the type

$$|\Phi_*\rangle=\sum_{i=1}^{N}\sum_{p=N+1}^{M} d_{pi}|\Phi_{i\to p}\rangle, \quad (3)$$

which yields an approximation to the excited state made consistent with the Hartree–Fock description of the ground state $|\Phi\rangle$. The configurational coefficients d_{pi} as well as the excitation energy λ are then found from the secular equations for the configurational interaction matrix $||\langle\Phi_{i\to p}|H|\Phi_{j\to q}\rangle||$. This model of the excited state will be called the Tamm–Dancoff model, as is usually done in modern investigations of molecular theory (see, for example, Refs. 15–17) and the theory of the nucleus[18]. The semiempirical version of this model for π-electron systems is associated with the familiar studies by Pariser, Parr, and Pople and is also referred to as the PPP model, which has been discussed in detail[7,11,13].

PPP calculations on the electronic states of organic molecules are widely used at the present time, which is also due to the relative simplicity of the relevant computer programs[19,20]. Subsequently, in many instances, particularly for triplet energy states, attempts have been made to improve the results of the calculation by including higher doubly excited $|\Phi_{\substack{i\to p\\ j\to q}}\rangle$ configurations,[21–23] and even triply excited configurations[24].

New approaches based on the application of the transition density matrix have been used[25–29]. An equation for the Hermitian transition density matrix D in terms of the Tamm–Dancoff approximation, convenient for computational purposes, has been formulated[26]. Its spin-orbital generalisation can be represented[29] with the aid of the operator modulus of the Fock operator f and a projected antisymmetrised potential of the Coulombic interaction of the electrons g^A (12):

$$u(12)=\rho(1)\rho_\ominus(2)g^A(12)\rho_\ominus(1)\rho(2)+\rho_\ominus(1)\rho(2)g^A(12)\rho(1)\rho_\ominus(2), \quad (4)$$

where $\rho=\sum_{i=1}^{N}|\phi_i\rangle\langle\phi_i|$ is the density matrix of the ground Hartree–Fock state $|\Phi\rangle$, and $\rho_\ominus=\sum_{p=N+1}^{M}|\phi_p\rangle\langle\phi_p|=1-\rho$ is a matrix projected on to vacant one-electron states. The superoperator $\hat{\Pi}$, which generates another operator by acting on an operator D in accordance with the rule

$$\hat{\Pi}(D)=D\cdot|f|+|f|\cdot D+2\operatorname{Sp}_{(2)}u(12)D(2), \quad (5)$$

is introduced by means of these quantities.

The fundamental equation of the Tamm–Dancoff model can then be formulated in terms of the equations for the eigenvalues of the superoperator $\hat{\Pi}$, each eigenvector of which plays the role of a transitional matrix D of an excited state. The eigenvalue of the superoperator $\hat{\Pi}$ is the excitation energy λ:

$$\hat{\Pi}(D)=\lambda D. \quad (6)$$

The transition matrix D permits a representation of the type

$$D=\sum_{i=1}^{N}\sum_{p=N+1}^{M}(d_{pi}|\varphi_p\rangle\langle\varphi_i|+d_{pi}^*|\varphi_i\rangle\langle\varphi_p|), \quad (7)$$

where d_{pi} can be regarded as the configurational coefficients of the excited state $|\Phi_*\rangle$ of the type of Eqn.(3).

In the construction of $|\Phi_*\rangle$ condition (2) is not the only possible requirement, particularly since the approximation to the ground state $|\Phi\rangle$ does not as a rule satisfy the exact Schrödinger equation. For example, in the method based on the equations of motion without an explicit construction of a wave function for the ground state more accurate than the Hartree–Fock function it is possible to take into account, particularly in the calculation of the oscillator strengths, the correlation effects in the excited states which are not included in the Tamm–Dancoff method[30]. However, the lack of explicit wave functions or correct density matrices corresponding to them precludes in this instance a well-founded analysis of the excited states. Another approach to the construction of $|\Phi_*\rangle$ can be devised on the basis of a self-consistent perturbation theory, various aspects of which have been discussed[11,29,31].

The general relations of the quantum-mechanical perturbation theory contain the so-called energy denominators, which in the case of a perturbation of the ground state have the values of the excitation energies. Indeed, for the first correction $|\delta\Phi\rangle$ to the wave function $|\Phi\rangle$ arising from the perturbation δH, one can write (E is the energy of the system and I a unit operator)

$$(H-E)|\delta\Phi\rangle=-(I-|\Phi\rangle\langle\Phi|)\delta H|\Phi\rangle. \quad (8)$$

Here $H-E$ is the excitation operator with the eigenvalues $\lambda=E_*-E$. After reducing formula (8) to one-electron quantities, the operator $H-E$ is transformed into the superoperator $\hat{\Lambda}$ and the correction $|\delta\Phi\rangle$ is replaced by the one-electron transition operator corresponding to the N-electron Hermitian operator $|\delta\Phi\rangle\langle\Phi|+|\Phi\rangle\langle\delta\Phi|$.

The explicit form of the superoperator $\hat{\Lambda}$ for singlet states has been obtained[26]. Its relation with the random phase approximation, which constitutes a special case of the method of equations of motion, has been discussed[32,33]: on this basis, the theory of spin perturbations has been developed[34] and a perturbation theory has been devised for open shells in the unrestricted Hartree–Fock method[35]. The spin–orbital definition of $\hat{\Lambda}$ is similar in form to the formulation of the superoperator $\hat{\Pi}(5)$, but the potential $u(12)$ is now replaced by the half-sum $\frac{1}{2}[u(12)+\nu(12)]$, where $\nu(12)$ is a correlation operator describing particle–hole pair interactions of the electrons in the $|\phi_p\rangle$ and $|\phi_i\rangle$ states:

$$v(12)=\rho(1)\rho(2)g^A(12)\rho_\ominus(1)\rho_\ominus(2)+\rho_\ominus(1)\rho_\ominus(2)g^A(12)\rho(1)\rho(2).$$

The operator $\nu(12)$ is encountered in calculations on the correlation interaction, since it is in fact responsible for the mixing of $|\Phi\rangle$ with the doubly excited configurations, for the superposition of $|\Phi_*\rangle(3)$ on $|\Phi_{\substack{i\to p\\ j\to q\\ k\to r}}\rangle$, etc.[29,36] The presence of an additional term of this kind in the expression for $\hat{\Lambda}$ therefore indicates an indirect, average allowance for the correlations in relation to the Tamm–Dancoff approximation, although the number of variational parameters (the coefficients d_{pi}) is the same in the two instances. At the same time, for the functions $|\Phi_*\rangle$, constructed with the aid of $\hat{\Lambda}$, the explicit wave function parameter remains in the form of the same operator D, which carries all the necessary information about the excited state, constituting a superposition of singly excited configurations (3). As a result of this, the analysis of $|\Phi_*\rangle$ for the $\hat{\Pi}$ and $\hat{\Lambda}$ versions can be carried out in the same way.

The $\hat{\Lambda}$ matrix had previously been introduced in a different form by Thoules[37] in connection with the introduction into the self-consistent field theory of the concept of stable and unstable solutions which do and do not require respectively a local minimum in the Hartree–Fock energy E. A stable

solution arises only for a rigorously positive quadratic form made up of local second derivatives of E with respect to the parameters for small deviations from the self-consistent solution. The matrix of this quadratic form, which corresponds to the variational derivative $\delta^2 E/\delta\rho^2$, is the same as the supermatrix $\hat{\Lambda}$, and its eigenvalues λ, which appear as energy denominators in the perturbation theory, are therefore at the same time stability numbers of some kind for the Hartree–Fock model.

It has been suggested that in the case of closed electron shells the stability numbers for spin-free distortions of $|\Phi>$ be identified[26] with the singlet excitation energies and that in the case of triplet states the Tamm–Dancoff description be retained, which can be justified to some extent by taking into account the tendency not to change the spin properties of a triplet wave function[29]. However, it is easy to find all the spectroscopic series (singlet–singlet, triplet–triplet, transitions, etc.) solely with the aid of stability numbers, adopting in each case the lowest state of the specified multiplicity as the ground state for the given series.

Such calculations can be most simply carried out with the aid of the unrestricted Hartree–Fock method, as suggested by the present author and Umanskii[35,38]. For example, with the same parametrisation, it is possible to calculate satisfactorily the singlet–singlet transitions in many aromatic molecules with the aid of singlet stability numbers; the energy of the $S_0 \to T_0$ transition can be found from the difference between the total energy of S_0 and the energy of the T_0 state calculated by the unrestricted method (the unrestricted method yields as a rule the same value for S_0 as the restricted method), while the energy of the triplet–triplet absorption is identified with the triplet spin-free stability numbers of the self-consistent state T_0 (see Table 1).

Table 1. The Hartree–Fock stability numbers corresponding to the singlet and triplet transitions (in eV).

Compound	$^1A_{1g}^- \to {}^1B_{3u}^-$	$^1A_{1g}^- \to {}^1B_{2u}^+$	$^1A_{1g}^- \to {}^3B_{2u}^+$	$^3B_{2u}^+ \to {}^3B_{1g}^-$	$^3B_{2u}^+ \to {}^3A_{1g}$
Naphthalene	3.90 (4.0)	4.48 (4.4)	2.87 (2.6)	3.18 (3.1)	4.11
Anthracene	3.44 (3.5)	3.45 (3.3)	1.82 (1.8)	2.83 (2.9)	4.09
Pyrene	3.25 (3.4)	3.57 (3.6)	2.04 (2.1)	2.43 (2.4)	3.27 (3.0)
Perylene	3.56 (3.4)	3.06 (2.8)	1.64	2.51 (2.6)	2.91 (4.4)

Note. The experimental data are given in brackets[8,11].

III. THE CONFIGURATIONAL–ORBITAL ANALYSIS OF EXCITED STATES. THE SPECIAL ROLE OF NATURAL ORBITALS

We shall now turn to the main problem discussed in this review—the analysis of excited states described by the standard superposition (3) of singly excited configurations. In the majority of studies involving specific calculations on excited states the largest configurational coefficients d_{pi}, from which one can infer the degree of configurational interaction[39–41], are usually quoted. This type of representation of the excited state is in certain respects (for example, as regards the cumbersome nature of the formulation) inapt and non-universal.

A form of the representation of Φ_*, which is independent of the explicit form of the occupied and vacant orbitals employed, can be regarded as universal in the given instance. In fact, these orbitals can be chosen quite arbitrarily not only as canonical molecular orbitals, i.e. as the eigenvectors of a single-particle Hamiltonian (the Fock operator f), but also as the eigenvectors of any other operator which commutes with the density matrix of the ground state ρ. This implies that the occupied orbitals $|\phi_i>$ can be mixed with one another in an arbitrary fashion but their orthonormalisation must be retained (i.e. unitary transformations are carried out). The vacant orbitals $|\phi_p>$ can also be subjected to a unitary transformation to the same extent. It is important that such transformations of the orbital set do not cause an overall alteration of the excited state Φ_*, but the configuration coefficients d_{pi} and the individual configurations $\Phi_{i\to p}$ are then considerably distorted. Consequently the coefficients d_{pi} do not yield an invariant description of the structure of the excited state (3) in the general case.

It is natural to attempt to isolate from all possible sets $\{d_{pi}\}$ an optimum set, which has the fewest members among all those permissible. The maximum number of configurations $\Phi_{i\to p}$, when all d_{pi} are non-zero (the least desirable situation from our point of view), can be found readily: it is equal to the product of the number of occupied orbitals N and the number of vacant orbitals $M-N$. As a rule the number of spin–orbital basis functions M is equal to or almost equal to twice the number of electrons $2N$. With increase in the size of the molecule, i.e. with increase of N, the maximum possible number of configurations $N(M-N) \cong N^2$ therefore increases in accordance with a quadratic law. It is found that there always exists a set of orbitals which the number of configurations is significantly smaller than and does not exceed the number of electrons in the system, i.e. varies linearly with N. It has been shown[42] that the most compact set of this kind is the set of natural spin–orbitals of the excited state Φ_*.

In the general case the natural orbitals of a certain state are the eigenvectors of a one-particle density matrix ρ_1 of this state[11]. In terms of the Hartree–Fock approximation, $\rho_1 = \rho$, so that the spin–orbitals $|\phi_i>$ are natural for any set of occupied molecular orbitals. The Tamm–Dancoff approximation (3) is characterised, in accordance with the work of Luzanov[17] and Mestechkin and Gutyrya[27], by a density matrix ρ_1^* of the type

$$\rho_1^* = \rho + D^2(\rho_\ominus - \rho). \tag{9}$$

The definition of the matrix D in form (7) makes it possible to find the identity $D\rho = \rho_\ominus D$, whence it follows, taking into account $\rho^2 = \rho$, that the occupied and vacant orbitals can be selected from the very beginning in the form of natural orbitals of the excited state investigated, because

$$\rho_1^*\rho = \rho\rho_1^*.$$

The natural orbitals are at the same time the eigenvectors of the matrix D^2.

This type of natural orbital will be designated by $|\phi_\alpha>$, if it is occupied in the ground state Φ, i.e. $\rho = \sum_{\alpha=1}^{N} |\phi_\alpha><\phi_\alpha|$ and by $|\phi_{N+\alpha}>$ if the natural orbital is populated only in the excited state. The matrix D then assumes the following form in terms of the basis set of the natural orbitals introduced[42]:

$$D = \sum_{\alpha=1}^{N} d_\alpha (|\varphi_\alpha\rangle\langle\varphi_{N+\alpha}| + |\varphi_{N+\alpha}\rangle\langle\varphi_\alpha|), \tag{10}$$

where the quantities d_α are the new configurational coefficients in the expansion of Φ_* in terms of (natural) configurations:

$$|\Phi_*\rangle = \sum_{\alpha=1}^{N} d_\alpha |\Phi_{\alpha\to N+\alpha}\rangle. \tag{11}$$

Here $\Phi_{\alpha\to N+\alpha}$ is formed as a result of the substitution of the natural occupied spin orbital $|\phi_\alpha\rangle$ in the main determinant Φ by the vacant orbital $|\phi_{N+\alpha}\rangle$. It follows from Eqns.(10) and (11) that the number of natural configurations never exceeds the number of electrons N; the transition to natural orbitals therefore sharply reduces the number of excited configurations and significantly simplifies the analysis of Φ_*, which can now be concentrated on only N values of d_α and not on N^2 coefficients d_{pi}. This reduction of the number of configurations (without a change in the overall wave function Φ_*) is clearly illustrated by the scheme of transitions in Fig.1.

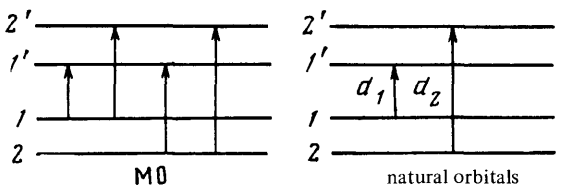


Figure 1. Decrease of the number of configurations on passing to natural orbitals of the excited state.

Fig.1 shows that, in the representation of the natural orbitals, all the cross-configurations $1\to 2'$, $2\to 1'$, etc. are missing; the excitation is described by the set of only the "diagonal" one-electron transitions $1\to 1'$, $2\to 2'$, etc. with the amplitudes d_1, d_2, etc. The numbers d_1, ..., d_α, ..., d_N are obtained from the matrix of the old configuration coefficients $d=||d_{pi}||$ by a kind of diagonalisation of this generally rectangular matrix, so that the number of non-zero terms of expansion (11) is equal to the rank $r\leq N$ of the matrix d:

$$|\Phi_*\rangle=\sum_{\alpha=1}^{r} d_\alpha|\Phi_{\alpha\to N+\alpha}\rangle. \qquad (12)$$

The number r is also an invariant characteristic of the matrix d, which remains constant in all the transformations of the basis set. In certain simple cases the rank of the matrix d is easily calculated and can yield direct information about the true nature of the configuration interaction.

As an example of this kind, we shall consider an excited state in which all the configurations $\Phi_{i\to p}$ are represented with the same weighting factor determined by the normalisation:

$$|\Phi_*\rangle=\frac{1}{\sqrt{N(M-N)}}\sum_{i;p}|\Phi_{i\to p}\rangle. \qquad (13)$$

It would appear that this is the extreme case of the maximum possible configuration interaction. Subject to condition (13), the matrix d assumes the following form:

$$d=[N(M-N)]^{-1/2}\begin{Vmatrix} 1 & 1 & \dots & 1\\ 1 & 1 & \dots & 1\\ . & . & \dots & .\\ . & . & \dots & .\\ 1 & 1 & \dots & 1 \end{Vmatrix}.$$

Evidently its rank is unity. Consequently the outwardly widest superposition (13), with the aid of which the idea of the delocalisation of transitions has been illustrated[43], can be reduced to only one determinant by a unitary transformation of vacant orbitals and orbitals occupied to different extents!

In this connection it is desirable to have a simple numerical characteristic which would indicate the number of significant configurations which cannot be reduced by any transformations. The average rank $\bar{r}$ of the matrix d, in which each natural configuration $\Phi_{\alpha\to N+\alpha}$ is included in proportion to its weighting factor d_α^2, can be used as such a quantity. An explicit expression for the average rank has been obtained[28,44]:

$$\bar{r}=1/\mathrm{Sp}\,(d^+d)^2=2/\mathrm{Sp}D^4, \qquad (14)$$

and a series of simple inequalities for Sp D^4 guarantees that the number $\bar{r}$ is between unity and the usual rank r of the matrix of configurational coefficients:

$$1\leq\bar{r}\leq r. \qquad (15)$$

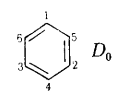
The natural nature of inequality (15) justifies the term "average rank" for the quantity defined by Eqn.(14). With the aid of Eqn.(14), it is easy to calculate the average rank of state (13) and to show that in this case $\bar{r}=1$.

On passing to configurations with a regular spin symmetry, the matrix D is replaced by the spin-free matrix D_0 and the average rank is always proportionally doubled as a result of the spin multiplier $(|\alpha(1)\beta(2)\rangle\pm|\beta(1)\alpha(2)\rangle)/\sqrt{2}$ used in the construction of the singlet and triplet configurations. It is therefore convenient to introduce the spin-free rank κ, which has been called[44] the delocalisation number, defined by the relations

$$\kappa=1/\mathrm{Sp}\,D^4=1/2\,\mathrm{Sp}\,D_0^4,\quad 1\leq\kappa\leq r_0, \qquad (16)$$

where r_0 is the rank of the matrix of the corresponding spin-free configurational coefficients, which does not exceed the number of spin-free occupied or vacant molecular orbitals.

We shall calculate, for example, the delocalisation number of the excited state B_{1u} of the π-electron shell of the benzene molecule, where, in accordance with the study of Mestechkin and Gutyrya[27], we have in terms of the basis set of atomic orbitals,



$$D_0(B_{1u})=\begin{Vmatrix}\Delta & 0\\ 0 & \Delta\end{Vmatrix},\quad \Delta=[6(y^2+1)]^{1/2}\begin{Vmatrix} y & 1 & 1\\ 1 & y & 1\\ 1 & 1 & y\end{Vmatrix}. \qquad (17)$$

Here the first block refers to the set of atoms in the 1-, 2-, and 3-positions and the second refers to the remaining atoms; y is the parameter of the configurational mixing equal to -2 for the Hückel solution, to -1.620 for the singlet, and to -2.818 for the triplet. Calculation by Eqn.(16) yields

$$\kappa=3(y^2+2)^2/(y^4+12y^2+8y+6). \qquad (17')$$

Table 2. The delocalisation numbers of the transitions corresponding to the α-, p-, and β-absorption bands.

Molecule	α	p	p'	β	Molecule	α	p	p'	β
Naphthalene	2.09	1.34	1.68	2.01	Perylene	2.11	1.13	5.15	2.84
$(\text{Naphthalene})^{2+}$	1.51	1.19	1.57	1.56	Aniline	1.61	1.38	1.82	2.00
Anthracene	2.17	1.19	1.66	2.02	Benzonitrile	1.97	1.42	1.85	2.00
$(\text{Anthracene})^{2+}$	1.50	1.12	2.36	1.57	*p*-Aminobenzonitrile	1.86	1.21	2.14	1.82

For the Hückel solution, we obtain the natural value $\kappa=2$ and, when account is taken of the electronic interaction, we have $\kappa(^1B_{1u})=2.04$ and $\kappa(^3B_{1u})=2.94$. As a result of symmetry, all the remaining π-transitions in the benzene

molecule correspond strictly to two configurations, since the matrix relation $D_0^2 = 4D_0^4$ holds for them. Taking y to infinity in Eqn.(17'), we obtain the maximum possible delocalisation number $\kappa = 3$ for Eqn.(17).

The delocalisation numbers for the lowest transitions in a series of conjugated hydrocarbons have been found[44] (Table 2). Table 2 permits the following conclusions. All the lowest transitions involve a small number of configurations, the number of natural configurations not exceeding five. In uncharged systems the p band (the B_{2u}^+ state) corresponds as a rule to virtually only one configuration, while the α and β bands (the $B_{3u}^{\mp}$ states) correspond to at least two configurations. This is consistent with the familiar qualitative picture of the transitions used for alternant systems[45] (Fig.2).

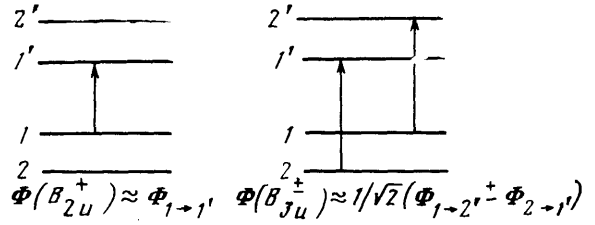


Figure 2. The principal one-electron transitions involved in the formation of the lowest excited states of alternant hydrocarbons.

For ions and substituted aromatic hydrocarbons, the alternant property disappears and the degree of delocalisation of these states diminishes. Table 2 also shows that the second transitions involve a higher degree of delocalisation compared with the first transitions of the same symmetry, i.e. the expansion of the set of configurations has a greater effect on the second and higher transitions than on the first.

One should note that the delocalisation numbers characterise not only the multiconfiguration nature of the excited state but also the degree of deviation of the excited state from the ground state. Indeed, the sum of squares of the changes in the charges and bond orders on excitation, which is the same as the quantity $\mathrm{Sp}\,(\rho_1^* - \rho)^2 = \mathrm{Sp}\,D^4 = 1/\kappa$, can serve as a characteristic of this deviation. Therefore, the higher the delocalisation number κ, the smaller the overall changes undergone by the molecular system as a result of the given excitation. In particular, those spectroscopic properties which are caused by changes in the electron density at the atoms (dipole moment, the influence of the substituent, etc.) should have the greatest influence on transitions with low delocalisation numbers. From this follows, for example (in conformity with the available experimental data[46]), a higher sensitivity to chemical substitution of the virtually one-configuration p bands than that of the two-configuration α and β bands. These factors can apparently also account for the greater polarisability of the excited p states, observed in the calculations[47], compared with the α states of aromatic hydrocarbons.

IV. THE METHOD OF EXCITATION LOCALISATION NUMBERS

While the degree of delocalisation of the transition is more in the nature of an "internal" than a purely theoretical characteristic necessary for the complete understanding of the structure of the wave function of the excited molecule, the localisation of the electronic transition plays a direct role in the interpretation of spectroscopic and certain other physicochemical experiments. The possibility of a real localisation of the excitation at individual fragments of the molecule is closely related to the additivity of a series of molecular properties described by the usual perturbation theory.

Suppose that the excitation is each time sufficiently localised at a particular group of atoms A. Then a certain observed property of the molecule, modelled as a second-order effect of the perturbation theory (polarisability, diamagnetic susceptibility, etc.)

$$E^{(2)} = \sum_a (1/\lambda_a) \cdot |\langle \Phi | \delta H | \Phi_*^{(a)} \rangle|^2,$$

can be represented by the sum of the contributions in terms of the fragments into which the molecule has been subdivided and in which each excitation $\Phi_*^{(a)}$ is significantly concentrated.

From the standpoint of the molecular orbital theory, it is to be expected that both occupied and vacant orbitals will in this case also be localised at individual atoms and bonds, which necessarily leads to the localisation of all possible transitions. Such localisation of orbitals is indeed possible but by no means obligatory. It can occur, as a rule, in saturated systems and this feature has been demonstrated by Lennard–Jones and coworkers for saturated hydrocarbons with a high degree of symmetry, while in the general case it has been demonstrated by Ruedenberg and coworkers[4] (see also Bazilevskii[48]).

However, in conjugated systems the additivity of properties of the type $E^{(2)}$ does not obtain, which indicates the impossibility of identifying all transitions with local transitions. This means that the localisation of the π orbitals is less extensive and the interaction of approximately localised orbitals cannot be neglected[4,5,13]. Therefore in the case of π systems it is difficult to expect the concentration of excitation at individual bonds. Nevertheless, in many instances large molecular fragments can be responsible for particular transitions. This factor has been frequently noted by spectroscopists[12,49–52] and required a theoretical interpretation. A logical quantum-chemical analysis must therefore extract directly from calculated data information about the localisation of transitions characterised by a readily calculable quantity. Until recently such a characteristic was not available and investigators usually confined themselves to a qualitative observation of the local nature of the transitions on the basis of the form of the molecular orbitals, provided that these orbitals had been localised beforehand (to the extent that this is possible)[53,54], or on the basis of the charges and bond orders, etc.[40,55]

The abandonment of the traditional orbital analysis and its replacement by the study of the transition density matrix D enabled Luzanov et al.[42] to put forward a logical quantitative characteristic of the localisation. We shall consider in greater detail the fundamental ideas of the above study[42] and the subsequent investigations[56–60]. As usual, we shall adopt the sum of squares of the moduli of the expansion coefficients $c_{\mu i}$ of the orbital $|\phi_i\rangle$ in terms of the atomic orbitals $|\chi_\mu\rangle$, referring to the fragment A investigated, as a measure of the degree of localisation of the molecular orbital. This quantity will be formulated thus:

$$L_A(\varphi_i) = \sum_{\mu \in A} c_{\mu i}^2, \qquad (18)$$

assuming for simplicity that all the quantities are real.

If we are dealing with a one-electron transition of the type $\Phi_{i\to p}$, then the localisation of the excitation of the fragment A can be naturally regarded as equally legitimately associated

with the localisation of both the occupied orbital $|\phi_i>$ and the vacant orbital $|\phi_p>$, i.e.

$$L_A\{\Phi_{i\to p}\} = \frac{1}{2}(L_A(\varphi_i) + L_A(\varphi_p)). \quad (19)$$

The coefficient 1/2 was introduced so that the sum of L_A and L_B, where B is the remainder of the molecule, was unity. The localisation number L_A introduced in this way represents the degree of involvement of the fragment A in the resultant excitation. If the molecule has been divided into a number of fragments larger than two, then a set of localisation numbers $\{L_A\}$, corresponding to the number of fragments, appears; these are also limited by the natural normalisation condition

$$\sum_A L_A = 1, \quad 0 \leqslant L_A \leqslant 1, \quad (20)$$

where the sum with respect to A is the sum with respect to all the fragments into which the molecule has been subdivided. In the limiting subdivision of the molecule into atoms, atomic localisation numbers L_μ arise, which we shall also refer to as the excitation indices. It is evident that

$$L_B = \sum_{\mu\in A} L_\mu. \quad (21)$$

The scheme described is in principle fairly natural and is in fact convenient for the analysis of one-configuration excited states.

We shall now consider the possible ways of extending it to the case of multiconfiguration excited state of type (3). A generalisation of the numbers L_A, which would take into account, with the aid of Eqn.(19), each configuration $\Phi_{i\to p}$ in proportion to its weighting factor d^2_{pi}, becomes immediately apparent, namely

$$L_A\{\Phi_*\} = \sum_{i,p} d^2_{pi} L_A\{\Phi_{i\to p}\}. \quad (22)$$

However, the numbers defined by Eqn.(22) suffer from a significant defect—they are not invariant relative to the transformation of the basis set of occupied and individually vacant molecular orbitals†. It is possible to eliminate this ambiguity by changing Eqn.(22) to the basis set of natural orbitals, which at the same time significantly simplifies Eqn.(22):

$$L_A = \sum_{\alpha=1}^{r} d^2_\alpha L_A\{\Phi_{\alpha\to N+\alpha}\}. \quad (22')$$

Using the explicit form [Eqn.(10)] of the Hermitian transition density operator D in terms of the natural basis set, we find an alternative form of Eqn.(22):

$$L_A = \sum_{\mu\in A} \langle\chi_\mu| D_0^2 |\chi_\mu\rangle. \quad (23)$$

Eqn.(23) does indeed exhibit the required invariance, because the transition operator D is, like the matrix ρ for the ground state, a fundamental invariant of the excited state (3). The requirement that L_A should be positive and the normalising condition (20) are satisfied automatically, because the matrix D_0^2 has been defined as a non-negative quantity and the normalisation of Φ_* yields $\mathrm{Sp}\, D_0^2 = 1$.

† Numbers of the type defined by Eqn.(22) have been introduced by Ohta et al.[61] to describe the localisation of the transition.

If each atom supplies several orbitals of different types (π, σ, etc.) to the valence shell, then the summation in Eqn. (23) must be carried out with respect to all the valence orbitals of the atoms of the fragment A. Accordingly, in calculating the excitation index of the atom L_μ, it is necessary to sum the elements D_0^2 for all the orbitals of each atom.

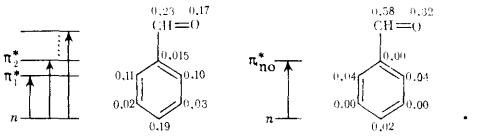
The choice of the quantity defined by Eqn.(23) as a measure of localisation was proposed by Luzanov et al.[42] on the grounds of other considerations. Namely, the localisation of the excitation was described in terms of the operator modulus of the change in the density matrix on excitation:

$$|\Delta\rho| = |\rho_1^* - \rho| = [(\rho_1^* - \rho)^2]^{1/2}, \quad (24)$$

which is exactly identical with the D^2 matrix in the Tamm–Dancoff model. The numbers L_A therefore automatically take into account the changes in both the charges and bond orders on excitation. In this connection, we may note that the employment in estimating the degree of localisation of the transition of only one of the above components, for example, only the changes in the charges, is not justified and the new quantity introduced on this basis[59] is not well founded.

With the aid of the quantities L_A in the form defined by Eqn.(22'), one observes immediately the fundamental role of the natural orbitals also in the localisation problem. Suppose that the excitation is almost fully localised at the fragment A, i.e. $L_A \cong 1$. Then, by virtue of the normalisation property $\Sigma d^2_\alpha = 1$, we must have $L_A\{\Phi_{\alpha\to N+\alpha}\} \cong 1$. Consequently $L_A(\phi_\alpha) = L_A(\phi_{N+\alpha}) \cong 1$; in other words, if the excitation is localised at a certain fragment, then the natural orbitals of the excited state are also localised at this fragment[42]. The natural orbitals as it were draw the excited electron cloud precisely to those sections of the molecule where the given excitation is largely concentrated. As regards the Hartree–Fock molecular orbitals, this claim is generally speaking invalid, so that the analysis of the degree of localisation of molecular orbitals can yield a distorted idea about the true nature of the distribution of the excitation.

A higher degree of localisation of natural orbitals compared with the molecular orbitals is manifested particularly clearly for the $n\pi^*$-states, where, as a consequence of the usual smearing of the n orbitals, the molecular orbital method cannot explain the experimental localisation of the excitation in the sections of the molecule adjoining the heteroatom which has an unshared electron pair[12,49]. The localisation numbers, defined by Eqn.(18), of the lowest vacant π_1^* molecular orbital and the natural orbital π_{no}^*, to which the electron of the unshared pair is transferred on excitation, are given below:



The numbers were taken from Luzanov and Pedash[60]. Evidently the degree of localisation of the natural orbital at the carbonyl group is a factor of two greater than the corresponding quantity for the π_1^* molecular orbital and reaches 90%. The use of the quantity defined by Eqn.(23) for carbonyl compounds made it possible[60] to estimate quantitatively the degree of localisation of the $n\pi^*$ excitation at C=O, which was found to diminish in a series of aromatic compounds investigated with increase in the size of the π system and amounted to $L_{C=O} = 0.88$–0.95. The decrease of the degree of localisation of the $n\pi^*$ transitions involving the carbonyl group as the conjugated system expands had been observed experimentally in a previous study[62].

It is significant that the determination of the numbers L_A from Eqn.(23) as well as the determination of the delocalisation numbers defined by Eqn.(16) do not require a special construction of natural states. It is sufficient to construct from the known configurational coefficients d_{pi} and the LCAO-MO coefficient $c_{\mu i}$ a matrix D_0 in terms of the atomic basis set, the elements of which can be identified with the quantities (n is the number of occupied molecular orbitals and m is the number of atomic orbitals)

$$D^0_{\mu\nu} = \frac{1}{\sqrt{2}} \sum_{i=1}^{n} \sum_{p=n+1}^{m} d_{pi} (c_{\mu p} c_{\nu i} + c_{i\mu} c_{\nu p}). \qquad (25)$$

Then one determines the atomic (orbital) excitation indices from the formula

$$L_\mu = \sum_{\nu=1}^{m} [D^0_{\mu\nu}]^2 \qquad (26)$$

and hence also the localisation numbers defined by Eqn.(21). In the methods for the calculation of the electronic spectra of molecules with the aid of the superoperators $\hat{\Lambda}$ or $\hat{\Pi}$ discussed in Section II, the matrix D_0 is usually calculated immediately in terms of the atomic basis set simultaneously with λ, so that the computational stage (25) becomes superfluous.

V. ISOLATION OF TRANSITIONS AT INDIVIDUAL FRAGMENTS AND MOLECULAR STRUCTURE

The relative simplicity of the calculation of the localisation numbers L_A and the clarity which they introduce into the interpretation of the electronically excited states permitted the analysis of the localisation of excitations for many molecular structures of an arbitrary degree of complexity[56-58,63]. With the aid of these calculations, it is natural to consider certain structural-chemical features, the presence of which favours the preferential concentration of excitation at an individual molecular fragment. Experimental studies, which stimulated such investigations, have been discussed in detail[12,49-52].

Numerous calculations have confirmed the natural hypothesis that a significant factor in the localisation of excitation at an individual section of the molecule is the asymmetry of the molecular structure. Indeed, for a combined system A+B, the type Λ excitation operator is described by the block supermatrix $||\Lambda_{AB,CD}||$, the diagonal blocks $\Lambda_{AA,AA}$ and $\Lambda_{BB,BB}$ of which characterise the excitation of the fragments A and B respectively and the blocks $\Lambda_{AB,AB}$ and $\Lambda_{BA,BA}$ characterise states with charge transfer from A to B and conversely, while the non-diagonal blocks $\Lambda_{AA,AB}$, etc. include the interaction between them. In the case of a weak interaction between the fragments, the approximate solutions (11) can be represented approximately by transitional matrices of three types generated by the corresponding diagonal blocks Λ:

$$\left\| \begin{matrix} D_A & 0 \\ 0 & 0 \end{matrix} \right\|, \left\| \begin{matrix} 0 & 0 \\ 0 & D_B \end{matrix} \right\|, \left\| \begin{matrix} 0 & D_{AB} \\ D^+_{AB} & 0 \end{matrix} \right\|. \qquad (27)$$

As a result of this, we have either $L_A \cong 1$, or $L_B \cong 1$, or even $L_A \cong L_B \cong 1/2$ [see Eqn.(23)].

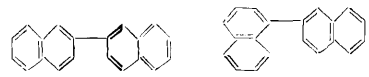
The first two cases correspond to the concentration of excitation alternately first in one and then in another fragment, while the third corresponds to excitation throughout the molecule, the first two solutions of Eqn.(27) being valid only when the fragments are non-equivalent, i.e. when the A+B system is asymmetric. On the other hand, if B is a copy of A and the symmetry of the system is not below C_2, then solutions which have the correct symmetry are

$$\frac{1}{\sqrt{2}} \left\| \begin{matrix} D_A & 0 \\ 0 & D_B \end{matrix} \right\|,$$

which evidently leads to a uniform localisation $L_A = L_B = 1/2$. Asymmetry is in fact the physically well-founded structural factor which distinguishes the so-called crossing conjugated systems where investigators sought, not without justification, quasi-autonomous excitation regions[51,52]. We may note that formally the same causes are responsible for the appearance of localised excitations in a molecular crystal, where the absorption bands of individual molecules are observed instead of exciton bands, but in the solid the asymmetry factors are the local deformation of the crystal, the presence of impurities, and defects, etc.[64]

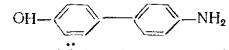
Proceeding now to specific illustrations, we shall consider initially the excited states of the styrene molecule Ph–CH=CH_2. According to estimates in the literature[56,58], one may claim that the first transition involves mainly the phenyl group, since $L_{Ph} = 0.92$, while the second transition involves the molecule as a whole ($L_{Ph} = 0.64$). The same interpretation follows also from experimental data which have been discussed in detail in a monograph[50]#.

An apt example of the structure containing two equivalent fragments which can be joined symmetrically and asymmetrically is provided by the binaphthyl system Nh–Nh:



(28)

Evidently, for all transitions in the first molecule $L_{Nh_1} = L_{Nh_2} = 1/2$, while in the second it is most likely that $L_{Nh_1} = L_{Nh_2}$. Specific calculations showed that, in the first excited state of the asymmetric 1,2'-binaphthyl, we have $L_{Nh_1} = 0.63$, i.e. there is an almost uniform distribution of excitation, the second transition involves mainly the β-naphthyl group ($L_{Nh_1} = 0.16$), and, finally, the third transition is almost entirely concentrated in the first fragment ($L_{Nh_1} = 0.94$). Thus, in this example all three situations illustrated in formula (27) are clearly manifested. Another asymmetric structure is that of α-phenylnaphthalene, the values of L_{Ph} for the first three electronic excitations of which are respectively 7, 15, and 88%. Finally, in the compound

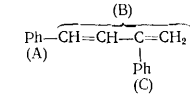


(29)

even a slight asymmetry (Ö is almost equivalent to N̈) leads to a sharp non-equivalence of the fragments in the first excited state (α-band)—95% of the entire excitation has been "collected" in the aniline fragment. These examples could be continued.

However, for asymmetry to have an effect in the direction indicated, it is necessary that the fragment should be weakly coupled, which obtains when the fragments are joined in the "minimal" manner, i.e. by only one bond (on dissociation of this bond, the molecule breaks up into at least two components). In the theory of graphs, such structures are assigned to graphs with edge connectivity 1 (graphs with a bridge). All the systems mentioned here belong to this type. In such systems the requirement that the interaction between the fragments is negligible compared with the overall interaction within the fragments, essential for the autonomy of the fragments[6], is readily fulfilled.

The 1,3-diphenylbutadiene molecule, where it is natural to distinguish three sections

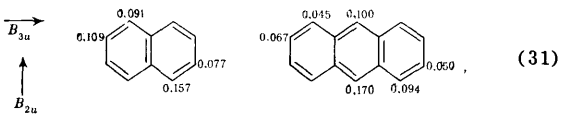


(30)

In contrast to the second band, the first band is hardly displaced following chemical substitution in –CH=CH_2.

has a remarkable structure as regards the non-equivalence of the fragments. The π-electronic excitation for the first two singlet transitions is very highly localised at the A+B fragment ($L_{A+B}=0.959$ and 0.999 respectively), while the next two transitions are localised at the B+C fragment (0.997 and 0.892). These data were obtained by Luzanov et al.,[42] while those for the keto-derivative of compound (30), called a chalcone, were obtained by Sukhorukov et al.[59] Example (30) illustrates an additional structural-chemical factor favouring localisation—the presence in the π-system of a branch associated with the bridges of the graph, which in chemistry is sometimes referred to as cross-conjugation.

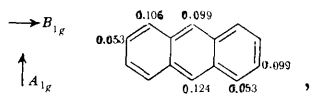
When the edge connectivity of the graph exceeds unity, rigidly bound systems of the type of condensed hydrocarbons are produced. Even when the fragments are differentiated within such molecules, the strong interaction between them via two or more carbon–carbon bonds significantly weakens the autonomy of the fragments on excitation. Nevertheless some non-uniformity is manifested in the distribution of excitation at the level of individual atoms. It has been shown[57] that under these conditions it is convenient to employ atomic excitation indices L_μ for the analysis of localisation. For example, in naphthalene and anthracene the following excitation index diagrams correspond to the two lowest energy transitions:



(31)

where the numbers in the upper half refer to the α band and those in the lower half refer to the *p* band, the arrow indicating the direction of polarisation of the transition. Comparison of the 1- and 2-positions of these molecules shows that the difference between the polarisations of the transitions of the α band (in the direction of the long molecular axis) and the *p* band (in the direction of the short axis) leads to the accumulation of excitation in the direction of polarisation.

However, for $T-T$ transitions this tendency is non-obligatory. For example, it has been reported[38] that the $^3B_{2u}\rightarrow{}^3B_{1g}$ (in the direction of the long axis) and $^3B_{2u}\rightarrow{}^3A_{1g}$ (in the direction of the short axis) transitions in anthracene can be represented by the following localisation diagram:



(32)

which shows that, despite the opposed polarisations of the bands, the excitation is localised in the direction of the short axis.

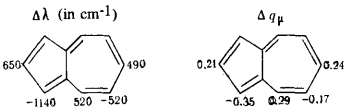
It has been suggested[57] that the excitation indices L_μ in alternant systems be used to estimate the spectral shifts $(\Delta\lambda)_\mu$ following the introduction of weak substituents X in the μ-position:

$$(\Delta\lambda)_\mu = K_X L_\mu. \qquad (33)$$

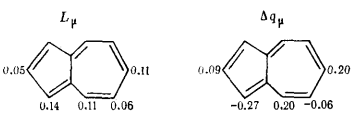
The spectroscopic substituent constant K_X was fitted on the basis of data for the corresponding benzene derivatives, where by virtue of symmetry $L_\mu = 1/6$. Conversely, it is possible to find by Eqn.(33) empirical localisation indices from the values of L_μ in an arbitrary alternant molecule and the previously determined substituent constants. For the naphthalene α band, the empirical $\bar{L}_\mu$ are $\bar{L}_1 = 0.081$ and $\bar{L}_2 = 0.108$, while for the phosphorescent $^1A_{1g}\rightarrow{}^3B_{2u}$ transition we have $\bar{L}_1 = 0.125$ and $\bar{L}_2 = 0.040$. These figures agree satisfactorily with the calculated values (0.091 and 0.109 for the α band and 0.174 and 0.072 for the $^2A_{1g}\rightarrow{}^3B_{2u}$ transition).

Thus we can assume that diagrams of types (31) and (32) make it possible to specify the substituent positions which are most sensitive as regards spectral shift. In the singlet case [formula (31)] one can therefore expect that the introduction of a substituent in the direction of the polarisation of the transition displaces the energy of this transition to a greater extent than the energy of the perpendicularly polarised transition. This rule, based on experimental observations, has been discussed[12,65] and has been extended to a triplet–triplet transition[65]. Diagram (32) shows, however, that this conclusion is by no means entirely general.

The influence of the insertion of a substituent X in the μ-position in non-alternant molecules can be estimated merely with the aid of the first correction to the excitation energy $\lambda_\mu^{(1)}$. Successive calculation of $\lambda_\mu^{(1)}$ shows that one of the main contributions to $\lambda_\mu^{(1)}$ is the term $\Delta q_\mu\cdot(\Delta\alpha)_X$, where Δq_μ is the change in the charge on the atom μ on excitation and $(\Delta\alpha)_X$ is the change in the Coulombic integral under the influence of the substituent X. In systems with a non-uniform distribution of charge both bathochromic and hypsochromic shifts can therefore arise[46]. For example, according to Godfrey and Murrell[66], reliable values of $(\Delta\lambda)_\mu$ for the first excited state of azulene are available and are satisfactorily correlated with the calculated Δq_μ[66]:



A similar correlation between Δq_μ and the values of $\lambda_\mu^{(1)}$ calculated exactly from the formulae of Luzanov et al.,[67] on the one hand, and the $(\Delta\lambda)_\mu$ for aromatic aza-hydrocarbons, on the other, have been discussed by Vysotskii[68]. In this case the excitation indices yield a distribution of excitation from which it is possible to infer only approximately the most reactive positions of the substituents in a given molecule without specifying the direction, which is apparently determined by the sign of Δq_μ[56]:



Excitation indices have found an unusual application in the qualitative description of the intercombination transition $S_1\rightsquigarrow T_0$. In the large molecules of aromatic hydrocarbons the symmetries of the fluorescent and phosphorescent states are the same. The spin–orbital coupling between these states, involving the cooperation of specific molecular vibrations, leads to the radiationless transition $S_1\rightsquigarrow T_0$, which is the main fluorescence quenching process in aromatic molecules. An exact calculation of the probability of this process is extremely difficult. In order to be able to draw qualitative inferences, it has been suggested[38] that one introduce the excitation overlap structure factor $\mathscr{P}$, which is defined as the product of the excitation indices $L_\mu(S_0\rightarrow S_1)$ of the fluorescent state S_1 and the excitation indices $L_\mu(S_0\rightarrow T_0)$ of the phosphorescent state T_0 as the quenching agent S_1:

$$\mathscr{P} = \sum_\mu L_\mu(S_0\rightarrow S_1)\,L_\mu(S_0\rightarrow T_0), \qquad (34)$$

where the summation is carried out with respect to all the atoms of the test system.

The factor $\mathscr{P}$ clearly reflects the likely assumption that the spin–orbital coupling of the states S_1 and T_0 is stronger the greater the degree of involvement of each atom μ simultaneously in the fluorescent and phosphorescent states. The greater the factor $\mathscr{P}$, the greater the probability of the

transition, and the lower the fluorescence quantum yield Φ_f. For molecules of a similar structural type, one may therefore hope for a correlation between $\mathscr{P}$ and the reciprocals of the quantum yields $1/\Phi_f$. In the class of condensed aromatic systems such correlation does in fact occur[69]:

Compound	Tetracene	Anthracene	Pyrene	Perylene
$\mathscr{P}$	0.271	0.121	0.091	0.088
$1/\Phi_f$[69]	0.58	0.38	0.17	0.13

In the case of a uniform distribution of excitations we have $\mathscr{P}=1/m$, in conformity with Eqn.(34), where m is the number of atoms in the molecule. If such uniformity did actually obtain, then, with increase of the size of the system, the probability of the transition would fall and the fluorescence quantum yield would increase. The non-uniformity of the distribution over the atoms in the excited state is in fact responsible for the greater overlap of the excitations and the lower yield Φ_f in tetracene (18 carbon atoms) than in the anthracene molecule with 14 carbon atoms. The data for polyphenyls show that $\mathscr{P}$ is close to $1/m$, since the decrease of $\mathscr{P}$ for these compounds is almost proportional to the increase of the number of rings.

VI. ANALYSIS OF CHARGE TRANSFER IN THE METHOD OF TRANSITION OPERATORS

In the discussion of the localisation of excitation in weakly coupled systems two significantly non-equivalent possibilities, reflected in Eqn.(27), were indicated: either the excitation is localised exclusively at the fragment A or B or there is excitation throughout the molecule, in which electrons, as it were, oscillate between different parts (A and B) of the molecule. Excited states of the latter type have come to be called charge-transfer states. The transition to such an excited state is as a rule characterised by a more pronounced redistribution of electron density and by a marked increase of the dipole moment (relative to the ground state) and hence by distinct solvatochromic effects, which in fact makes them attractive for spectroscopic investigation[70-72].

Charge-transfer states can be realised in a virtually "pure" form in excimers and charge-transfer complexes, whence both the terminology and the methods of identification have been taken[73]. Intramolecular charge-transfer is rarely fairly complete and the need to estimate the relative contributions of charge-transfer states led in its time to the development of special computational methods differing from the standard Pariser–Parr model. We have in mind primarily the so-called "molecule in molecule" method, which was initially developed by Longuet-Higgins and Murrell[1,66] and has found numerous adherents up to very recent times[2,74-77]. The essential feature of the method is that, having specified a certain subdivision of the molecule into fragments A, B, ..., C and using the orbitals for the individual fragments, one constructs the wave functions for the combined A + B + ... + C system. The basis set of N-electron functions employed in this procedure consists of products, antisymmetrised with the aid of the antisymmetrisation operator $\mathscr{A}$, comprising mainly the ground configuration $\Psi_0=\mathscr{A}\Phi_A\Phi_B\ldots\Phi_C$, where Φ_A denotes the determinant made up of the occupied molecular orbitals in the ground state in the fragment A and of different types of locally excited molecular orbitals:

$$\Psi_A^*=\mathscr{A}\Phi_A^*\Phi_B\ldots\Phi_C,\ \ldots,\ \Phi_C^*=\mathscr{A}\Phi_A\Phi_B\ldots\Phi_C^*, \qquad (35)$$

where the wave function of each fragment of the entire molecule is replaced by a singly excited configuration or a superposition of such configurations Φ_A^* made up of the molecular orbitals of only this fragment. In addition, all possible charge-transfer configurations are introduced:

$$\Psi_{A\to B}=\mathscr{A}\Phi_A^+\Phi_B^-\ldots\Phi_C,\ \ldots,\ \Phi_{C\to A}=\mathscr{A}\Phi_A^-\Phi_B\ldots\Phi_C^+, \qquad (36)$$

in which the occupied molecular orbital of one fragment is replaced by the vacant molecular orbital of another fragment.

In the basis set of the functions Ψ_0, $\{\Psi_A^*\}$, $\{\Psi_{A\to B}\}$ set up in this way one diagonalises the overall Hamiltonian of the molecule $H_{A+B+\ldots+C}$, the eigenvectors of which are identified (on the basis of the increase of the energy) with the resultant ground and excited states of the entire system. Since the molecular orbitals of the fragments are not self-consistent for the combined system, the resultant ground state comprises the locally excited states Ψ_A and charge-transfer states of the type $\Psi_{A\to B}$, apart from the ground configuration Ψ_0. Accordingly the excited states of the entire system include a contribution from the ground configuration Ψ_0. This factor leads to some inconsistency of the "molecule in molecule" method for the analysis of the structure of excited states in terms of the localisation of charge-transfer useful to the investigator.

In the method of Baba et al.[3] one begins with the Pariser–Parr wave functions of the excited states obtained from self-consistent molecular orbitals by the usual method of configuration interaction (see Section II). However, the contribution of charge-transfer states is estimated by a procedure similar to that in the "molecule in molecule" method. Namely, having selected for each fragment specific reference molecular orbitals, for example, the self-consistent molecular orbitals of these fragments, the coefficients of expansion of the functions Φ_* of type (3) for excited states in terms of the basis set $\Psi_0\{\Psi_A,\Psi_{A\to B}\}$ are found by linear transformations of the self-consistent molecular orbitals of the entire system into the reference molecular orbitals of the fragments. Thus the given method of analysis does not eliminate the difficulties in interpretation associated with the method of Murrell and Longuet-Higgins.

As a typical example of studies on electronic states in terms of this approach, we shall consider data for the ground and the lowest excited $\pi\pi^*$-states of the aniline molecule[78]. Charge-transfer states $\Psi_{NH_2\to Ph}$ with an overall contribution of 11.8%, reflecting the electron-donating function of the amino-group when it is incorporated in the overall π-system, are "imposed" on the ground state of this molecule. In the first $\pi\pi^*$-excited state the contribution of the above states increases to 28.5%. In the second excited state the contribution of $\Psi_{NH_2\to Ph}$ reaches 37.4%, but the ground configuration Ψ_0 with a 6% contribution also appears. As a result, it is difficult to understand how these figures reflect the charge transfer proper on excitation, this being a consequence of the lack of self-consistency of the reference molecular orbitals of the individual fragments in relation to the entire system made up of the given fragments. It is therefore difficult to compare such contributions even for different excited states of the same molecule. Apart from the cumbersome nature of the methods described, the contributions obtained are not invariant, because they depend on the form of the reference molecular orbitals of the fragments.

We may also note studies[53,54] where a set of orbitals localised at atoms and bonds is used in the construction and analysis of the Tamm–Dancoff excited state (3). However, the approximate nature of the localisation of the molecular orbitals, found by the Ruedenberg method or some other procedure, permits only qualitative inferences, which, owing to the lack of numerical characteristics, also hinder a comparative analysis of the excitations.

We shall now show how the problem of charge transfer is solved in the method of localisation numbers described in Section V. In order to extract the maximum amount of

information, it is necessary to employ in this case, instead of the Hermitian transition density matrix D, the overall one-electron matrix τ of the transition, which can be readily expressed in terms of D, and the density matrix ρ of the ground state, namely

$$\tau = D\rho. \tag{37}$$

The excited state (3) can then be represented as the result of the action of the operator (37) on the Hartree–Fock ground state Φ for each electron i:

$$|\Phi_*\rangle = \sum_{i=1}^{N} \tau(i)|\Phi\rangle.$$

The matrix elements $\tau_{\mu\nu}$ of the operator τ in terms of the atomic basis set can therefore be regarded as amplitudes of the electron transfer from the atom ν to the atom μ. Proceeding further to the spin-free quantities τ_0 and, putting, as before, $(\tau_0)_{\mu\nu} = \tau_{\mu\nu}$, we assume that the probability of a jump of the excited electron from the atom μ to the atom ν is characterised by the number

$$l_{\mu\to\nu} = 2\tau^2_{\nu\mu}. \tag{38}$$

If we are interested in the probability $l_{A\to B}$ of the electron transfer on excitation from the fragment A to the fragment B, it is necessary to carry out a summation of the probability defined by Eqn.(38) with respect to the corresponding atoms (orbitals):

$$l_{A\to B} = \sum_{\mu\in A}\sum_{\nu\in B} l_{\mu\to\nu}. \tag{39}$$

The positive quantities defined by Eqns.(38) and (39) will be called the *charge-transfer numbers*[79,80]. On the other hand, if A = B, then Eqn.(39) is converted into the partial localisation number:

$$l_A = 2\sum_{\mu,\nu\in A} \tau^2_{\mu\nu}, \tag{40}$$

which describes the probability that the excited electron is located in the fragment A, i.e. the probability of its local excitation. In particular, for the local excitation of the atom μ we have $l_\mu = 2\tau^2_{\mu\mu} = [(D_0)_{\mu\mu}]^2$.

There exists a simple relation, established with the aid of Eqn.(37), between the charge-transfer numbers defined by Eqns.(39) and (40) and the localisation numbers defined by Eqn.(23) and introduced previously:

$$L_A = l_A + {}^1/_2(l_{A\to B} + l_{B\to A}), \tag{41}$$

where B is a component of the overall molecule A + B in addition to A. If the molecule has been divided into a large number of fragments A + B + ... + C, then

$$L_A = l_A + {}^1/_2(l_{A\to B} + l_{B\to A} + \cdots + l_{A\to C} + l_{C\to A}). \tag{42}$$

Thus the overall localisation of the excitation in a certain fragment consists of the local excitation of the fragment proper (the number l_A), the charge transfer from the given fragment to all the remaining fragments, and the reverse transfer from all the remaining fragments to the given fragment. This conclusion is quite natural, because charge-transfer states involving simultaneously two fragments cause a rearrangement, on excitation, of the electron shells of the fragments and make a specific contribution, like local excitations, to the overall distribution of the excitation in the molecule.

An important feature of this approach is the fact that the introduction of the transfer numbers defined by Eqn.(39) eliminates the discrepancy, noted previously, between the charge transfer arising following the appearance of states of the type $\Psi_{A\to B}$ and the observed charge transfer (the change in electron density Δq_A in the fragment or the dipole moment of the molecule on excitation). Eqns.(9) and (37) permit the claim that the following relation is valid for the molecule A + B:

$$\Delta q_A = l_{B\to A} - l_{A\to B}, \tag{43}$$

while for the system A + B + ... + C we have

$$\Delta q_A = \sum_{B\neq A} (l_{B\to A} - l_{A\to B}). \tag{44}$$

Eqn.(43) implies that an increase of electron density in the fragment A takes place only at the expense of states involving charge transfer from the remainder of the molecule to the fragment A, while states with electron transfer from A to the remainder of the molecule merely decrease Δq_A. In other words, the transfer numbers $l_{A\to B}$ and $l_{B\to A}$ represent a kind of virtual charges of opposite sign, which are induced in the fragments following the excitation of the neutral molecule.

Thus Δq_A is a difference characteristic of the charge transfer and in the general case it can therefore yield only indirect evidence concerning the "charge transfer" nature of the excited state. Only in the case of an absolutely strong donor or acceptor does one of the components of Eqn.(43) disappear ($l_{B\to A}$ for the donor and $l_{A\to B}$ for the acceptor) and Δq_A is equal to the contribution of the charge states ($l_{A\to B}$ or $l_{B\to A}$).

In alternant systems $\Delta q_A = 0$ for any fragment, since, in conformity with the parity theorem, the excitation of such systems does not cause any changes in the charge density[27]. Hence follows also the finding that the charge-transfer numbers associated with transfer in opposite directions ($l_{A\to B}$ and $l_{B\to A}$) are the same. The contribution of the charged states of alternant molecules can therefore be characterised by the overall quantity $l_{AB} = 2l_{A\to B}$, and in the general case we have

$$l_{AB} = l_{A\to B} + l_{B\to A}. \tag{45}$$

A method based on the employment of only the transition matrix D has been proposed[80] for the estimation of the overall charge transfer defined by Eqn.(45). The results of the calculation of l_{AB} by the two methods usually yields similar values.

We may note that, by analogy with the theory of excitons, locally excited states ($l_{AB} \cong 0$) can be naturally referred to also as small-radius excitations while charge-excitations involving the entire molecule ($l_{AB} \cong 1$) can be called large-radius excitations.

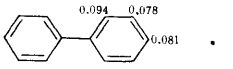
We shall now consider the results of the calculation of the charge-transfer numbers for specific hydrocarbon systems. For the α-, p-, and β-bands of biphenyl, these quantities have the following values:

Band	α	p	β
l_{Ph}, %	43	31	5
$l_{Ph,\,Ph}$, %	14	38	90

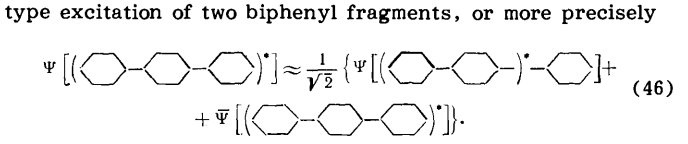
Evidently the α-band is caused by the small-radius excitation and can be identified with the benzene absorption band[81], in the p-band the contributions of the charged and locally excited states are comparable, while the large-radius excitation and hence the strongest linkage between the fragments correspond to the β-band. Naturally the asymmetric introduction of substituents into biphenyl leads to the removal of "degeneracy with respect to localisation" for the α-band and this results in the isolation of this excitation in one of the benzene rings; as a consequence of the strong interaction between the rings, the excitation involving the molecule as a whole persists for the p- and β-bands. The example of the 4-amino-4'-hydroxybiphenyl molecule [formula (29)] examined in Section V is fully consistent with this interpretation.

The similarity of the biphenyl α-band to the benzene band is manifested by the fact that the atomic localisation indices L_μ can be inferred fairly accurately from the values of L_μ

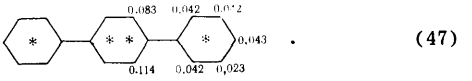
for the corresponding band in the benzene spectrum, where all the L_μ are 1/6 by virtue of symmetry. Then, having superimposed two diagrams of the benzene molecule and having renormalised the resulting numbers to unity, we find that all the L_μ should be close to $1/12 \cong 0.083$. Direct quantum-chemical calculation yields a diagram close to this uniform picture:



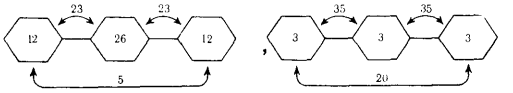
In terphenyl the α-band is also of the benzene type, but the central and lateral rings are not equivalent, since the excitation can be regarded as the result of alternate benzene-type excitation of two biphenyl fragments, or more precisely



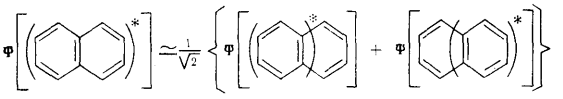
The central ring therefore contributes to the resultant excitation twice as much as the side rings, which can be represented by means of a scheme in which the indices L_μ, arising in this description, are indicated on top and the values calculated by Eqn.(25) are given below:



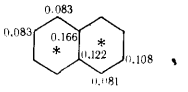
In the spectrum of the same molecule the p- and β-absorption bands are characterised by charge-transfer number diagrams similar to those for biphenyl:



The existence of a benzene-type α absorption band in the spectra of polyacenes indicates the possibility of a structural-chemical description of the corresponding excitation similar to that in formula (46). However, owing to topological features of such systems (marked edge connectivity), their molecules cannot be subdivided into a set of non-intersecting purely benzene-type fragments. Alternate excitation of superimposed benzene rings therefore corresponds to the α-band. For example, in naphthalene we have

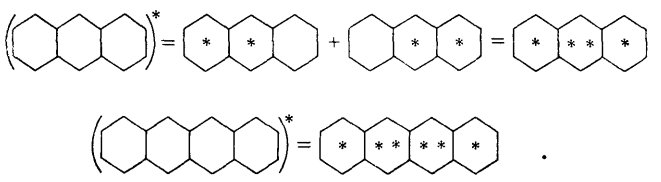


which gives rise to a diagram of L_μ indices of the type



where the numbers below are empirical values estimated by Luzanov and Umanskii[57].

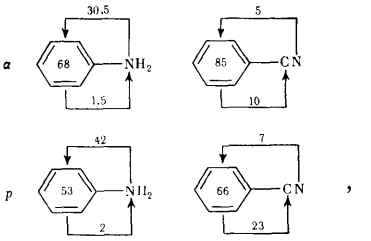
In higher polyacenes benzene-type absorption arises as a result of the alternate benzene-type excitation of the naphthalene fragment migrating throughout the molecule. For anthracene and tetracene, this has the following implication:



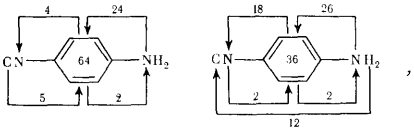
Thus, despite the rigid connectivity, in condensed hydrocarbons benzene-type absorption is also of a local type and therefore constitutes a small-radius excitation.

The study of the charge-transfer numbers in non-alternant molecules due to the charged states which lead to the observed physical effects, because $l_{A\to B} \neq l_{B\to A}$ is of special interest.

As an illustration, we shall consider the results of the calculation of the α- and p-bands of benzene derivatives. For aniline and benzonitrile, the charge-transfer number diagrams have the following form:



while for p-aminobenzonitrile we have



The absence in some of them of an arrow from A to B implies that the corresponding charge-transfer number $l_{A\to B} = 0$.

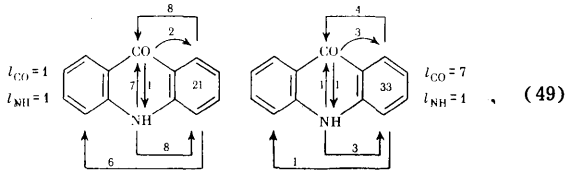
It is noteworthy that the charge transfer at right angles to the polarisation vector of the transition is smaller than in the case where the fragments between which charge transfer takes place are located on a line parallel to the polarisation vector. The α-bands therefore correspond to a less polar transition than the p-bands (cf. the numbers κ in Section II). In the same case, when the fragments are linear in a molecule with a symmetry of C_{2v} and higher, the charge-transfer number for a band polarised at right angles to the line of the fragments become rigorously equal to zero owing to symmetry factors, for example, in the case of $l_{NH_2 \rightleftharpoons CN}$ for p-aminobenzonitrile.

The case of p-aminobenzonitrile is of additional interest, because this compound contains electron-donating and electron-accepting groups simultaneously. As a consequence of symmetry factors, the long-wavelength band reflects the situation where there is no charge transfer whatever between the donor and the acceptor, while in the case of the p-band, which is identified as the charge-transfer band for molecules of this kind, the degree of charge transfer between the acceptor and the donor is smaller than the degree of charge transfer from the amino-group to the phenyl group and from the phenyl group to the nitrile group. However, since the change in the charge on CN following excitation is 0.28 and that on NH_2 is approximately −0.36, it may turn out that the charge is mainly transferred directly from the donor to the acceptor. Furthermore, diagram (48) shows that only one-third of the entire charge Δq_{NH_2} is removed in this way. The assignment of the corresponding band as one associated with charge transfer between the donor and the acceptor is therefore somewhat arbitrary, although the polar nature of such transitions, which are large-radius transitions, is significantly greater than that of the more localised small-radius transitions giving rise to α-bands. Additional illustrations have been published elsewhere[79].

Valuable information about the local nature of the transition can be obtained by considering the fine structure of molecular spectra[12]. Since electronic excitation is from the zero-point vibrational level of the ground state to the vibrational

levels of the excited state, the absorption spectra should exhibit progressions associated with the frequencies of the vibrational spectrum of the excited molecule and their intensity should be proportional to the square of the overlap of the vibrational functions of the ground and excited states. As a result of the concentration of the excitation in a certain molecular fragment, progressions generated by the characteristic vibrations of the given fragment in the excited state are the most intense. In the luminescence spectra one then observes the vibrational frequencies of the fragment in the ground state (corresponding to the infrared spectrum), because emission usually takes place as a result of the transition from the zero-point vibrational level of the excited molecule to the vibrational levels of the ground state.

We shall therefore consider the excitation diagrams for acridone, the spectrum of which has been studied in detail[82]. In the first excited singlet and triplet states the partial localisation and charge-transfer numbers yield the following distribution of excitations:



(49)

The degree of polarity of the singlet transition, treated as the sum of all the charge-transfer numbers $l_{AB}(A \neq B)$ is more than 50%. In the lowest triplet state, many of the properties of which are closer to those of the ground state than to the corresponding excited singlet state, the degree of polarity is smaller (26%). The vibrational structure of the phosphorescence spectrum makes it possible to determine the characteristic frequencies in the infrared spectrum of the benzene ring and the carbonyl group; in the latter they are not dominant (in contrast to $n\pi^*$-phosphorescence). Diagram (49) agrees with these observations—the local numbers for the benzene rings (0.33) prove to be much greater than for the carbonyl group (0.07).

We may note that the relation between the charge-transfer numbers and the fine structure of the band in the electronic spectrum is not unambiguous. However, one can assume that the individuality of the fragments under the conditions of pronounced charge transfer between them is lost, so that, other conditions being equal, the manifestation of the vibrational structure of the excited fragments is hindered.

The intensity of the corresponding transition is related to the polar nature of the excited state. Strictly speaking, theory does not predict a parallel variation of the degree of charge transfer and one can claim that, if $l_{AB}=1$, i.e. there is complete charge transfer, then the intensity of the π-band becomes zero. Complete charge transfer does not usually occur and the intensity of the transition is influenced by the topology of the molecule, its size, vibronic effects, intermolecular interaction, etc. In the systems considered above charge-transfer bands arose for transitions polarised in the direction of the long molecular axis. Their intensity is therefore greater than that of the α-bands polarised at right angles and related genetically to transitions of purely benzenoid systems, which are prohibited by the alternant properties.

For short-radius excitations, it is possible to establish in many instances definite relations between the parameters of the molecular shape and the intensity of the transition[83].

In conclusion we shall state an analogue of formula (22′) for charge-transfer numbers, namely, in terms of the basis set of natural orbitals, we have[80] $\tau=\Sigma\mu_\alpha^{1/2}\times|\phi_{N+\alpha}\rangle\langle\phi_\alpha|$; consequently, the charge-transfer numbers defined by Eqn.(39) can be expressed in terms of localisation orbitals defined by Eqn.(19):

$$l_{A\to B}=\sum_{\alpha=1}^{r}\mu_\alpha L_A(\varphi_\alpha)\cdot L_B(\varphi_{N+\alpha}).$$

This representation does not hold in terms of the basis set of canonical molecular orbitals, although attempts had been made earlier to use the corresponding quantities in order to estimate the degree of charge transfer[61].

VII. DISTRIBUTION OF EXCITATION ENERGY AMONG THE STRUCTURAL ELEMENTS OF THE MOLECULE

We shall now attempt to elucidate in what way selective localisation of excitation is related to changes in the properties of the molecule in the electronic transition. Apparently marked isolation of excitation in a single fragment implies that all the changes in the molecular characteristic $\mathscr{X}$ on excitation are associated precisely with this fragment, i.e. the corresponding physical quantity $\Delta\mathscr{X}=\mathscr{X}_*-\mathscr{X}$ is, as it were, localised in a given limited region of the molecule. In this connection the study of the spatial distribution of excitation energy assumes particular interest.

There is much experimental evidence for the possibility of the preferential concentration of the transition energy $\lambda=E_*-E$ at individual bonds or in other structural elements of the molecules[9]. In particular, the photochemical instability of the fragment is attributed to the localisation in the latter of a considerable proportion of the excitation energy[84].

The first attempts to explain what should be understood in terms of the spatial distribution of the electronic energy were made by Tatevskii[85]. However, the method of analogies which he used did not enable him to obtain any specific results, since the distribution of energy proved to be simply proportional to the electron density. This conclusion should have been surprising, since the energy of the system is determined not only by the one-particle density matrix, but also by the two-particle density, which averages the Coulombic interaction between the electrons in the calculation of E.

It must be emphasised that in the steady state the quantum-mechanical system possesses the total energy E observed in direct experiments as a unique quantity and the assignment to an isolated region of the molecule of a proportion of the energy localised in this region constitutes a non-trivial procedure with a controversial physical interpretation[86].

Strictly speaking steady states in which one could observe simultaneously with E also a local energy $\mathscr{E}(\mathbf{r})$ concentrated at a point $\mathbf{r}$ do not exist in the general case in quantum mechanics. However, in principle the operator corresponding to the required energy density $\mathscr{E}(\mathbf{r})$ can be set up on the basis of rules developed in the quantum field theory, where such an operator is known as the density of the Hamiltonian $\mathscr{H}(\mathbf{r})$.[87] Then, by calculating the average value of $\mathscr{H}(\mathbf{r})$ for the states of the system under investigation, we thereby obtain the required information about the spatial distribution of the energy in this state. The applied aspects of this approach[88] become evident if one takes into account the fact that regions with a low energy density (as a negative quantity) are most likely to exhibit the highest reactivity and the concentration of excitation energy (as a positive quantity) in the vicinity of specific atoms in the molecule indicates an increased photochemical reactivity of these atoms.

In order to calculate $\mathscr{E}(\mathbf{r})$, we should determine the density of the Hamiltonian as a Hermitian operator $\mathscr{H}(\mathbf{r})$, having the following form in terms of atomic units[87]:

$$\mathscr{H}(\mathbf{r})=\tfrac{1}{2}\nabla\psi^+(\mathbf{r})\cdot\nabla\psi(\mathbf{r})+U(\mathbf{r})\psi^+(\mathbf{r})\psi(\mathbf{r})+\tfrac{1}{2}\int\psi^+(\mathbf{r})\psi^+(\mathbf{r}')g(\mathbf{r},\mathbf{r}')\psi(\mathbf{r}')\psi(\mathbf{r})\,d\mathbf{r}',$$

where $\Psi^+(\mathbf{r})$ and $\Psi(\mathbf{r})$ are the electron generation and annihilation operators, the function $U(\mathbf{r})$ describes a one-particle interaction potential, and the function $g(\mathbf{r},\mathbf{r}')$ describes a two-particle interaction potential. In conformity with the approach adopted here, the required energy density $\mathscr{E}(\mathbf{r})$ is obtained by averaging $\mathscr{H}(\mathbf{r})$ with respect to the state investigated $|\Phi>$ in terms of a secondary quantisation representation:

$$\mathscr{E}(\mathrm{r}) = \langle\Phi|\mathscr{H}(\mathrm{r})|\Phi\rangle,$$

The total energy of the system E is obtained by integration with respect to the entire configurational space:

$$E = \int \mathscr{E}(\mathrm{r})\, d^3\mathrm{r}.$$

After introducing the spin-free single-particle density matrix $P(\mathbf{r}|\mathbf{r}')$ and the two-particle density matrix $R(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_1',\mathbf{r}_2')$,

$$P(\mathrm{r}|\mathrm{r}') = \langle\Phi|\psi^+(\mathrm{r})\psi(\mathrm{r}')|\Phi\rangle, \qquad (50)$$

$$R(\mathrm{r}_1,\mathrm{r}_2|\mathrm{r}_1',\mathrm{r}_2') = \langle\Phi|\psi^+(\mathrm{r}_1)\psi^+(\mathrm{r}_2)\psi(\mathrm{r}_2')\psi(\mathrm{r}_1')|\Phi\rangle,$$

we find a more detailed expression for the density:

$$\mathscr{E}(\mathrm{r}) = \left[\left(\tfrac{1}{2}\frac{\partial}{\partial \mathrm{r}}\frac{\partial}{\partial \mathrm{r}'} + U(\mathrm{r})\right)P(\mathrm{r}|\mathrm{r}')\right]_{\mathrm{r}=\mathrm{r}'} + \int g(\mathrm{r},\mathrm{r}')\,R(\mathrm{r},\mathrm{r}'|\mathrm{r},\mathrm{r}')\,d^3\mathrm{r}'. \qquad (51)$$

In the special case of a system of non-interacting particles, only the first term remains in Eqn.(51) and, when a one-particle system is investigated, we have

$$\mathscr{E}(\mathrm{r}) = \tfrac{1}{2}|\nabla\varphi(\mathrm{r})|^2 + U(\mathrm{r})|\varphi(\mathrm{r})|^2,$$

where $\varphi(\mathbf{r})$ is the wave function of the particle. Even in this simple case $\mathscr{E}(\mathbf{r})$ differs from the electron density $E|\varphi|^2$ by the momentum $\frac{1}{2}(\varphi^* p^2\varphi - |p\varphi|^2)$, where $\mathbf{p}$ is the momentum operator.

We shall now turn to the details of the general formula (51) for a one-determinant description of the ground state of the molecule in terms of the Hartree–Fock approximation. For this purpose we express Eqn.(51) in a more convenient form by introducing the Hermitian energy density operator $\hat{\mathscr{E}}$ in the specified state $|\Phi>$ described by the overall density matrices of type (50) with the spin variables ρ_1 and ρ_2:

$$\hat{\mathscr{E}} = \tfrac{1}{2}([h,\rho_1]_+ - 1/2\,[\mathrm{p},[\mathrm{p},\rho_1]_-]_- + \underset{(2)}{\mathrm{Sp}}[g(1,2),\rho_2(1,2)]_+),$$

where the one-particle Hamiltonian $h = \frac{1}{2}\mathbf{p}^2 + U$ has been introduced. It can be readily shown that the diagonal elements $\hat{\mathscr{E}}$ in the coordinate representation $<\mathbf{r}|\hat{\mathscr{E}}|\mathbf{r}'>$ coincide exactly with the energy density (51) and $\mathrm{Sp}\,\hat{\mathscr{E}} = E$. In terms of the Hartree–Fock approximation, $\rho_1 = \rho \equiv \sum_{i=1}^{N}|i\times i|$, where $|i>$ is the population of the spin-orbital of the ground state and the two-particle density $\rho_2(1,2)$ is given by an antisymmetrised direct product: $\rho_2(1,2) = A_2\rho(1)\rho(2)$. Hence we find immediately the structure of the energy density operator in terms of the self-consistent field approximation:

$$\hat{\mathscr{E}} = \tfrac{1}{4}([f+h,\rho]_+ - [\mathrm{p},[\mathrm{p},\rho]_-]_-), \qquad (52)$$

where $f = h + 2G(\rho)$ is the Fock operator of the many-electron system investigated and $G(X) \equiv \underset{(2)}{\mathrm{Sp}} A_2 g(1,2)X(2)$.

The distribution of energy among the structural elements of the molecule, primarily atoms and bonds, rather than the local density $\mathscr{E}(\mathbf{r})$ is of direct interest for quantum-chemical purposes. The corresponding index can be determined by integrating $\mathscr{E}(\mathbf{r})$ in the region A investigated and leads to the replacement of $\mathscr{E}(\mathbf{r})$ by the quantities $\mathscr{E}_\mu = <\chi_\mu|\hat{\mathscr{E}}|\chi_\mu>$ in terms of the basis set of the atomic orbitals χ_μ, and $\mathscr{E}_A = \sum_{\mu\in A}\mathscr{E}_\mu$.

We shall now consider the special cases $\mathscr{E}_\mu$ in terms of the self-consistent field approximation [formula (52)]. Firstly, for neutral states of alternant hydrocarbons, one can show that, in terms of the π-approximation, the contributions of momentum to $\mathscr{E}_\mu$ become zero whatever the multiplicity of the electronic energy state. Furthermore, neglect of the inter-electron interaction in an alternant molecule is known to result in the Hückel model, for which we obtain, taking into account $\hat{\mathscr{E}} = h\rho = \rho h$, the following index of the localisation of energy§ at the atom μ, expressed in terms of the spin-free bond orders $P_{\mu\nu}$: $\mathscr{E}_\mu = \beta\sum_\sigma P_{\mu\sigma}$, where σ represents only centres adjoining μ. This is clearly none other than the free valence index of the atom to within constant terms. Thus the energetic indices $\mathscr{E}_\mu$ extend the reactivity index to the case of the Hartree–Fock description of arbitrary molecular systems.

In the light of the foregoing, it is not difficult to find the excitation energy density $\lambda(\mathbf{r})$, which we defined naturally as the difference between the densities in the ground $\mathscr{E}(\mathbf{r})$ and excited $\mathscr{E}_*(\mathbf{r}) = <\Phi_*|\mathscr{H}(\mathbf{r})|\Phi_*>$ states. We shall adopt the superposition of all the singly excited configurations, for which the density matrices have been obtained[17], as a fairly adequate approximation for the excited state Φ_* in relation to the Hartree–Fock ground state Φ. The final result of the calculation of $\lambda(\mathbf{r}) = \mathscr{E}_*(\mathbf{r}) - \mathscr{E}(\mathbf{r})$ leads to the following excitation localisation operator:

$$\hat{\lambda} = -\tfrac{1}{4}([f+h, D^2Y]_+ + [G(DY), DY]_+ - [G(D), D]_- + 2\,[G(D^2Y),\rho]_+ - [\mathrm{p},[\mathrm{p}, D^2Y]_-]_-),$$

the diagonal elements of which are the same as $\lambda(\mathbf{r})$ in terms of the coordinate representation, while combinations of the matrix elements in terms of the atomic basis set of type $\mathscr{E}_A$ are the same as the indices of excitation at atoms and bonds. In the stability matrix method we have a similar expression but without the second anticommutator ($Y \equiv 2\rho - I$).

As for the ground state, in the case of neutral alternant systems in the π-electron approximation the momentum contributions to the diagonal elements $\hat{\lambda}$ in terms of the atomic orbital basis set disappear. If we then again resort to the Hückel model, then the spin-free operator $\hat{\lambda}_0$ reduces merely to a single anticommutator, which can be readily transformed into a product:

$$\hat{\lambda}_0 = -[h, D_0^2Y_0]_+ = -2hD_0^2Y_0,$$

where the subscript 0 indicates a spin-free quantity here and henceforth.

We shall consider in the same systems a one-electron transition from the $|i>$ orbital to the corresponding, in terms of alternant symmetry, vacant orbital $|i'>$, i.e. $D_0 = (|i><i'| + |i'><i|)/\sqrt{2}$, and, on the basis of the theory of parity, the one-electron energy is $\mathscr{E}_i = -\mathscr{E}_{i'}$. It is then easy to observe that $\hat{\lambda}_0(i\to i') = 2|\mathscr{E}_i|D_0^2$ and if we now introduce the energy localisation operator as the operator $\hat{\lambda}_0$ normalised with respect to unity and the corresponding localisation indices

$$\hat{L}_0 = 1/\lambda\hat{\lambda}_0, \quad L_A^{\mathscr{E}} = \sum_{\mu\in A}\langle\chi_\mu|\hat{L}_0|\chi_\mu\rangle,$$

we observe in this instance ($\lambda = 2|\mathscr{E}_i|$) the identity of $\hat{L}_0$ and the matrix D_0^2.

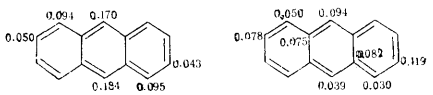
Consequently the energetic localisation indices $L_A^{\mathscr{E}}$ for the diagonal transitions $i\to i'$ in terms of the Hückel approximation are identical with the localisation numbers L_A described

§ The Hückel energy indices (without momentum contributions) have been introduced[99] on the basis of intuitive considerations.

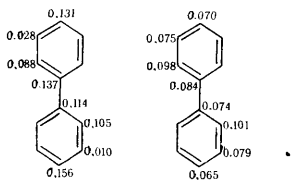
above. The inclusion of electronic interaction in terms of a self-consistent scheme for alternant systems causes an insignificant deviation of L_A^{ε} from L_A. However, in systems with an inhomogeneous charge distribution the excitation indices calculated from the operator $\hat{L}_0$ differ appreciably from the quantities defined by Eqn.(23).

For non-alternant systems, one fundamental difference between these operators is clearly manifested. In contrast to D_0^2 and despite the evident normalising property $\mathrm{Sp}\,\hat{L}_0 = 1$, the operator $\hat{L}_0$ is not in the general case defined as a non-negative quantity and its diagonal elements are therefore not definite. The possible negative sign of $\langle\chi_\mu|\hat{L}_0|\chi_\mu\rangle$ can, however, be interpreted as evidence for the existence of regions in the molecule which are not loosened on excitation but are actually stabilised to an even greater extent than in the ground state. This factor makes the localisation indices obtained from the energetic criterion particularly informative as regards the photochemical aspect.

The localisation numbers L_A (above) and the energetic indices L_A^{ε} (below) are given below for the p- and β-bands of anthracene

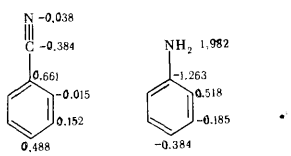


and biphenyl



The above diagrams show that, on excitation to the $^1B_{2u}$ state, the transition energy is distributed fairly non-uniformly among the atoms in the molecule, being concentrated in the 9- and 10-positions in anthracene (approximately 40% of the overall value of λ) and in the 4- and 4′-positions in biphenyl (>30% of λ). Data for the photodimerisation of anthracene and the Diels–Alder photoaddition[89] show that the atoms in the 9- and 10-positions are indeed photochemically active in anthracene.

An example of excitations for which positive and negative values of L_A^{ε} are possible is provided by the intense long-wavelength transitions (p-bands) in non-alternant molecules—benzonitrile and aniline:



The negative values of L_A^{ε} for the CN group indicate the photochemical stability of the latter. At the same time, the ring carbon atom closest to CN is greatly destabilised ($L_C^{\varepsilon} = 0.66$) and the chemical reactions in the excited state should therefore involve primarily this atom. In fact there is a tendency towards the photoaddition of trimethylethylene to benzonitrile in precisely this position[89]. On the other hand, in aniline the outer NH_2 group is the most active section of the excited molecule and this feature promotes the experimentally observed photoabstraction of hydrogen from the aniline NH_2.[90] The different signs of L_μ^{ε} in these molecules are consistent with the opposite directions of the charge transfer in them.

The uniform distribution of the excitation involving the molecule as a whole leads to smaller energetic localisation indices than for excitation isolated in a fragment and hence excited molecules which are photochemically more stable. In asymmetric systems the charge-transfer states are of this kind, as stated in Section V. In excited charge-transfer systems the photochemical stability is therefore higher than for local excitations[91].

The data presented in this review permit the formulation in a specific form of the quantum-chemical aspects of the concept of the "structure of electronic excitation".

The "internal" structure of the wave function Φ_* describing the excited state, namely the existence of the most important invariant elements of Φ_* of the type of independent singly excited configurations, the determination of orbitals which impart to Φ_* the simplest form, etc., was studied in the first place. The search for such invariant elements inevitably leads to natural orbitals of the excited state which are reconstructed anew for each electronic transition from the usual self-consistent molecular orbitals of the ground state. Analysis of model (3) yielded an important and somewhat unexpected conclusion—the greater the number of natural independent configurations in Φ_*, the smaller the changes undergone by the molecule as a whole on electronic excitation. This assertion shows how the internal structure determines the characteristic features of the external excitation structure in model (3). Our analysis of the external structure was concentrated on the study of the distribution of excitation in the direct structural-chemical sense (in atoms, bonds, whole fragments, etc.), on the elucidation of the physicochemical consequences of the selective localisation of excitation in fragments, on the determination of the relation between the localisation of excitation and charge transfer, etc.

The localisation numbers L_A and l_A, the charge-transfer numbers $l_{A\to B}$, and the energetic excitation indices L_μ^{ε} are all quantities arising in the method of transition density operators, which have demonstrated, in our view, a certain elegance and clarity in the interpretation of the external excitation structure mentioned above, which is important primarily for applied purposes.

The range of problems in the solution of which excitation indices defined by Eqns.(23) and (26) are used continues to be extended. An attempt has been made to apply the excitation localisation numbers in the analysis of data on the photoisomerisation of stilbene derivatives[92]. Studies have been made on the use of the indices L_A and l_{AB} for new classes of molecules[93–96]. Different analytical methods for excited states have been compared[97] and definite advantages of localisation numbers introduced by Luzanov and coworkers[42,80], compared with similar numbers introduced by other workers[59,61], have been pointed out.

Further efforts to generalise the above numerical characteristics of the wave function Φ_* (more accurate than in the initial model), adopted in this review (superposition of all singly excited configurations), therefore merit attention. One of the versions of such generalisation has been discussed by the present author in a paper[80], where it was suggested that the generalised matrix $\tilde{D}^2$ be constructed by analogy with Eqn.(34) using the normalised operator modulus of the change in the one-particle density matrix $|\rho_1^* - \rho_1|$ on transition from the ground state, not necessarily of the Hartree–Fock type, to an excited state, which does not necessarily reduce to approximation (3).

The internal excitation structure could be studied in a manner similar to the entropic analysis of wave functions considered by Bochvar et al.[98] In terms of the applied aspect, the application of the method of excitation indices[42,79] to nonconjugated molecules is not of interest solely as regards the

π-electron model, which has been used in all the computational studies quoted in this review. Such are apparently the likely prospects for the development of the methods of description of the electronic excitation structure of molecules discussed here.

REFERENCES

1. H.Longuet-Higgins and J.Murrell, Proc.Phys.Soc., **A68**, 901, 969 (1955).
2. K.Kimura and S.Nagakura, Theor.Chim.Acta, **3**, 164 (1965).
3. H.Baba, S.Suzuki, and T.Takemura, J.Chem.Phys., **50**, 2078 (1969).
4. W.England, L.Salmon, and K.Ruedenberg, Fortsch. chem.Forsch., **23**, 31 (1971); H.Weinstein, R.Pauncz, and M.Cohen, Adv.Atom.Mol.Phys., 7, 97 (1971).
5. "Localisation and Delocalisation in Quantum Chemistry", Dordrecht–Boston, Vol.1, 1975; Vol.2, 1976.
6. I.B.Bersuker, Teor.Eksper.Khim., **9**, 3 (1973).
7. T.E.Peacock, "Electronic Properties of Aromatic and Heterocyclic Molecules" (Translated into Russian), Izd.Mir, Moscow, 1969.
8. S.P.McGlynn, T.Azumi, and M.Kinoshita, "Molecular Spectroscopy of the Triplet State" (Translated into Russian), Izd.Mir, Moscow, 1972.
9. L.A.Gribov, "Vvedenie v Molekulyarnuyu Spektroskopiyu" (Introduction to Molecular Spectroscopy), Izd.Nauka, Moscow, 1976.
10. V.A.Gubanov, V.P.Zhukov, and A.O.Litiinskii, "Poluempiricheskie Metody Molekulyarnykh Orbitalei v Kvantovoi Khimii" (Semiempirical Molecular Orbital Methods in Quantum Chemistry), Izd.Nauka, Moscow, 1976.
11. M.M.Mestechkin, "Metod Matritsy Plotnosti v Teorii Molekul" (The Density Matrix Method in Molecular Theory), Izd.Naukova Dumka, Kiev, 1977.
12. R.N.Nurmukhametov, "Pogloshchenie i Lyuminestsentsiya Aromaticheskikh Soedinenii" (The Absorption and Luminescence of Aromatic Compounds), Izd. Khimiya, Moscow, 1971.
13. I.A.Misurkin and A.A.Ovchinnikov, Uspekhi Khim., **43**, 2195 (1974) [Russ.Chem.Rev., No.12 (1974)]; **44**, 393 (1975) [Russ.Chem.Rev., No.3 (1975)].
14. S.Epstein, "The Variational Method in Quantum Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1977, Chapter III.
15. W.Ostlund and M.Karplus, Chem.Phys.Letters, **11**, 450 (1971).
16. T.-I.Shibuya and V.McKoy, J.Chem.Phys., **54**, 1738 (1971).
17. A.V.Luzanov, Teor.Eksper.Khim., **9**, 723 (1973).
18. J.M.Eisenberg and W.Greiner, "Microscopic Theory of the Nucleus" (Translated into Russian), Atomizdat, Moscow, 1976.
19. Yu.A.Kruglyak, G.G.Dyadyusha, V.A.Kuprievich, G.I.Kagan, and L.M.Podol'skaya, "Metody Rascheta Elektronnoi Struktury i Spektrov Molekul" (Methods for the Calculation of the Electronic Structure and Spectra of Molecules), Izd.Naukova Dumka, Kiev, 1969.
20. G.I.Kagan, Candidate's Thesis, Institute of General Chemistry, USSR Academy of Sciences, Moscow, 1968.
21. H.Kashiwagi, Bull.Chem.Soc.Japan, **44**, 624 (1971).
22. Y.H.Méyer, R.Astier, and J.M.Leclercq, J.Chem. Phys., **56**, 801 (1972).
23. J.Panzir and R.Zagradnic, J.Phys.Chem., **77**, 107 (1973).
24. G.Olbrich and F.Fratev, Izv.Khim.B'lg.Akad.Nauk, 11, 98 (1978).
25. R.McWeeny, in "Reports, Density Matrix Seminar", Queen's University, Ontario, 1968, p.25; Mol.Phys., **30**, 1203 (1975).
26. M.M.Mestechkin, Symposium, "Stroenie Molekul i Kvantovaya Khimiya" (Molecular Structure and Quantum Chemistry), Izd.Naukova Dumka, Kiev, 1970, p.111.
27. M.M.Mestechkin and L.S.Gutyrya, Optika i Spektrosk., **26**, 159 (1969).
28. M.M.Mestechkin, L.S.Gutyrya, and V.N.Poltavets, Optika i Spektrosk., **28**, 454 (1970); **30**, 1022 (1971); **31**, 847 (1971).
29. A.V.Luzanov, Teor.Eksper.Khim., **11**, 3 (1975); "Konstruktivnye Metody v Teorii Perekhodnykh Matrits Plotnosti" (Constructive Methods in the Transition Density Matrix Theory), Preprint from the Physical Technical Low-Temperature Institute, Kharkov, 1976.
30. P.Jorgensen and J.Oddershede, J.Chem.Phys., 57, 277 (1972).
31. M.N.Adamov and N.P.Borisova, Symposium, "Problemy Teoreticheskoi Fiziki" (Problems of Theoretical Physics), Izd.Leningrad.Gos.Univ., 1974, No.1, p.117.
32. Yu.B.Malykhanov and M.M.Mestechkin, Optika i Spektrosk., **33**, 469 (1972).
33. A.V.Luzanov, Teor.Eksper.Khim., **9**, 733 (1973).
34. A.V.Luzanov, M.M.Mestechkin, and Yu.B.Vysotskii, Zhur.Strukt.Khim., 12, 289 (1971); **16**, 195 (1975).
35. A.V.Luzanov and V.E.Umanskii, Zhur.Strukt.Khim., 18, 3 (1977).
36. A.V.Luzanov, Teor.i Mat.Fiz., **30**, 361 (1971).
37. D.Thoules, Nucl.Phys., **22**, 78 (1962).
38. A.V.Luzanov, V.F.Pedash, Yu.F.Pedash, and V.E.Umanskii, Izv.Akad.Nauk SSSR, Ser.Fiz., **42**, 294 (1976).
39. H.Kashiwagi and S.Iwata et al., Bull.Chem.Soc.Japan, **46**, 417 (1973).
40. A.E.Lutskii and N.I.Gorokhova, Teor.Eksper.Khim., **6**, 490 (1970).
41. B.E.Zaitsev and V.M.Allenov, Zhur.Prikl.Spektrosk., **20**, 109 (1974).
42. A.V.Luzanov, A.A.Sukhorukov, and V.E.Umanskii, Teor.Eksper.Khim., **10**, 456 (1974).
43. Yu.Yu.Dmitriev and L.N.Labzovskii, Teor.Eksper. Khim., **6**, 3 (1970).
44. A.V.Luzanov and V.E.Umanskii, Teor.Eksper.Khim., **14**, 217 (1977).
45. A.Streitwieser, "Molecular Orbital Theory for Organic Chemists" (Translated into Russian), Izd. Mir, Moscow, 1965.
46. E.S.Stern and C.J.Timmons, "Gillam and Stern's Introduction to Electronic Absorption Spectroscopy in Organic Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1974.
47. Yu.B.Malykhanov, Optika i Spektrosk., **43**, 431 (1977).
48. M.V.Bazilevskii, "Metod Molekulyarnykh Orbitalei i Reaktsionnaya Sposobnost' Organicheskikh Molekul" (The Molecular Orbital Method and the Reactivity of Organic Molecules), Izd.Khimiya, Moscow, 1969.
49. D.N.Shigorin, Zhur.Fiz.Khim., **44**, 2681 (1970) [Russ.J.Phys.Chem., No.11 (1970)].

50. O.B.Sverdlova, "Elektronnye Spektry v Organicheskoi Khimii" (Electronic Spectra in Organic Chemistry), Izd.Khimiya, Leningrad, 1973.
51. V.A.Izmail'skii, Symposium, "Fiziko-Khimicheskie Svoistva Organicheskikh Veshchestv i Ikh Svyaz' so Stroeniem i Mikrostrukturoi" (Physicochemical Properties of Organic Substances and Their Relation with Structure and Microstructure), Izd. MGPI, Moscow, 1974, p.5.
52. V.I.Stepanov, "Vvedenie v Khimiyu i Tekhnologiyu Organicheskikh Krasitelei" (Introduction to the Chemistry and Technology of Organic Dyes), Izd. Khimiya, Moscow, 1977.
53. V.A.Kuprievich, Stud.Biophys., **58**, 1973 (1976).
54. A.Denis, J.Longlet, and J.Malrien, Theor.Chim. Acta, **29**, 117 (1973).
55. A.E.Lutskii, I.I.Naidenova, N.I.Gorokhova, I.S.Romodanov, and Z.A.Shevchenko, Izv.Vys. Ucheb.Zaved., Khim.i Khim.Tekhnol., **18**, 249 (1975).
56. M.Reinhardt, A.A.Sukhorukov, and A.V.Luzanov, Symposium, "Qvantovaya Khimiya" (Quantum Chemistry), Izd.Shtiintsa, Kishinev, 1975, p.200.
57. A.V.Luzanov and V.V.Umanskii, Optika i Spektrosk., **41**, 156 (1976).
58. A.A.Sukhorukov et al., Teor.Eksper.Khim., **11**, 747 (1975).
59. A.A.Sukhorukov, V.E.Umanskii, B.A.Zadrozhnyi, and V.F.Lavrushin, Teor.Eksper.Khim., **12**, 681 (1976).
60. A.V.Luzanov and V.F.Pedash, Optika i Spektrosk., **43**, 176 (1977).
61. T.Ohta, H.Kuroda, and T.Kunii, Theor.Chem.Acta, **19**, 167 (1970).
62. I.L.Belaits, N.I.Kunavin, R.N.Nurmukhametov, and A.E.Podol'skaya, Optika i Spektrosk., **38**, 908 (1975).
63. A.V.Luzanov and V.E.Umanskii, Optika i Spektrosk., **40**, 201 (1976).
64. A.F.Davydov, "Teoriya Molekulyarnykh Eksitonov" (Theory of Molecular Excitons), Izd.Nauka, Moscow, 1968.
65. T.G.Pavlopoulous, IEEE J.Quant.Electr., **9**, 510 (1973).
66. M.Godfrey and J.Murrell, Proc.Roy.Soc., **A278**, 64 (1964).
67. A.V.Luzanov, Yu.B.Malykhanov, and M.M.Mestechkin, Teor.Eksper.Khim., **6**, 723 (1970).
68. Yu.B.Vysotskii, Optika i Spektrosk., **44**, 1025 (1978).
69. S.L.Murov (Editor), "Handbook of Photochemistry", Marcel-Dekker, New York, 1973.
70. N.G.Bakhshiev, "Spektroskopiya Mezhmolekulyarnogo Vzaimodeisteviya" (Spectroscopy of Intermolecular Interaction), Izd.Nauka, Leningrad, 1972.
71. P.Suppon, J.Mol.Spectr., **30**, 17 (1969).
72. A.E.Lutskii, Optika i Spektrosk., **34**, 1976 (1973).
73. E.N.Gur'yanova, I.P.Gol'dshtein, and I.G.Romm, "Donorno-Aktseptornaya Svyaz'" (The Donor–Acceptor Bond), Izd.Khimiya, Moscow, 1973.
74. T.Hinohara, S.Cho, and T.Morita, Bull.Chem.Soc. Japan, **44**, 629 (1971).
75. T.G.Edwards, Theor.Chim.Acta, **30**, 267 (1973).
76. V.N.Mochalkin, Teor.Eksper.Khim., **9**, 357 (1973).
77. I.N.Fundyler and V.M.Ryaboi, Izv.Akad.Nauk SSSR, Ser.Khim., 573 (1974).
78. S.Suzuki and T.Fujii, Bull.Chem.Soc.Japan, **48**, 835 (1975).
79. A.V.Luzanov and V.F.Pedash, Teor.Eksper.Khim., **15**, 436 (1979).
80. A.V.Luzanov, Teor.Eksper.Khim., **14**, 579 (1977).
81. K.R.Popov, L.V.Smirnov, L.G.Grebeneva, and L.A.Nakhimovskaya, Optika i Spektrosk., **37**, 1070 (1974).
82. R.N.Nurmukhametov, D.N.Shigorin, L.A.Mileshina, and G.A.Ozerova, Zhur.Fiz.Khim., **40**, 2206 (1966) [Russ.J.Phys.Chem., No.9 (1966)].
83. A.I.Kiprianov and G.G.Dyadyusha, Ukrain.Khim. Zhur., **35**, 608 (1969).
84. N.A.Borisevich and V.V.Gruzinskii, Symposium, "Kvantovaya Elektronika i Lazernaya Spektroskopiya" (Quantum Electronics and Laser Spectroscopy), Izd. Nauka i Tekhnika, Minsk, 1971, p.81.
85. V.M.Tatevskii, "Kvantovaya Mekhanika i Teoriya Stroeniya Molekul" (Quantum Mechanics and the Theory of Molecular Structure), Izd.Moskov.Gos. Univ., Moscow, 1965.
86. W.Heisenberg, "Principles of the Quantum Theory" (Translated into Russian), GTTI, Moscow, 1932.
87. A.I.Akhiezer and S.E.Peletminskii, "Metody Statisticheskoi Fiziki" (Methods of Statistical Physics), Izd.Nauka, Moscow, 1977.
88. A.V.Luzanov and V.F.Pedash, Preprint ITF-77-59R, Kiev, 1977.
89. N.J.Turro, "Molecular Photochemistry" (Translated into Russian), Izd.Mir, Moscow, 1967.
90. A.I.Terenin, "Fotonika Molekul Krasitelei i Rodstvennykh Organicheskikh Soedinenii" (Photonics of the Molecules of Dyes and Related Organic Compounds), Izd.Nauka, Moscow, 1967.
91. V.A.Krongauz, Uspekhi Khim., **41**, 852 (1972) [Russ. Chem.Rev., No.5 (1972)].
92. L.A.Sleta, Yu.A.Ershov, G.G.Kononenko, and L.Ya.Malkes, Teor.Eksper.Khim., **14**, 331 (1978).
93. Yu.L.Frolov, Yu.M.Sapozhnikov, N.N.Chipanina, V.F.Sidorkin, and N.A.Tyukavina, Izv.Akad.Nauk SSSR, Ser.Khim., 301 (1978).
94. V.A.Shagun, V.F.Sidorkin, V.L.Usov, and M.G.Voronkov, Teor.Eksper.Khim., **15**, 58 (1979).
95. O.M.Tsyguleva, I.M.Gella, and I.V.Krivoshei, Teor.Eksper.Khim., **15**, 441 (1979).
96. V.A.Kuz'mitskii, "Issledovanie Vozbuzhdennykh Elektronnykh Sostoyanii Dimerov Metalloporfina Metodom SSP MO LKAO" (The Study of the Excited Electronic States of Metalloporphin Dimers by the LCAO-MO SCF Method), Preprint No.188 from the Institute of Physics of the Academy of Sciences of Belorussian SSR, Minsk, 1979.
97. J.Fabian, A.Mehlhorn, and F.Fratev, Int.J.Quant. Chem., **17**, 235 (1980).
98. D.A.Bochvar, I.V.Stankevich, and A.L.Chistyakov, Uspekhi Khim., **43**, 655 (1974) [Russ.Chem.Rev., No.4 (1974)].
99. O.B.Tomilin and I.V.Stankevich, Izv.Akad.Nauk SSSR, Ser.Khim., 1275 (1975); 936, 1166 (1980).

Kharkov State University, Kharkov

Translated from *Uspekhi Khimii*, 49, 2118-2131 (1980) U.D.C. 546.147

Heptavalent Bromine Compounds

V.V.Gavrilov and V.K.Isupov

Publications on heptavalent bromine compounds which have appeared during the last 10 years are reviewed. The discussion includes the preparation and analysis of perbromates, the physical and chemical properties of perbromic acid and its salts, the "hot atom" chemistry and radiation chemistry of perbromates, and the practical utilisation of heptavalent bromine compounds. 80 references.

CONTENTS

I.	Introduction	1049
II.	Methods of preparation of heptavalent bromine compounds	1049
III.	Physical and chemical properties of perbromic acid and its salts	1050
IV.	Analytical chemistry of heptavalent bromine compounds	1051
V.	"Hot atom" chemistry of crystalline perbromates	1052
VI.	Radiation chemistry of heptavalent bromine compounds	1053
VII.	Practical applications of perbromic acid and its salts	1054

I. INTRODUCTION

Perbromates have long been classified among the compounds which cannot be prepared by ordinary chemical methods. However, the existence and widespread applications of their homologues (the perchlorates and the periodates) have stimulated renewed interest from theoreticians and experimentalists in the preparation of perbromates. The first attempts to prepare heptavalent bromine compounds were made in the middle of the 19th century. Experimental and theoretical work in this area is reviewed in Refs.1–4. The first successful preparation of perbromate (Appelman[5]) by the β^- disintegration of ^{83}Se in a selenate composition was described as recently as in 1968. By studying the chemical properties of microquantities of perbromate Appelman was able to develop[5] a macro-synthetic method for heptavalent bromine compounds.

Several dozen papers on heptavalent bromine compounds have appeared since the first successful synthesis of perbromate, but they do not include general reviews of the subject. The aim of this paper is to generalise existing information on heptavalent bromine compounds.

II. METHODS OF PREPARATION OF HEPTAVALENT BROMINE COMPOUNDS

The first successful synthesis of perbromate was carried out by the "hot atom" chemistry method, using the β^- disintegration of ^{83}Se in a selenate composition[5]. The resulting bromine-83 is radioactive, with a half-life of 2.4 h. Therefore the method does not yield weighable amounts of perbromates, but it does show that heptavalent bromine compounds are relatively stable and therefore can be prepared (in principle) in macro-amounts. The preparation was demonstrated by electrochemically oxidising lithium bromate in a neutral solution[5], using a partitioned cell with a platinum anode and an anodic current density of 10 A cm^{-2}. The yield of perbromate was ~2%.

The electrolytic oxidation of bromate was therefore not acceptable as a preparative method, because its yield was too low, and a search for more effective methods of preparing heptavalent bromine compounds was started. An aqueous solution of xenon difluoride, whose oxidation potential is 2.62 V, was added[6] to a fairly concentrated bromate solution, giving perbromate in 12% yield (calculated from the initial amount of xenon difluoride[7]).

Shortly after Appelman's preparation of heptavalent bromine compounds Brown and coworkers[8] demonstrated the formation of perbromate by irradiating caesium bromate with gamma-rays from ^{60}Co. The yield of caesium perbromate was 0.86% of the initial amount of caesium bromate. Irradiation of lithium bromate did not produce perbromate. No heptavalent bromine compounds were obtained by oxidising aqueous bromate solutions with sodium perxenate and persulphate at 100 °C,[5] or by treating bromate solutions with hydrogen peroxide in the presence of acid[9].

A more convenient method of preparing heptavalent bromine compounds relies[10] on the oxidation of sodium bromate by fluorine in an alkaline solution. This reaction gave a sodium perbromate yield of 20% of the initial amount of bromate:

$$F_2 + BrO_3^- + 2OH^- \rightarrow BrO_4^- + 2F^- + 2H_2O.$$

The preparation of sodium perbromate by this method is described in detail in Ref.11.

A simple method of separating sodium perbromate from the reaction mixture is extraction with acetone[12]. The sodium bromate solution after being oxidised with fluorine is evaporated to dryness under a heat lamp, and the residue is washed with acetone. Under these conditions the sodium perbromate is extracted into the liquid phase, and the sodium bromate and fluoride remain in the solid phase. The acetone is evaporated off, and the sodium perbromate is recrystallised first from acetone and then from ethanol.

The following perbromates have been prepared by neutralising perbromic acid with the appropriate hydroxide or oxide: lithium, sodium, potassium, rubidium, and caesium[13], magnesium, calcium, strontium, and barium[14], ammonium[15], silver[16], and uranyl[17]. Potassium, rubidium, caesium, and uranyl perbromates are recrystallised from aqueous solutions, silver perbromate by adding hexane to a benzene solution, and the other perbromates are usually recrystallised from acetone.

The reaction of potassium perbromate with antimony pentafluoride yields the highly reactive compound perbromyl fluoride[18–22], BrO_3F, which rapidly hydrolyses in air[23] and attacks glass even at room temperature. Isopropyl perbromate[16] also is unstable at room temperature, though it can be prepared by the reaction between isopropyl bromide and silver perbromate. On the other hand tetraphenylarsonium perbromate, prepared from tetraphenylarsonium chloride and sodium perbromate[8], is a very stable compound.

Thus, several compounds of heptavalent bromine have already been prepared.

III. PHYSICAL AND CHEMICAL PROPERTIES OF PERBROMIC ACID AND ITS SALTS

Perbromic acid is a strong monobasic acid. Potentiometric titration of 0.6 M $HBrO_4$ with a 0.6 M solution of sodium hydroxide gives a curve very similar to that of $HClO_4$ under the same conditions[10]. In aqueous solutions perbromic acid is stable up to a concentration of 55% (6 M), but it decomposes at higher concentrations. A 6 M solution of $HBrO_4$ is stable indefinitely at room temperature. When heated on a water bath the solution becomes weakly yellow after one hour, but its oxidising power is reduced by only 1%. Mass spectrometric measurements have shown[24] that perbromic acid is a very stable compound, and is less volatile than perchloric acid. Samples in which the concentration of perbromic acid is as high as 83% can be obtained by vacuum distillation at room temperature. Rapid removal of the water produces crystals of $HBrO_4 \cdot 2H_2O$, which quickly become liquid when stored in air.

Perbromic acid is a slow-acting oxidising agent. In dilute solutions it oxidises iodide and bromide ions quite slowly, and it does not react with chloride ions. This may explain early failures to detect perbromates, which were always sought among the most reactive (rather than the most inert) compounds. On the whole, perbromates are the least reactive of all oxy-halogen compounds (except the perchlorates). However, at high concentrations perbromic acid is no longer a slow-acting oxidiser. Thus, 12 M $HBrO_4$ rapidly oxidises chloride ions and reacts explosively with filter paper; 3 M $HBrO_4$ rapidly oxidises stainless steel, and 6 M $HBrO_4$ at 100 °C easily oxidises bivalent manganese to MnO_2, tervalent chromium to dichromate, and tervalent cerium to Ce(IV).[10] These reactions occur also at room temperature if the acid is dehydrated under vacuum.

Perbromic acid and its salts have the same u.v. and Raman spectra, showing that identical anions are present in both cases. The similarity between the Raman spectra of solid $KBrO_4$ and those of its solutions[25] confirms that these anions are also present in the crystals. By comparing the Raman and the i.r. spectra of solid $KBrO_4$ we find that two of the four Raman bands are active in the i.r.: assignment of these frequencies suggests a tetrahedral structure for $KBrO_4$. The fundamental vibrational frequencies of BrO_4^- [10] are compared with those of ClO_4^- and IO_4^- [26] in Table 1.

Table 1. Vibrational frequencies of ClO_4^-, BrO_4^-, and IO_4^- ions in the i.r. region.

Anions	Vibrational frequencies, cm^{-1}			
	ν_1	ν_2	ν_3	ν_4
ClO_4^-	935	460	1060	630
BrO_4^-	798	331	883	410
IO_4^-	791	256	853	325

The lack of fast oxygen exchange between the perbromate ion and water shows that this ion (unlike the periodate ion[27]) does not undergo the fast hydration reaction

$$IO_4^- + 2H_2O \rightleftarrows H_4IO_6^- .$$

The most fully investigated of the salts of perbromic acid is potassium perbromate: $KBrO_4$, a white crystalline substance with a density of 3.08 g cm^{-3}.[28] The enthalpy of formation of potassium perbromate is -68.74 ± 0.14 kcal $mole^{-1}$, and its enthalpy of dissolution is 11.61 kcal $mole^{-1}$.[29] The potassium perbromate crystals belong to the $BaSO_4$ structure type, with the rhombic lattice parameters $a = 8.930$, $b = 5.921$, and $c = 7.488$ Å. The BrO_4^- ion has a tetrahedral structure, with a Br–O bond length of 1.61 Å and an O–Br–O bond angle of 109–110°.[28] The bond order, calculated by the Long–Plane–Pauling formula, is 1.93,[30] as compared with a Br–O bond order of 1.56 [31] in perbromyl fluoride. The mean-square vibrational amplitudes and the Coriolis interaction constants have also been calculated[32–35].

The chemical shift in the photo-electronic spectra of potassium perbromate (as compared with potassium bromide) was lower than for the corresponding chlorine compounds but higher than for the iodine analogues[36]. This is consistent with the differences in bond energy for the three halogens calculated by the Hartree–Fock method. Quantum-chemical calculations[37,38] have shown that the perbromate ion can be less stable than the perchlorate and the periodate, but that the difference is very small. The standard electrode potential of the bromate–perbromate couple is variously reported as 1.74 V,[39] 1.76 V,[29,40] and 1.82 V,[41] which should be compared with 1.23 V for the chlorate–perchlorate couple and 1.64 V for the iodate–periodate couple.

Ammonium perbromate is another salt of perbromic acid which has been adequately studied[15]. It is a white crystalline compound, indefinitely stable in air. Its density is 2.5 g cm^{-3}, and its crystal lattice has a rhombic unit cell with lattice parameters $a = 9.20$, $b = 6.04$, and $c = 7.63$ Å.[15] NH_4BrO_4 is very much less hygroscopic than ammonium perchlorate. Thus at 95% relative humidity ammonium perbromate absorbs only 4% of water, after which its weight remains constant, whereas ammonium perchlorate absorbs 23% of water and becomes visibly wet. The solubility of ammonium perbromate in water increases with temperature[15] (9.5, 13.9, 17.8, and 26.3 g per 100 g of solution at 0, 15, 25, and 45 °C respectively). Ammonium perbromate is soluble in methanol, acetone, ethanol, and acetonitrile.

In the alkali metal perbromates the solubility in water decreases in the sequence from lithium perbromate to caesium perbromate. Whereas lithium and sodium perbromates are very soluble in water, the solubility of $KBrO_4$ is only 0.2 mole $litre^{-1}$, and rubidium and caesium perbromates are only sparingly soluble at room temperature. On the other hand the perbromates of the alkaline earth metals, magnesium, silver, and uranyl are very soluble in water as well as in acetone.

When stored in air the anhydrous perbromates of lithium and sodium are converted into crystal hydrates of composition $LiBrO_4 \cdot 2H_2O$ and $NaBrO_4 \cdot H_2O$ respectively, but potassium, rubidium, and caesium perbromates are much less hygroscopic. Crystals of alkaline-earth, magnesium, and uranyl perbromates deliquesce very rapidly in the air, and have to be handled in a dry-box.

Alkali, alkaline-earth, and magnesium perbromates decompose to the bromates, after losing all their water, when heated[13,14], whereas the decomposition products of ammonium perbromate are N_2, Br_2, H_2O, and small amounts of N_2O and NO_2.[15] Temperature ranges and decomposition temperatures of the alkali, alkaline-earth, magnesium, and ammonium perbromates are listed in Table 2.

It is clear from Table 2 that the thermal stability of the alkali metal perbromates increases in the sequence $LiBrO_4 < NaBrO_4 < KBrO_4 < RbBrO_4 < CsBrO_4$, whereas the alkaline-earth and magnesium perbromates are indistinguishable as regards thermal stability (within experimental error). The alkali metal perbromates decompose at higher temperatures than the perbromates of the alkaline-earth metals, but the decomposition temperatures are very sensitive to the purity

of the sample. Thus, a sample of $KBrO_4$ which had been prepared without recrystallisation began to decompose at 150 °C, whereas a recrystallised sample remained unchanged up to 260 °C.[10] Obviously, even traces of bromate impurity are able to catalyse the thermal decomposition of perbromates.

Table 2. Temperature ranges and decomposition temperatures of alkali, alkaline-earth, magnesium, and ammonium perbromates.

Compound	Decompn. temperature range, °C	Decompn. temperature, °C	References
$LiBrO_4$	185—220	210±10	13
$NaBrO_4$	246—289	226±10	13
$KBrO_4$	255—282	271±5	13
$KBrO_4$	260—280	275	10
$RbBrO_4$	272—300	291±5	13
$CsBrO_4$	200—319	302±5	13
NH_4BrO_4	180—260	—	15
$Mg(BrO_4)_2$	181—199	191±5	14
$Ca(BrO_4)_2$	180—201	193±5	14
$Sr(BrO_4)_2$	180—207	192±5	14
$Ba(BrO_4)_2$	174—203	187±5	14

Other salts of perbromic acid, such as silver and uranyl perbromates, have been much less fully investigated. Baum and coworkers[16] prepared $AgBrO_4$ as a white, hygroscopic salt which was stable for several months at room temperature. Silver perbromate is soluble in benzene but insoluble in saturated hydrocarbons. Uranyl perbromate is a light-green, very hygroscopic salt. As in the case of the uranyl perchlorates[42], samples of $UO_2(BrO_4)_2 \cdot nH_2O$ containing up to 7 moles of water per mole of salt can be prepared[17]. Uranyl perbromate pentahydrate (unlike the perchlorate) can be obtained only in a narrow range of water vapour pressures. From the i.r. and Raman spectra of the uranyl perbromates we may conclude[17] that the force constants of the UO_2^{2+} bonds in $UO_2(BrO_4)_2$ are similar to the corresponding values for $UO_2(ClO_4)_2$. The i.r. spectra of the hydrated uranyl perbromates indicate the existence of different types of bond in these compounds [as in the case of $UO_2(ClO_4)_2 \cdot .nH_2O$].[43]

IV. ANALYTICAL CHEMISTRY OF HEPTAVALENT BROMINE COMPOUNDS

Various methods can be used to detect and to determine perbromates. For qualitative analysis the main reaction is a drop test with an acidified solution of potassium iodide. The perbromate spot, unlike that of many other oxidising agents, does not appear at once: the rate of development of the spot increases with the concentration of potassium iodide and with the acidity of the solution. The perbromate ion can be detected by a Methylene Blue drop reaction, which produces a crimson spot of perbromate on a blue background[44], and also by the reaction with manganese sulphate in phosphoric acid, which produces a violet colour[45].

The most sensitive spot test for perbromate ions on paper is the benzidine reaction[46]. The chromatograms are sprayed with a 2% solution of benzidine in 10% acetic acid, and heated in a jet of hot air. The spot due to the perbromate ion is initially blue, but on being heated it becomes dark grey. The sensitivity of the reaction is 0.01 μg of potassium perbromate. The main drawback of all these qualitative reactions is their lack of specificity: many oxidising agents will seriously interfere with the detection of heptavalent bromine compounds.

Perbromates can be determined quantitatively by a variety of methods. One of the simplest is the reduction of perbromate to bromide ions, using 12 M HBr.[10] A five-fold (by volume) excess of concentrated HBr is added to the sample for analysis, and the resulting solution is allowed to stand for 10 min in a closed vessel. The reaction goes to completion in this time if the concentration of HBr is not less than 11.5 M: at an HBr concentration of 10.4 M 40 min are required to complete the reaction. The solution is then diluted 10-fold with a 2% solution of sodium iodide containing NaH_2PO_4, and titrated with thiosulphate. If the perbromate solution contains substantial amounts of lower oxygen compounds of bromine it is first reduced with dilute HBr, and the resulting bromine is swept out of the solution by a stream of argon. If the concentration of HBr is held between 0.5 and 1 M the perbromate is practically unaffected by this operation.

An alternative oxidation–reduction method uses $SnCl_2$ for the determination of perbromate ions[5]. The perbromate solution is made 6 M in hydrochloric acid, and Mo(VI) is added to it to a 0.04 M concentration. After adding an excess of $SnCl_2$ an aliquot of the solution is heated for 30 min on the water bath, in order to reduce the perbromate to bromide, and the latter is oxidised by chlorine to BrCN in a neutral solution of cyanide. The solution thus obtained is acidified and titrated with thiosulphate after adding KI.

Another method of determining perbromate in the presence of bromate includes the reduction of BrO_4^- to BrO_3^- by iodine in a weakly alkaline medium (pH 7–9) at 100 °C.[47] Evolution of free iodine is prevented by adding a known amount of Na_3AsO_3, and the excess of this reagent is titrated with iodine with starch indicator. The total amount of bromate is determined by titration with acidified thiosulphate. The perbromate ion can be reduced to bromate simply by adding a solution of KI, but in this case two weeks must be allowed for the reaction to go to completion, whereas with hydroiodic acid the reduction of BrO_4^- to Br^- is instantaneous at room temperature[48].

In addition to the redox methods, gravimetry methods of determining perbromate have been described. They involve precipitation of the perbromate as $RbBrO_4$ [5] or as tetraphenylarsonium perbromate[8]. The latter is precipitated by adding tetraphenylarsonium chloride to the solution containing perbromate and bromate ions. The precipitate is washed with water to remove traces of bromate and with 50% aqueous ethanol, and dried in a vacuum desiccator at room temperature.

As an alternative to the gravimetric end-determination, perbromate can be determined as tetraphenylarsonium perbromate by potentiometric titration with a solution of tetraphenylarsonium chloride[49]. Anions such as chlorate, chloride, bromate, bromide, fluoride, sulphate, and chromate do not interfere with the titration. However, in the presence of periodate ions this method cannot be used.

Polarographic measurements have given a single wave for solutions containing bromate and perbromate ions in 0.05 M $HClO_4$, corresponding to the reduction of BrO_4^- and BrO_3^- to Br^-, whereas in neutral or in alkaline media two distinct waves are observed. The first corresponds to the reduction of perbromate ions to bromate, and the second to the reduction of bromate to bromide, thus allowing the method to be used for the determination of BrO_4^- in the presence of BrO_3^-.[50] The error of the determination of perbromate by this method is 2%. The electrochemical reduction of BrO_4^- is discussed also in Refs. 51–54.

Small amounts of perbromate in the presence of traces of other bromine anions have been determined by colorimetric methods[55] and by extraction photometry, using Crystal Violet[56]. In the latter method the presence of bromate at concentrations up to 10^{-3} g-ion litre^{-1} does not interfere with the determination of perbromate, whereas bromide at concentrations greater than 5×10^{-4} M lowers the optical density of solutions of Crystal Violet containing BrO_4^-. The method is suitable for determining perbromate ions at concentrations between 10^{-6} and 10^{-5} M.

Perbromate ions can be separated from mixtures with other anions by ion-exchange, thin-layer, and paper chromatography methods. Lederer and Sinibaldi[44] studied the chromatographic behaviour of perbromate ions on paper and on thin cellulose and silica gel layers, using the ethanol–water–ammonia and butanol–pyridine–1 M NH_4OH systems. BrO_4^- was found to be more mobile than BrO_3^- under these conditions. The same is true in the isopropanol–1.5 M NH_4OH system[45], but in this case substantial reduction of the perbromate ion occurs, and therefore the system is not suitable for the quantitative determination of perbromate.

Table 3. Chromatographic separation of chemical forms of bromine by thin-layer and paper chromatography.

Chemical form	R_f values for chromatography on Al_2O_3		R_f values for paper chromatography	
	Acetone–water (8:1)	Acetone–water–ethanol (6:2:1)	Acetone–water–ethanol (6:2:1)	Acetone–water–pyridine (6:1:2)
BrO_4^-	0.60±0.02	0.68±0.02	0.89±0.02	0.82±0.02
BrO_3^-	0.08±0.01	0.14±0.02	0.39±0.01	0.26±0.02
Br^-	0.27±0.02	0.41±0.02	0.53±0.05	0.14±0.01

A method free from this drawback is described in Ref. 57. Bromine compounds were separated on thin layers of Al_2O_3 and on paper by using the following solvent systems: acetone–water, acetone–water–ethanol, and acetone–water–pyridine. The R_f values were determined by measuring the ^{82}Br activity with an MST-17 end-window counter: the results are summarised in Table 3.

Separation of bromate and perbromate ions on a thin layer of Al_2O_3 has been achieved also by using aqueous solutions of the salts, acids, and bases[58]. As in the case of paper electrophoresis, the perbromate ion has the higher mobility. The sharpest separation was obtained with solutions of thorium nitrate and zirconyl chloride[44].

A reliable method of separating the different chemical forms of bromine is ion-exchange chromatography on the strongly basic anion exchangers AV-17 and Dowex-1.[57] Selective separation of bromine compounds in different states of oxidation was achieved by elution with potassium bicarbonate and nitrate solutions. Bromite ions were washed out by elution with 0.5 M $KHCO_3$, bromate ions with 1 M $KHCO_3$, bromide ions with 1 M KNO_3, and perbromate ions with 2 M KNO_3. On the other hand, hypobromite ions were absorbed at the top of the column and were not eluted: apparently, these ions react with the anion exchange resin by brominating it.

On anion-exchange paper the perbromate ions are adsorbed as strongly as perchlorate and periodate ions: the Rf values of all these ions are very similar[45]. The best separation of BrO_4^- from BrO_3^- is obtained by using diethylaminocellulose.

V. "HOT ATOM" CHEMISTRY OF CRYSTALLINE PERBROMATES

The "hot atom" chemistry of crystalline perbromates has great theoretical and practical interest. Its theoretical importance stems from the possibility of predicting chemical forms and of setting up a kinetic theory of chemical reactions involving atoms with an excess of energy. The practical interest lies in the preparation of sources of radioactive bromine with a high specific activity.

One possible way of obtaining radioactive isotopes of bromine is to irradiate perbromates in a nuclear reactor. The radioactive isotopes are usually stabilised in chemical forms different from the original compound. The distribution of atoms of the radioactive isotope ^{82}Br over the different chemical forms after irradiation with thermal neutrons is shown in Table 4 for the perbromates of alkali[59] and alkaline-earth metals, and of magnesium and ammonium[60].

Table 4. Yield of chemical stabilisation forms of ^{82}Br in neutron-irradiated perbromates.

Irradiated compound	Yield of bromine-82, %				
	BrO_4^-	BrO_3^-	BrO_2^-	BrO^-	Br^-
$LiBrO_4 \cdot H_2O$	2.1±0.3	44±2	4.4±0.5	4.4±0.5	45±2
$NaBrO_4$	2.1±0.4	36±1	1.0±0.6	0.8±0.3	60±1
$KBrO_4$	2.3±0.4	44±3	1.1±0.3	1.7±0.3	51±3
$RbBrO_4$	2.6±0.4	33±1	3.0±0.3	2.0±0.3	59±2
$CsBrO_4$	2.2±0.4	31±1	5.1±0.5	3.5±0.5	58±2
NH_4BrO_4	1.6±0.4	<0.3	<0.3	0.4±0.3	98±1
$Mg(BrO_4)_2 \cdot 6H_2O$	4.4±0.4	68±2	1.8±0.5	1.7±0.5	24±1
$Ca(BrO_4)_2 \cdot 6H_2O$	9.2±0.7	42±2	3.8±0.5	2.2±0.5	43±2
$Sr(BrO_4)_2 \cdot 3H_2O$	8.0±0.3	26±1	1.9±0.3	1.7±0.3	62±1
$Ba(BrO_4)_2 \cdot 2H_2O$	6.0±0.3	27±1	1.1±0.3	3.1±0.3	63±1

The distribution of ^{82}Br over the different chemical forms in alkali metal perbromates irradiated with neutrons was studied also by Hassan and Heitz[61], who found that 74% of the ^{82}Br was present as bromide, 24% as bromate, and 1% as perbromate, in general agreement with other workers[59,60], but (surprisingly) they claim that the $^{82}BrO_4^-$ ions remained in the original spot in their paper electrophoresis method of analysis whereas $^{82}BrO_3^-$ had a much higher mobility (in contrast to earlier reports[44,58]).

After thermal annealing of neutron-irradiated perbromates the yields of the chemical forms of ^{82}Br show some major changes[60–62]. In the alkali metal perbromates the content of ^{82}Br as BrO_4^- increases initially to a maximum, and then decreases, but in this case the changes are not very great. The main reaction occurring when alkali metal perbromates are annealed is the oxidation of $^{82}Br^-$ to $^{82}BrO_3^-$, the size of the effect being very dependent on the nature of the cation. For example, in neutron-irradiated lithium perbromate the yield of $^{82}BrO_3^-$ was 98% at the end of the heat treatment, for $NaBrO_4$ it was 93%, for $KBrO_4$ 89%, for $RbBrO_4$ 80%, and for $CsBrO_4$ 58%. Similar effects are reported in Ref. 63, but thermal annealing of neutron-irradiated potassium perbromate near its decomposition temperature (275 °C) was found to give a sudden increase in retention, similar to the increased retention of ^{128}I produced by heating irradiated potassium periodate[64]. The maximum retention of ^{82}Br (80%) was reached after heating $KBrO_4$ for 1 h at 275 °C. Above 300 °C all the bromine oxy-anions decompose.

In the alkaline-earth metal and magnesium perbromates the retention of ^{82}Br decreases, and at the end of the heat treatment it is as low as 2.0%. The changes in yield of $^{82}BrO_3^-$ caused by thermal annealing again depend on the nature of the cation[60]. The bromine and oxygen recoil atoms recombine with formation of bromate ions during thermal annealing of neutron-irradiated perbromates. On the other hand, the oxygen atoms can recombine together to give oxygen molecules. Therefore the oxidation of $^{82}Br^-$ to $^{82}BrO_3^-$ is not usually quantitative, in spite of the fact that stable perbromate molecules give off oxygen atoms during radiolysis.

Table 5. Yield of chemical stabilisation forms of ^{82}Br and ^{80m}Br recoil atoms in neutron-irradiated lithium and sodium perbromates.

Irradiated compound	Isotope	Yield of radioactive bromine, %				
		BrO_4^-	BrO_3^-	BrO_2^-	BrO^-	Br^-
$LiBrO_4$	^{82}Br	2.1±0.2	45±1	3.4±0.8	4.8±0.6	46±1
	^{80m}Br	1.9±0.2	60±2	2.9±0.6	4.2±0.9	31±1
$NaBrO_4$	^{82}Br	2.0±0.1	41±2	1.5±0.3	0.7±0.2	55±2
	^{80m}Br	1.1±0.1	55±2	0.9±0.2	1.2±0.5	41±1

Irradiation of perbromates with thermal neutrons produces, in addition to ^{82}Br, also ^{80m}Br, and this allows us to compare the yields of the chemical forms of these isotopes, i.e. to look for an isotope effect. The results of these experiments, made with lithium and sodium perbromates[65], are shown in Table 5.

During thermal annealing the yield of $^{82}BrO_3^-$ in neutron-irradiated sodium perbromate increases from 41 to 91% in 15 min at 150 °C, whereas the yield of $^{80m}BrO_3^-$ increases from 55 to 86% during the same time. Longer heating times have no effect, and at the end of the anneal the isotope effect amounts to 5%. In lithium perbromate the yields of ^{82}Br and ^{80m}Br as bromate ion are equal at the end of the anneal, possibly as a result of the production of fission fragments from ^6Li by the thermal neutrons. These fragments cause strong ionisation of their surroundings and tend to mask any differences in the dislocation regions where the ^{82}Br and ^{80m}Br recoil atoms are accommodated.

Crystal defects play an important role in determining the fate of the bromine recoil atoms during thermal annealing of neutron-irradiated perbromates. In order to quantify the influence of crystal defects on the annealing operation the effect of previous heat treatment of the crystals (before neutron irradiation) has been investigated[66]. These experiments showed that in sodium perbromate which has been heat treated before irradiation the retention of ^{82}Br is unchanged by annealing, and the yield of bromate ions is lower than in ordinary samples which have been similarly annealed. Since all the samples had been irradiated under identical conditions, differences in behaviour of the recoil atoms during annealing can be interpreted as differences between the crystals, i.e. as differences in the relative distribution over energy levels with activation energies corresponding to different temperatures.

Whereas the retentions of ^{82}Br and ^{80m}Br formed by neutron irradiation of crystalline perbromates of the alkali metals seldom exceed 2.6%, the retention of the radioactive bromine isotopes formed by isomeric transition and β^- disintegration is substantially higher. Thus, the retention of ^{80}Br formed by isomeric transition from ^{80m}Br in a lithium perbromate composition is 31 ± 1%,[60] and the retention of ^{83}Br formed by β^- disintegration from ^{83}Se in potassium selenate is 24%.[67]

Whereas irradiation of perbromates in a nuclear reactor produces radioactive bromine isotopes, the interaction of stable bromine atoms with high-energy protons produces a whole series of radioactive isotopes of different elements. Radiochemical and gamma-spectroscopic analyses have shown that the irradiation of crystalline sodium perbromate with 1 GeV protons leads to the formation of oxygenated krypton compounds, produced from bromine by a (p, xn) reaction[68]. The retention of radioactive krypton isotopes in a chemically bound state was 30 ± 9% for krypton-74, 7 ± 3% for krypton-76, and not more than 0.3% for krypton-77 and krypton-79. No attempt was made to identify the krypton compounds formed. However, by analogy with the formation of xenon compounds by β^- disintegration of ^{131}I, ^{133}I, and ^{135}I in periodate, iodate, and iodine pentoxide compositions[69], in which the preferred chemical form of the bound xenon is XeO_3, we may assume the formation of KrO_3. Krypton trioxide may be formed by the interaction of krypton recoil atoms with various fragments, produced in sodium perbromate by the radiolytic interaction of the proton beam, secondary particles, gamma radiation, and the recoil atoms themselves. One possible fragment is O_3^-, which has been detected by ESR in potassium perbromate irradiated with X-rays[70]. The interaction of these ions with krypton recoil atoms can stabilise the latter in the form of KrO_3. The formation of oxygen compounds of krypton, xenon, and radon has been observed also after irradiation of uranyl sulphate with high-energy protons[71].

Thus, previously unknown oxygen compounds of krypton have been prepared by studying perbromates. The perbromates themselves, on the other hand, can be prepared by using xenon difluoride[7] and krypton difluoride[72].

VI. RADIATION CHEMISTRY OF HEPTAVALENT BROMINE COMPOUNDS

Boyd and Brown[73] have studied the stable radiolysis products formed in crystalline potassium perbromate irradiated with gamma rays from ^{60}Co. The irradiation was carried out at ~35 °C with two sources, having activities of 3 and 11.5-kCi respectively. The dose of radiation absorbed was 9.3×10^{17} eV g^{-1} H_2O min^{-1} for the first source and 3.8×10^{18} eV g^{-1} H_2O min^{-1} for the second source. The dose absorbed by crystalline potassium perbromate was calculated by multiplying the dose for water by the ratio of the number of electrons per gramme of $KBrO_4$ to the number of electrons per gramme of H_2O: it was found to be 1.5×10^{23} eV $mole^{-1}$. The i.r. spectrum of $KBrO_4$ irradiated with this dose contains, in addition to the BrO_4^- absorption bands, only the absorption bands due to BrO_3^-. No bands which could be assigned to BrO_2^- were detected. A possible explanation[73] is that the dose to which the sample was exposed was too small.

However, even at higher doses the bromate ion is practically the only product of the radiolysis of crystalline potassium perbromate (4.36×10^{24} eV $mole^{-1}$) and sodium perbromate (3.98×10^{24} eV $mole^{-1}$).[60] The preferential formation of bromate ions during radiolysis of perbromates is explained by the far higher probability of breaking one bromine–oxygen bond than two, three, or (especially) all four bonds in a perbromate ion irradiated with gamma rays from ^{60}Co.

Irradiation of alkali metal perbromates in a reactor also leads to extensive radiolysis with formation of bromate ions, the radiation-chemical yield $G(-BrO_4^-)$ being 3.9 ± 0.3 for

lithium perbromate, 2.8 ± 0.3 sodium, potassium, and rubidium perbromates, and 3.2 ± 0.3 for caesium perbromate. These yields are very large in comparison with $G(Br^-)$, which is never greater than 0.02.[60]

Hassan and Heitz[74] studied the radiolytic reduction of potassium perbromate in aqueous solutions (both aerated and de-aerated) under the influence of gamma rays from ^{60}Co. In acid solutions only one reaction is observed: $H^{\bullet}(HO_2^{\bullet}) + BrO_4^-$ [with a yield $G(-BrO_4^-) = 3.5$]. In a neutral solution the perbromate ion is reduced by solvated electrons. However, the yield of this reaction [$G(-BrO_4^-) = 5.3$] suggests that species other than solvated electrons are also involved in the reduction. The photolysis and the radiolysis of potassium perbromate solutions are discussed also by Byberg and Linderberg[75].

Irradiation of potassium perbromate single crystals with X-rays (of 50 kV energy) at 10, 26, and 77 K produces four types of centre [A, BrO_4^{2-}; C, $BrO_4^{\bullet}$; D, $(BrO_4)_2^-$; G, O_3^-] which can be detected by ESR. At 10 K only BrO_4^{2-}, $BrO_4^{\bullet}$, and $(BrO_4)_2^-$ are observed, but at temperatures above 20 K O_3^- is produced by thermal processes from BrO_4^{2-}, and BrO_2 from $BrO_4^{\bullet}$. As a result of these annealing effects only O_3^- and BrO_2 can be detected in the potassium perbromate single crystal at 240 K.

The ESR method has been used also to study the radiolysis products of frozen solutions of potassium perbromate[76]. $BrO_3^{\bullet}$, $BrO_4^{\bullet}$, and BrO_4^{2-} were identified in an irradiated polycrystalline solution of potassium perbromate; the $KBrO_4$ reacted with electrons even in a frozen (glassy) solution in 10 M NaOH, but under these conditions bromine-containing radicals could not be detected.

The pulsed radiolysis of aqueous solutions of potassium perbromate with electrons of 10 MeV energy in a neutral solution saturated with argon produced the reaction

$$BrO_4^- + e^-_{hybr} = BrO^- + O^-,$$

whose rate constant was 7×10^9 litre mole^{-1} s^{-1}.[77] Measurements of the yield of $OH^{\bullet}$ radicals in acid or neutral argon-saturated solutions and of the yield of O_3^- in alkaline oxygen-saturated solutions of potassium perbromate showed that interactions of $H^{\bullet}$, $OH^{\bullet}$, and O^- with BrO_4^- all have rate constants smaller than 10^7 litre mole^{-1} s^{-1}.

Polarographic, optical spectroscopy, and ESR methods have been used to study the photolysis products of aqueous solutions of potassium perbromate at room temperature and at 77 K.[78] Irradiation was carried out at a wavelength $\lambda = 253.7$ nm. At 77 K the O^- centre was detected, but this centre disappears at 160 K with formation of O_2^- and O_3^-. BrO_3^-, BrO_2^-, HO_2^-, and molecular oxygen were detected when a solution of potassium perbromate in 0.1 M NaOH was irradiated.

VII. PRACTICAL APPLICATIONS OF PERBROMIC ACID AND ITS SALTS

Perbromates are still laboratory compounds, and are not yet handled on an industrial scale. However, they are beginning to find wide uses in the laboratory, for example in studies of the electrical double layer[79,80] and of the synthesis of oxygen compounds of krypton[68]. Perbromic acid and its salts can be used as special oxidising agents, and also for the quantitative determination of rubidium and caesium (whose perbromates are sparingly soluble in water at 0 °C). Mixed with nitric acid, $HBrO_4$ has been used for wet ashing organic compounds. Concentrated perbromic acid is one of the strongest oxidising agents, whereas dilute perbromic acid (like perchloric acid) can be used as a reaction medium. Since most perbromates are fairly soluble, perbromic acid and its salts can be used in metal treatment processes such as electroplating, etching, and polishing. Perbromic acid can also be used in organic synthesis for separating alcohols, ketones, and amines from resinous materials.

Perbromates can be used as sources of radioactive bromine (in the form of bromide ions) with a high specific activity, because most of the radioactive bromine isotopes in neutron-irradiated perbromates are stabilised as bromide ions, and the yield of Br^- during radiolysis is negligible. A high specific activity is important in medical and biological investigations, in which the application of radioactive bromine isotopes is increasing every year.

Thus, heptavalent bromine compounds will undoubtedly find increasingly wide applications in industry and in the national economy as well as in scientific research.

REFERENCES

1. G.M.Bancroft and H.D.Gesser, J.Inorg.Nuclear Chem., **27**, 1545 (1965).
2. A.Y.Herrell and K.H.Gayer, J.Chem.Education, **49**, 583 (1972).
3. E.H.Appelman, Acc.Chem.Res., **6**, 113 (1973).
4. D.S.Urch, J.Inorg.Nuclear Chem., **25**, 77 (1963).
5. E.H.Appelman, J.Amer.Chem.Soc., **90**, 1900 (1968).
6. J.G.Malm and E.H.Appelman, Atomic Energy Rev., **7**, 21 (1969).
7. E.H.Appelman, Inorg.Chem., **10**, 138 (1971).
8. L.C.Brown, G.M.Begun, and G.E.Boyd, J.Amer. Chem.Soc., **91**, 2250 (1969).
9. T.A.Turney, New Zealand J.Sci., **14**, 299 (1971).
10. E.H.Appelman, Inorg.Chem., **8**, 223 (1969).
11. E.H.Appelman, Inorg.Chem.Synthesis, **13**, 1 (1972).
12. V.V.Gavrilov, V.K.Isupov, and I.S.Kirin, USSR P.497220/1974; Byull.Izobr., **48** (1975).
13. V.K.Isupov, V.V.Gavrilov, and I.S.Kirin, Zhur. Neorg.Khim., **20**, 1492 (1975)[Russ.J.Inorg.Chem., No.6 (1975)].
14. V.K.Isupov, V.V.Gavrilov, and I.S.Kirin, Zhur. Neorg.Khim., **22**, 2592 (1977)[Russ.J.Inorg.Chem., No.9 (1977)].
15. J.N.Keit and I.J.Solomon, Inorg.Chem., **9**, 1560 (1970).
16. K.Baum, C.D.Beard, and V.Grakauskas, J.Amer. Chem.Soc., **97**, 267 (1975).
17. N.G.Gorshkov, Yu.K.Gusev, V.D.Klimov, L.G.Mashirov, and D.N.Suglobov, Symposium "Vtoraya Vsesoyuznaya Konferentsiya po Khimii Urana" (Second All-Union Conference on the Chemistry of Uranium), Moscow, 1978, p.64.
18. E.H.Appelman and M.H.Studier, J.Amer.Chem.Soc., **91**, 4561 (1969).
19. H.H.Claasen and E.H.Appelman, Inorg.Chem., **9**, 622 (1970).
20. G.Nagarajan and M.J.Redom, Monatsh., **103**, 1406 (1972).
21. E.H.Appelman and M.A.A.Clyne, J.Chem.Soc., Faraday Trans., I, **71**, 2072 (1975).
22. E.H.Appelman, B.Beagley, D.Cruikshank, A.Ford, S.Rustad, and V.Ulbrecht, J.Mol.Structure, **35**, 139 (1976).
23. G.K.Johnson, P.A.G.O'Hare, and E.H.Appelman, Inorg.Chem., **11**, 800 (1972).
24. M.H.Studier, J.Amer.Chem.Soc., **90**, 1901 (1968).
25. H.Schulze, N.Weinstock, A.Müller, and G.Vandrish, Spectrochim.Acta, **29A**, 1705 (1973).

26. K.Nakamoto, "Infrared Spectra of Inorganic and Co-ordination Compounds" (Translated into Russian), Izd.Mir, Moscow, 1966.
27. C.E.Grouthemal, A.M.Hayes, and D.S.Martin, J.Amer.Chem.Soc., **73**, 82 (1951).
28. S.Siegel, B.Tani, and E.H.Appelman, Inorg.Chem., **8**, 1190 (1969).
29. G.K.Johnson, P.N.Smith, E.H.Appelman, and W.N.Hubbard, Inorg.Chem., **9**, 119 (1970).
30. D.J.Witt and R.M.Hammaker, Inorg.Chem., **10**, 1093 (1971).
31. E.J.Baran and J.P.Aymonino, Z.Naturforsch., **276**, 1568 (1972).
32. N.K.Sanyal, A.N.Pandey, H.S.Singh, and B.P.Singh, J.Quant.Spectrosc.Radiat.Transfer, **10**, 1343 (1970).
33. E.J.Baran, P.J.Aymonino, and A.Müller, Anales Asoc.quím.argentina, **58**, 71 (1970).
34. A.Müller, N.Mohan, and F.Königer, J.Mol.Structure, **18**, 357 (1973).
35. D.K.Sharma, A.N.Pandey, A.K.Dullish, and S.N.Rai, Z.Naturforsch., **29A**, 1504 (1974).
36. L.D.Hullet and T.A.Carlson, Appl.Spectrosc., **25**, 33 (1971).
37. M.M.Cox and J.W.Moor, J.Phys.Chem., **74**, 267 (1970).
38. B.F.Shchegolev and M.E.Dyatkina, Zhur.Strukturnoi Khim., **15**, 325 (1974).
39. F.Schreiner, D.W.Osborne, A.V.Pocious, and E.H.Appelman, Inorg.Chem., **9**, 2320 (1970).
40. A.J.Downs and C.J.Adams, "Comprehensive Inorganic Chemistry", Vol.2, Pergamon Press, Oxford, 1972.
41. J.R.Brand and S.A.Bunck, J.Amer.Chem.Soc., **91**, 6500 (1969).
42. V.M.Vdovenko, L.G.Mashirov, and D.N.Suglobov, Radiokhimiya, **6**, 299 (1964).
43. N.W.Alcock and S.E.Speras, Inorg.Chem., **9**, 893 (1977).
44. M.Lederer and M.Sinibaldi, J.Chromatogr., **60**, 275 (1971).
45. L.Ossicini and N.Balzoni, J.Chromatogr., 79, 311 (1973).
46. S.K.Shukla, Analyt.Letters, **7**, 691 (1974).
47. R.Keil, Z.analyt.Chem., **281**, 123 (1976).
48. S.K.Shukla, S.Fanali, and L.Ossicini, J.Chromatogr., **114**, 451 (1975).
49. J.R.Brand and M.L.Smith, Analyt.Chem., **43**, 1105 (1971).
50. B.Jaselskis and J.L.Huston, Analyt.Chem., **43**, 581 (1971).
51. M.L.Foresti, D.Cozzi, and R.Guidelli, J.Electroanalyt.Chem., **53**, 2235 (1974).
52. F.Pergola, J.Electroanalyt.Chem., **51**, 461 (1974).
53. R.De Levie and M.Nemes, J.Electroanalyt.Chem., **58**, 123 (1975).
54. N.V.Fedorovich and F.S.Sarbash, Dokl.Akad.Nauk SSSR, **243**, 1231 (1978).
55. R.Belcher, J.Pure Appl.Chem., **31**, 537 (1972).
56. L.C.Brown and G.E.Boyd, Analyt.Chem., **42**, 291 (1970).
57. I.S.Kirin, V.V.Gavrilov, and V.K.Isupov, Radiokhimiya, **16**, 416 (1974).
58. M.Lederer and C.Polcaro, J.Chromatogr., **84**, 379 (1973).
59. V.V.Gavrilov, V.K.Isupov, and I.S.Kirin, Radiokhimiya, **17**, 130 (1975).
60. V.V.Gavrilov, Thesis, Leningrad, 1978.
61. N.Hassan and C.Heitz, J.Inorg.Nuclear Chem., **37**, 395 (1975).
62. V.V.Gavrilov, V.K.Isupov, and I.S.Kirin, Radiokhimiya, **17**, 254 (1975).
63. S.Bulbulian, J.J.Shleiffer, and J.P.Adloff, Radiochim.Acta, **25**, 31 (1978).
64. G.E.Boyd and Q.V.Larson, J.Amer.Chem.Soc., 91, 4639 (1969).
65. V.V.Gavrilov, V.K.Isupov, I.S.Kirin, and V.S.Gusel'nikov, Radiokhimiya, **18**, 526 (1976).
66. V.V.Gavrilov and V.K.Isupov, Radiokhimiya, **20**, 312 (1978).
67. D.Tenorio, S.Bulbulian, and J.P.Adloff, Radiochem. Radioanalyt.Letters, **24**, 61 (1976).
68. V.V.Gavrilov, V.I.Tikhonov, and V.K.Isupov, Radiokhimiya, **20**, 627 (1978).
69. V.K.Isupov, Thesis, 1971.
70. J.R.Byberg, J.Chem.Phys., **55**, 4867 (1971).
71. A.N.Murin, V.D.Nefedov, V.V.Avrorin, V.V.Gavrilov, S.D.Golos, V.M.Zaitsev, V.I.Tikhonov, and M.A.Toropova, Lenigrad.Inst.Yadernoi Fiz., Preprint No.400, 1978.
72. V.N.Prussakov and V.B.Sokolov, Atomnaya Energiya, **31**, 259 (1971).
73. G.F.Boyd and L.C.Brown, J.Phys.Chem., **74**, 3490 (1970).
74. N.Hassan and C.Heitz, J.Chim.phys., 72, 119 (1975).
75. J.R.Byberg and J.Linderberg, Chem.Phys.Letters, **33**, 612 (1975).
76. K.J.Olesen, Trans.Faraday Soc., **67**, 1041 (1971).
77. K.J.Oleson, K.Schested, and E.H.Appelman, Chem. Phys.Letters, **19**, 213 (1973).
78. U.K.Kläning, K.J.Olesen, and E.H.Appelman, J.Chem.Soc., Faraday Trans.I, **71**, 473 (1975).
79. N.V.Fedorovich and F.S.Sarbash, "Dvoinoi Elektricheskii Sloi i Adsorbtsiya na Tverdykh Elektrodakh" (The Electrical Double Layer and Adsorption on Solid Electrodes), Izd.Tartu.Univ., 1978.
80. N.V.Fedorovich, F.S.Sarbash, E.I.Mikhailova, V.K.Isupov, and V.V.Gavrilov, Elektrokhimiya, **15**, 587 (1979).

Khlopin Radium Institute

Translated from *Uspekhi Khimii*, **49**, 2132-2158 (1980) U.D.C. 547.324;547.402

Synthesis of Corroles and Octadehydrocorrins

N.S.Genokhova, T.A.Melent'eva, and V.M.Berezovskii

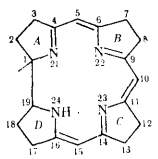
A survey has been made of methods for the synthesis of corroles and their complexes with various metals, and also methods for the synthesis of metal complexes of 1,19-disubstituted octadehydrocorrins from biladienes, bilenes, and bilatrienes and of nickel complexes of 1-substituted octadehydrocorrins by the oxidative and non-oxidative cyclisation of biladienes. Aspects of the structure of corroles and metal complexes of corroles and octadehydrocorrins are discussed. A list of 76 references is included.

CONTENTS

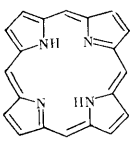
I.	Introduction	1056
II.	Synthesis of corroles	1056
III.	Synthesis of metal complexes of corroles	1058
IV.	Synthesis of metal complexes of 1,19-disubstituted octadehydrocorrins	1060
V.	Synthesis of nickel complexes of 1-substituted octadehydrocorrins	1065

I. INTRODUCTION

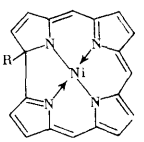
Corroles and octadehydrocorrins are tetrapyrrole macrorings related both to corrin (I)—a partly hydrogenated tetrapyrrole system present in biological catalysts, e.g.vitamin B_{12} and its coenzymes—and to porphyrin (II), which forms the framework of chlorophyll, haemin, and cytochromes.



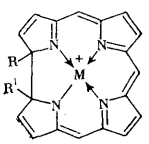
(I)



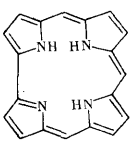
(II)



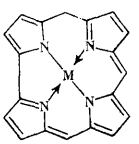
(III)



(IV)



(V)



(VI)

Octadehydrocorrins† are known as the neutral nickel complexes of 1-substituted derivatives (III) and in the cationic form of metal complexes of 1,19-disubstituted derivatives (IV). Corroles (V), like octadehydrocorrins, contain a direct $\alpha\alpha'$-bond between two pyrrole rings, but unlike them are aromatic compounds, thereby approaching the porphyrin system (II). Corroles are known also as metal complexes (VI).

Corroles and metal complexes of octadehydrocorrins differ from porphyrins and also corrins both in chemical and physicochemical properties and in methods of synthesis. Furthermore, the cobalt complexes of octadehydrocorrins catalyse the oxidation of reduced nicotinamide–adenine dinucleotide, one of the most important links in the electron-transport system of the living cell[2]. It is therefore of undoubted interest to examine routes and methods for the synthesis of corroles and octadehydrocorrins.

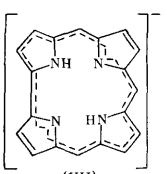
Foreign reviews[3–8] covering the synthesis of tetrapyrrole macrorings devote only individual chapters to corroles and octadehydrocorrins. The main advances in this field were surveyed[9] in 1969. The present Review covers all published information on methods for the synthesis of corroles and octadehydrocorrins, paying special attention to work appearing during the past decade.

† The name *octadehydrocorrin* applies to the macroring in (III) and (IV); it has been recommended by the Commission for Biochemical Nomenclature of the International Union of Pure and Applied Chemistry and the International Union of Biochemistry[1].

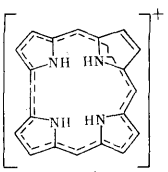
II. SYNTHESIS OF CORROLES

1. Structure and Properties of Corroles

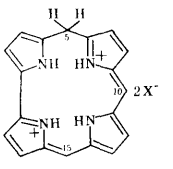
The search for synthetic routes to corrin led to the synthesis of corroles (V), which forms red crystals. It contains an aromatic cyclic system with eighteen π-electrons, as indicated by an intense Soret band (~400 nm) in its electronic absorption spectrum, which contains also bands in the region of 540, 550, and 600 nm.[10]



(VII)



(VIII)



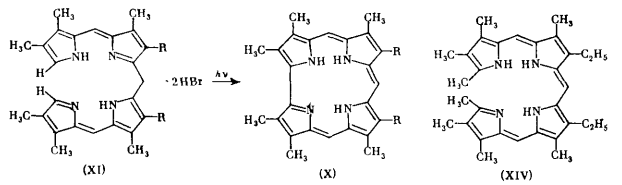
(IX)

Addition of dilute alkali to solutions of corroles readily converts them into stable aromatic anions (VII),[10–12], which distinguishes them in particular from porphyrins[13]. Corroles readily undergo monoprotonation when treated with a dilute solution of hydrobromic acid in acetone. This involves formation of crystalline monohydrobromides, existing as aromatic ambident cations (VIII).[12] The green solutions of corroles in concentrated sulphuric acid do not contain a Soret band in the electronic spectrum, which indicates the appearance of the "blocked" conjugated structure of the tautomeric non-aromatic dication (IX) with the additional protonation at carbon atom 5,[11] not at $C_{(10)}$ as assumed previously[10,11]. Addition of alkali to a solution of the dication (IX) converts the latter back into the original corrole (V).

2. Synthesis of Corroles from Biladienes-*ac*

The free bases of corroles (X) have been synthesised from 1,19-dideoxybiladienes-*ac* (XI) containing hydrogen atoms at positions 1 and 19, by the photocyclisation of their dilute methanolic solutions in the presence of a small excess of

ammonia or aqueous sodium acetate[11,14], and also by the photocyclisation of aqueous solutions in the presence of ammonia and potassium hexacyanoferrate(III):[15]

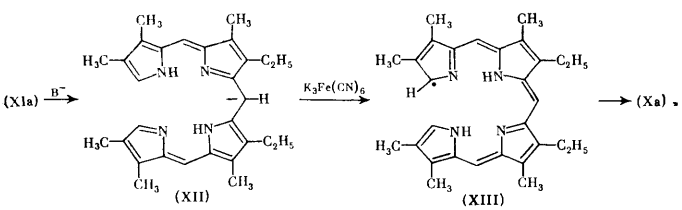


(XI) (X) (XIV)

a) R = C_2H_5, b) R = $CH_2CH_2COOH_3$

On the assumption that formation of corroles had a free-radical mechanism[16,17] an examination was made of the influence of various initiators (of free-radical processes) and one-electron oxidising agents on cyclisation of the 1,19-unsubstituted biladiene-*ac* (XIa). It was found that cyclisation occurred very rapidly in the presence of ammonia and potassium hexacyanoferrate(III), iron(III) chloride, cerium sulphate, and hydrogen, benzoyl, and t-butyl peroxides; in all cases the corresponding corrole (X) was isolated in 68 to 84% yield[16].

These reactions require the presence of a base, which indicates initial detachment of a proton from a 10-methylene group of biladiene during photocyclisation. This is confirmed by the fact that 10,10-dimethylbiladienes are not cyclised to a corrole[18]. Formation of corroles is appreciably accelerated by ultraviolet irradiation of solutions of biladienes; yet replacement of atmospheric oxygen by nitrogen has no appreciable effect on the course of the reaction. Cyclisation apparently involves successive formation of an anion (XII) and an intermediate radical (XIII):

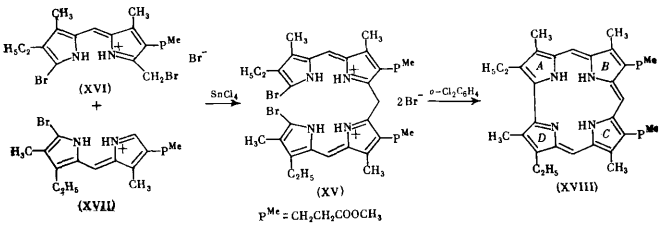


(XII) (XIII)

In an attempt to synthesise the corrole (X) from 1,19-dimethylbiladiene-*ac* ultraviolet irradiation of the methanolic solution yielded mainly the bilatriene (XIV) with some porphyrin[19].

The synthesis of corroles[10] by the photolysis of alkaline solutions of biladienes-*ac* in which positions 1 and 19 are unsubstituted is restricted by the methods for obtaining these intermediate compounds, in whose formation the degree of symmetry of the β-substituents plays an important part.

Corroles having an unsymmetrical arrangement of β-substituents have been obtained by the thermal cyclisation of 1,19-dibromobiladienes-*ac*. Thus 1,19-dibromo-1,19-dideoxybiladiene-*ac* dihydrobromide (XV), obtained by condensation of the dipyrromethene (XVI) with the 5′-unsubstituted 5-bromodipyrromethene (XVII) in the presence of tin(IV) chloride, was converted into the corrole (XVIII) by boiling with *o*-dichlorobenzene[20]:

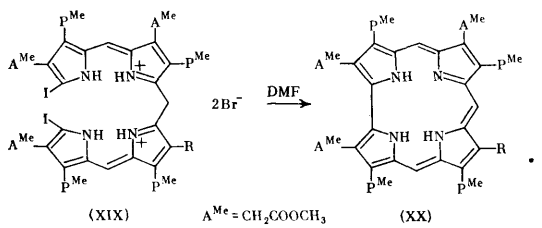


(XVI) (XVII) (XV) (XVIII)

P^{Me} = $CH_2CH_2COOCH_3$

Corroles having non-alkyl β-substituents in rings A and D were unknown until 1975,[21] perhaps because groups larger than methyl in positions 2 and 18 prevent the photocyclisation of 1,19-biladienes-*ac*.[10]

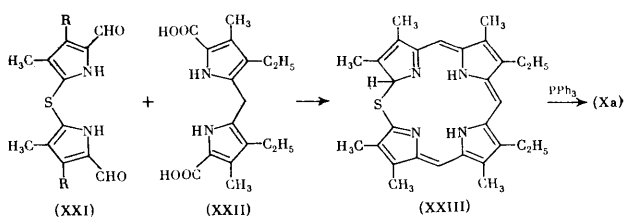
A more promising method for synthesising corroles having different substituents in rings A and D was thermal cyclisation of 1,19-dibromobiladienes-*ac* (XV) in *o*-dichlorobenzene[20] or of 1,19-di-iodobiladienes-*ac* (XIX: R = CH_3, A^{Me}) in dimethylformamide (DMF).[21] 1,19-Dideoxy-1,19-di-iodobiladienes-*ac* (XIX) with acetic and propionic residues in β-positions were more reactive than the corresponding 1,19-dibromo-derivatives[20], the former yielding corroles (XX: R = CH_3, A^{Me}) when heated in DMF:[21]



(XIX) A^{Me} = CH_2COOCH_3 (XX)

3. Synthesis of Corroles via Sulphur-containing Compounds

Corroles have been obtained by cyclising linear dipyrrole compounds containing sulphur. The condensation of bis-5-formylpyrrol-2-yl sulphide (XXIa) with methane-2,2′-dipyrrole-5,5′-dicarboxylic acid (XXII) at −10 °C in the presence of hydrogen chloride gives a 10–20% yield of a dark red product (XXIII), which when boiled with excess of triphenylphosphine in *o*-dichlorobenzene is converted into the corresponding corrole (Xa):[22]

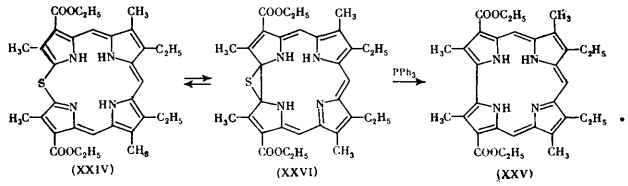


(XXI) (XXII) (XXIII)

a) R = CH_3, b) R = $COOC_2H_5$

However, when the sulphide (XXIb) is condensed with the dicarboxylic acid (XXII), the dark blue crystalline *meso*-thiaphlorin (XXIV) of non-aromatic character is obtained[22], whose desulphurisation in boiling *o*-dichlorobenzene leads to

formation of the corrole (XXV) in 35–40% yield, apparently with intermediate formation of a thi-iran derivative (XXVI):[8]



(XXIV) (XXVI) (XXV)

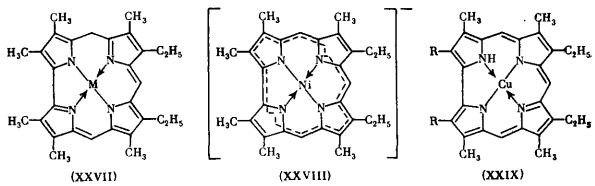
Conducting the reaction in the presence of triphenylphosphine increases the yield of the corrole (XXV) to 60%.

III. SYNTHESIS OF METAL COMPLEXES OF CORROLES

1. Structure of Complexes of Corrole with Bivalent Metals

In metal complexes of corrole a bivalent metal (zinc, nickel, palladium) replaces only two of the three imino-hydrogen atoms; the third hydrogen atom moves to another site in the chromophore. The aromatic conjugated system is disrupted in such complexes, as indicated by the absence of an intense Soret band from the electronic spectra of the above three metal complexes[10,15,23,24]. Such absence indicates that these complexes (XXVII: M = Ni, Pd) are derivatives of a tautomeric non-aromatic base corresponding to a dication of type (IX).[12]

For a long time the site of the "extra" hydrogen atom in the ligand could not be established, since the paramagnetic nature of nickel octa-alkylcorroles prevented the use of nuclear magnetic resonance spectroscopy for this purpose. The atom was arbitrarily located at $C_{(10)}$.[15] In order to solve this structural problem an examination was made of the protonation of corrole in fluorosulphuric acid, which established that in the formation of dications protonation is considerably more rapid at $C_{(5)}$ than at $C_{(10)}$.[12] On this basis the structure (XXVII) was ascribed to complexes of corroles with bivalent metals.



(XXVII) (XXVIII) (XXIX)

a) R = C_2H_5, b) R = CH_3.

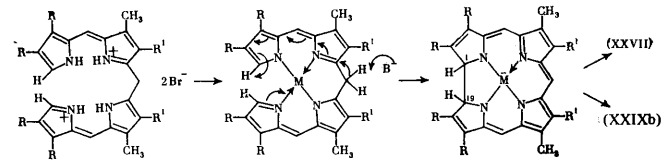
Addition of alkali to the green solutions of the nickel complex of corrole (XXVII: M = Ni) produces a Soret band in the electronic spectrum, apparently owing to formation of the stable ambident aromatic anion (XXVIII), whose solutions are red. This colour change is reversed on acidification.

Spectral data for the copper complexes of corroles indicate the presence of a continuous π-chromophore, and therefore the formula (XXIX) was suggested[15].

2. Synthesis of Nickel, Copper, Zinc, and Palladium Complexes of Corrole

Metal complexes of corroles can be obtained both by the cyclisation of 1,19-disubstituted 1,19-dideoxybiladienes-*ac* in the presence of metal acetates in hot methanol and by introduction of the metal into the free base of corrole[10].

Corrole complexes of nickel (XXVII: M = Ni) and copper (XXIXb) have been synthesised by the ultraviolet irradiation of methanolic solutions of biladienes-*ac* (XXX) containing terminal hydrogen atoms, in the presence of nickel or copper ions and a base[10,11]. Initially a metal–biladiene complex (XXXI) is apparently formed, in which the metal has a coordinating effect on positions 1 and 19, draws them together, and thereby facilitates cyclisation:

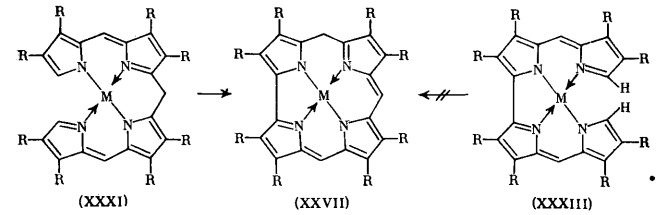


(XXX) (XXXI) (XXXII), M=Ni, Cu

a) R = CH_3, R' = C_2H_5; b) R = R' = CH_3; c) R = R' = C_2H_5.

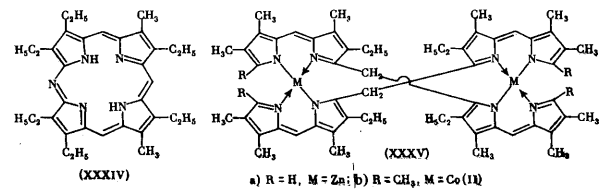
In the presence of a base a proton is detached from the $C_{(10)}$ atom in the metal complex (XXXI) and an anion (XXXII) is formed, which then passes into a neutral metal–corrole complex, (XXVII) [10,11] or (XXIX) [15] depending on the metal.

Whereas metal–corrole complexes (XXVII) are readily formed from metal–biladiene complexes (XXXI),[10] it has not proved possible to cyclise metal complexes of 5,5'-bisdipyrromethenes (XXXIII), which also contain terminal hydrogen atoms[18]:



(XXXI) (XXVII) (XXXIII)

Bulky β-substituents present at positions 2 and 18 in a biladiene-*ac* deactivate positions 1 and 19, and have an adverse influence on formation of a direct αα'-bond. Other reactions can then occur, e.g. formation of the azaporphyrin (XXXIV) by photocyclisation of an ammoniacal solution of the biladiene-*ac* (XXXc) containing ethyl groups at positions 2 and 18, whereas the corresponding 2,18-dimethylated compounds are converted under these conditions into a corrole[10].

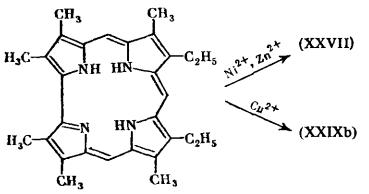


(XXXIV) (XXXV)

a) R = H, M = Zn; b) R = CH_3, M = Co(II).

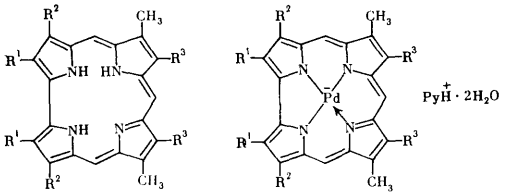
Zinc–biladiene-*ac* complexes could not be converted into corroles[10], since they have a tetrahedral configuration (XXXVa),[25] with the terminal α-hydrogen atoms occupying positions unfavourable to formation of a direct αα'-bond.

Corrole complexes of bivalent zinc and nickel (XXVII: M = Ni, Zn) and also copper (XXIXb) were obtained[10] by adding the cations to a solution of the corrole (XXXVI) in either pyridine or aqueous ammonia:



(XXXVI)

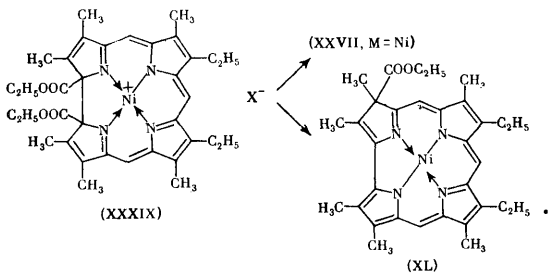
Treatment of the corrole (XXXVII) with palladium acetate in pyridine solution leads to the formation of crystalline pyridinium salts of palladium–corrole anions (XXXVIII) in 89–92% yield, isolated as the dihydrates[15], which are aromatic like the original corrole (XXXVII). On treatment with acids these salts pass into unstable, apparently neutral palladium complexes of the corroles, which could not be isolated.



(XXXVII) (XXXVIII)

a) $R^1 = R^3 = CH_3$, $R^2 = C_2H_5$; b) $R^1 = R^3 = C_2H_5$, $R^2 = CH_3$

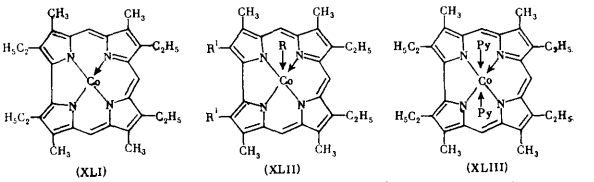
Nickel–corrole complexes can be obtained[26,27] from the corresponding complex of the octadehydrocorrin (XXXIX) containing angular ethoxycarbonyl substituents. Successive hydrolysis and decarboxylation of the angular groups in the complex (XXXIX: X = NO_3) gave the nickel–corrole complex (XXVII),[26] but heating the nitrate or chloride of octadehydro-1,19-diethoxycarbonylcorrin (XXXIX: X = NO_3, Cl) in chlorobenzene led to isolation of the nickel–corrole complex (XL):[27]



(XXXIX) (XL)

3. Structure and Properties of Cobalt Complexes of Corrole

Two types of cobalt–corrole complexes are known, the first of which do not contain axial ligands. Because of their paramagnetism they were originally regarded as cobalt(II) complexes[10], but are paramagnetic square–planar cobalt(III)–corrole complexes (XLI).[26–30] Complexes of the second type are formed in the presence of pyridine, triphenylphosphine, or *p*-tolyl isocyanate, and are five-coordinated cobalt(III)–corrole complexes (XLIIa–d) containing these compounds as axial ligands[31]. Addition of excess of pyridine to solutions of both types of complexes leads to the formation of octahedral dipyridine–cobalt(III)–corrole (XLIII), which is stable only in the presence of excess of pyridine[31].



(XLI) (XLII) (XLIII)

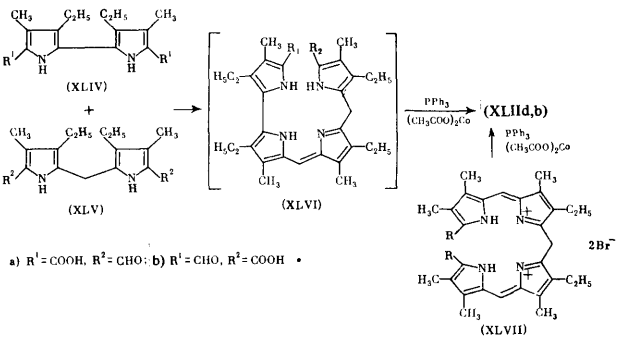
a) R = Py, $R^1 = C_2H_5$; b) R = PPh_3, $R^1 = CH_3$; c) R = *p*-$CN \cdot C_6H_4 \cdot CH_3$, $R^1 = C_2H_5$; d) R = PPh_3, $R^1 = C_2H_5$

Thus cobalt is tervalent in all its complexes with corroles: i.e. in these compounds all three imino-hydrogen atoms have been replaced. The complexes are either square–planar, pyramidal, or octahedral depending on the number of axial ligands[31]. In contrast, nickel[24], palladium, and copper[15] form only square–planar complexes of corroles in which these metals are bivalent.

4. Synthesis of Cobalt Complexes of Corrole

The synthesis of tetrapyrrole macrocycles such as corroles[10], octadehydro-1-methylcorrins[32], and 1,19-dialkyloctadehydrocorrin salts[33], which contain a direct bond between two pyrrole rings, involves the cyclisation of linear tetrapyrrole derivatives, e.g. 1,19-dideoxybiladienes-*ac*, bilenes-*b*, or bilatrienes. In 1973 the first [2 + 2] synthesis of corrole was accomplished that did not involve formation of a direct bond in the last stage of cyclisation[31].

Reaction between 3,3′-diethyl-4,4′-dimethyl-2,2′-bipyrrole-5,5′-dicarboxylic acid (XLIVa) [19] and 3,3′-diethyl-5,5′-diformyl-4,4′-dimethyldipyrromethane (XLVa) [10] in the presence of hydrobromic acid in methanol at 0 °C gives a red deposit, which when heated in methanol containing cobalt(II) acetate and triphenylphosphine is converted into the cobalt(III) complex (XLIId) having a triphenylphosphine group as an axial ligand:



a) R^1 = COOH, R^2 = CHO; b) R^1 = CHO, R^2 = COOH

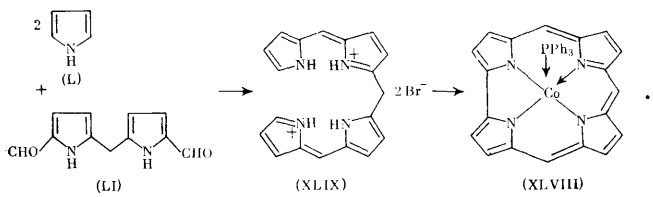
The same product (XLIId) can be obtained by condensing the bipyrrolyl (XLIVb) with the dipyrromethanedicarboxylic acid (XLVb).

These reactions may involve intermediate formation of *a*-norbilenes-*c* (XLVIa,b). The successful cyclisation of (XLIV) and (XLV) into a corrole emphasises the importance of cobalt both in stabilising the intermediate compound and in conferring a favourable configuration on it, since it had previously proved impossible to convert (XLIV) and (XLV) into a corrole in the absence of a complexing metal[31].

The corresponding cobalt(III) complex of corrole containing an axial triphenylphosphine ligand (XLIIb: R = $(C_6H_5)_3P$) has been obtained by cyclising 1,19-dideoxybiladiene-*ac*

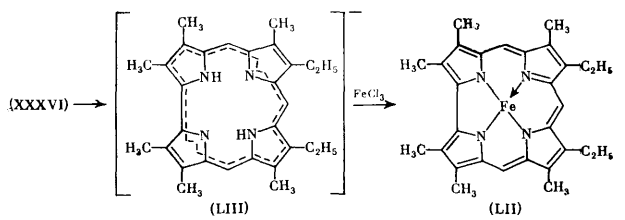
dihydrobromide (XLVII: R = H) in the presence of cobalt(II) acetate and triphenylphosphine in hot methanol. On the other hand, when a biladiene-*ac* containing methyl groups at the terminal positions 1 and 19 (XLVII: R = CH_3) is heated with cobalt(II) acetate and triphenylphosphine in methanol, a paramagnetic green product separates that proves to be a dimeric form of the cobalt complex of the biladiene (XXXVb).[25,31,33,34]

The stabilising effect of a coordinated triphenylphosphine ligand in the synthesis of cobalt corroles has been used in the synthesis of the triphenylphosphinecobalt(III) complex of corrole itself (containing no β-alkyl substitutents). This complex (XLVIII) has been obtained[31] by cyclising in the presence of cobalt(II) acetate and triphenylphosphine the dihydrobromide of 1,19-dideoxybiladiene-*ac* (XLIX), which is formed when pyrrole (L) is condensed with 5,5'-diformylmethane-2,2'-dipyrrole (LI) [35,36] and which, like its 1,19-disubstituted analogue[36], decomposes when an attempt is made at isolation or cyclisation in the absence of triphenylphosphine[37]:



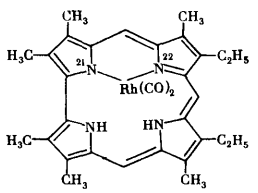
5. Synthesis of Iron Complex of Corrole

Besides the cobalt(III)—corrole complexes a paramagnetic crystalline complex of tervalent iron (LII) has been synthesised by treating with iron(III) chloride the corrole anion (LIII) obtained from 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole (XXXVI):[31]



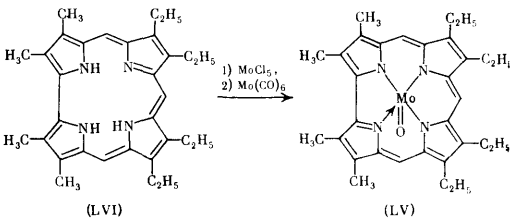
6. Synthesis of Rhodium and Molybdenum Complexes of Corroles

Rhodium[38,39] and molybdenum[40] complexes of corroles have been obtained quite recently. Reaction between the corroles (XXXVI) and di-μ-chlorobisdicarbonylrhodium $Rh_2(CO)_4Cl_2$ leads to formation of a monorhodium complex



as in the case of thiaphlorins, whereas dirhodium complexes are formed with porphyrins and azaporphyrins. The type of rhodium complex depends on the number of imino-hydrogen atoms present in the central portion of the tetrapyrrole macroring[38]. Each coordinated dicarbonylrhodium unit requires the presence of one imino-group and one nitrogen atom devoid of a hydrogen atom. Since corroles on alkylation form di-*N*-alkyl derivatives at the adjacent nitrogen atoms 21 and 22,[12] the structure (LIV) has been suggested for the monorhodium—corrole complex. The latter breaks down on crystallisation, and is less stable than the bisdicarbonylrhodium complex of porphyrin.

The discovery of superconducting materials[41] was followed by attempts to obtain conductors comprising planar metal complexes located one above the other and containing a metal—metal bond. These led to synthesis of the molybdenum—corrole complex (LV) [40] by the action of the corrole (LVI) either on molybdenum pentachloride or on hexacarbonylmolybdenum in decalin in an atmosphere of nitrogen:



However, the resulting oxomolybdenum(V) 7,8,12,13-tetraethyl-2,3,17,18-tetramethylcorrole (LV) proved to be a monomeric five-coordinated oxomolybdenum complex having an axial oxygen atom.

IV. SYNTHESIS OF METAL COMPLEXES OF 1,19-DISUBSTITUTED OCTADEHYDROCORRINS

1. Structure and Properties of Metal Complexes of 1,19-Disubstituted Octadehydrocorrins

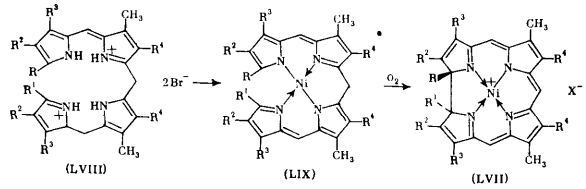
The metal complexes of 1,19-disubstituted octadehydrocorrins are macrocyclic tetrapyrrole compounds in which two pyrrole rings form a direct bond between the αα-carbon atoms at positions 1 and 19. They contain 1,19-angular substituents having a *trans* configuration. This series of compounds became known only in 1964.[26]

1,19-Disubstituted octadehydrocorrins form crystals of violet or dark cherry colour. Their electronic absorption spectra contain three principal bands in the ranges 280—300, 350—365, and 500—580 nm, and are devoid of the Soret band (at ~400 nm) characteristic of aromatic macrocycles such as corroles and porphyrins. The metal atom cannot be removed from an octadehydrocorrin complex without destruction of the organic macroring.

2. Synthesis of Nickel Complexes of 1,19-Disubstituted Octadehydrocorrins from Biladienes-*ac*

The traditional method for obtaining nickel complexes of 1,19-disubstituted octadehydrocorrins (LVII) is base-catalysed oxidative cyclisation of the 1,19-disubstituted 1,19-

dideoxybiladienes-*ac* (LVIII) [42] in alcoholic solution in the presence of excess of nickel acetate[33,43]:



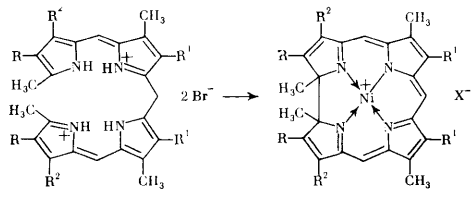
(LVIII) (LIX) (LVII)

(a) R=R¹=R²=R³=CH₃, R⁴=C₂H₅, X=NO₃, Cl;
(b) R=R¹=R³=R⁴=CH₃, X=ClO₄;
(c) R=R¹=R³=R⁴=CH₃, R²=OCH₂C₆H₅, X=Br;
(d) R=R¹=R³=R⁴=CH₃, R²=COOC₂H₅, X=ClO₄.
(e) R=R¹=R³=R⁴=CH₃, R²=CN, X=ClO₄;
(f) R=R¹=COOC₂H₅, R²=R³=CH₃, R⁴=C₂H₅;
(g) R=R¹=OCH₃, R²=R³=R⁴=CH₃;
(h) R=COOC₂H₅, R¹=R²=R³=CH₃, R⁴=C₂H₅;
(i) R=R¹=R³=R⁴=CH₃, R²=CH₂COOH, X=ClO₄;
(j) R=R¹=R²=R³=CH₃, R⁴=CH₂CH₂COOH, X=ClO₄;
(k) R=R¹=R³=CH₃, R²=CH₂COOH, R⁴=CH₂CH₂COOH, X=ClO₄.

Thus boiling 8,12-diethyl-1–3,7,13,17–19-octamethylbiladiene-*ac* (LVIIIa) with nickel and sodium acetates in methanol for a short time (30 s) gives the nickel–biladiene complex (LIXa), which on further aeration followed by treatment with nitrate ions is converted into the nitrate of the crystalline nickel–octadehydrocorrin complex (LVIIa), and into the corresponding crystalline chloride (LVIIa) when chloride ions are used. The decasubstituted octadehydrocorrin–nickel compex has been obtained as the perchlorate (LVIIb).[44,45] Similarly, cyclisation of the biladiene-*ac* (LVIIIc) gives the nickel complex (LVIIc) with benzyloxy-groups at positions 3 and 17,[46] and a nickel complex (LVIId) with ethoxycarbonyl substituents at positions 2 and 18 has been obtained from the biladiene (LVIIId).[47] A nickel complex of 2,18-dicyano-octadehydrocorrin (LVIIe) could not be synthesised in the usual way[47]: it has been obtained by aerating a chloroform solution of the biladiene (LVIIIe) containing hydrobromic acid, since in alcoholic solution or on addition of sodium acetate this biladiene is converted into a bilatriene, which under these conditions cannot be cyclised to the octadehydrocorrin.

The oxidative cyclisation of biladienes enables us to obtain metal complexes of octadehydrocorrins containing angular ethoxycarbonyl (LVIIf) [33] and methoxyl (LVIIg) [48] substituents. The 1,19-diethoxycarbonyl derivative (LVIIf) could be obtained in higher yield (85%) than the compounds (LVIIa, b). Nickel complexes of octadehydrocorrins having two different angular substituents have also been synthesised by oxidative cyclisation, e.g. the nickel complex (LVIIh) from 1,19-dideoxy-1-ethoxycarbonyl-19-methylbiladiene-*ac* (LVIIIh).[33]

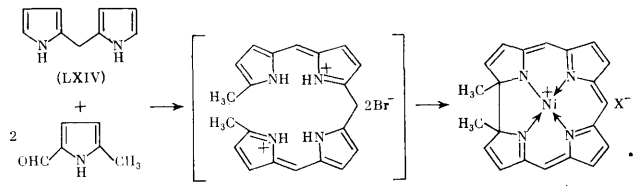
Oxidative cyclisation of biladienes[43,49] has been used also to obtain nickel complexes of 1,19-disubstituted oxydehydrocorrins having partly vacant β-positions[43,50,51]. Nickel complexes with unsubstituted positions 2 and 18 (LXa,b),[43,51,52] 8 and 12 (LXc),[50] and also 2, 3, 17, and 18 (LXd) [43] are obtained in the usual way[33] from the corresponding biladienes-*ac* (LXIa–d):[42]



(LXI) (LX)

(a) R=H, R¹=C₂H₅, R³=CH₃, X=ClO₄;
(b) R=H, R¹=R²=CH₃, X=ClO₄;
(c) R=R²=CH₃, R¹=H, X=ClO₄;
(d) R=R²=H, R¹=CH₃.

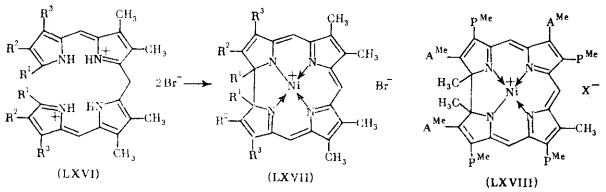
However, several difficulties were encountered in synthesis of the nickel complex (LXII) of octadehydro-1,19-dimethylcorrin with completely unsubstituted β-positions[36,53]. The initial 1,19-dideoxy-1,19-dimethylbiladiene-*ac* (LXIII), formed by the condensation of 2,2′-dipyrrolylmethane (LXIV)[35] with excess of 2-formyl-5-methylpyrrole (LXV) in chloroform solution in the presence of hydrogen bromide, was subjected to cyclisation without being isolated, owing to its extreme instability:



(LXIV) (LXV) (LXIII) (LXII)

The reaction was conducted in methanol in the presence of nickel and sodium acetates at room temperature for 3 h, and gave 2–22% yields of the nickel–octadehydrocorrin complex (LXII). If DMF is used as solvent, cyclisation goes more smoothly for 15 min even without the addition of sodium acetate, and the yield rises to 26%.[36,53]

The interest in the synthesis of octadehydrocorrins containing residues of acetic and propionic acids as β-substituents arises understandably from the presence of such substituents in naturally occurring corrin and porphyrin macrocycles. As early as 1969 perchlorates were obtained of several nickel complexes of octadehydrocorrins containing propionic ester groups in various positions in the pyrrole rings[54]. It then proved possible by the cyclisation of biladienes-*ac* (LXVI) to prepare nickel complexes of octadehydrocorrins (LXVII) [55] containing acetic and propionic ester groups at positions 2, 3, 17, and 18 in rings A and D:



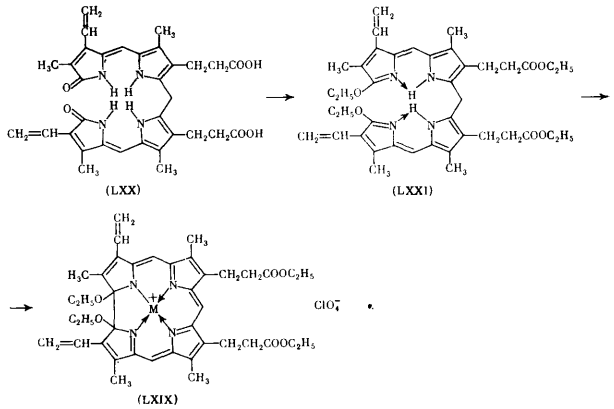
(LXVI) (LXVII) (LXVIII)

R¹=CH₃, COOC₂H₅, COOCH₂C₆H₅; R² и R³=CH₃, CH₂COOCH₃, CH₂COOC₂H₅, CH₂CH₂COOCH₃, CH₂CH₂COOC₂H₅
A^Me=CH₂COOCH₃, P^Me=CH₂CH₂COOCH₃.

Finally, a nickel–octadehydrocorrin complex (LXVIII) containing propionic and acetic ester groups at all β-positions in the macroring was obtained[56] in 1975. Cyclisation of the corresponding biladiene was accomplished in the presence of nickel acetate. It is noteworthy that this biladiene is an intermediate compound in the synthesis of porphyrins[54] and corroles[10]. Other nickel–octadehydrocorrin complexes contain acetic ester residues at positions 2 and 18 (LVIIi) [50] and propionic ester groups at positions 8 and 12 (LVIIj) [47] have also been obtained; in the complex (LVIIk) all four positions are occupied by ester substituents[47].

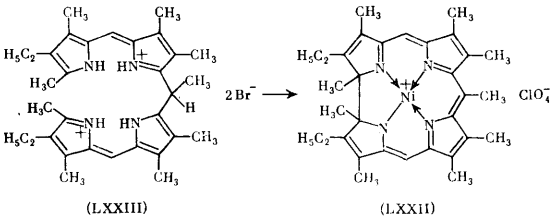
A nickel–octadehydrocorrin complex has been prepared also from the natural yellow pigment bilirubin (LXX),[57] which on treatment with triethyloxonium tetrafluoroborate in di-isopropylethylamine and dichloromethane was converted into the biladiene-*ac* (LXXI),[58] cyclisation of which in the presence of

nickel acetate and sodium perchlorate with heating in air led to formation of the complex (LXIX: M = Ni):[57]



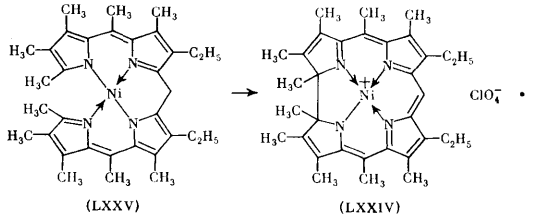
(LXX) (LXXI) (LXIX)

An interesting extension of the cyclisation of 1,19-disubstituted biladienes-*ac* is its application to biladienes containing *meso*-methyl groups. The nickel complex of octadehydro-2,18-diethyl-1,3,7,8,10,12,13,17,19-nonamethylcorrin (LXXII) was obtained by cyclising the corresponding 10-methylbiladiene (LXXIII):[33]



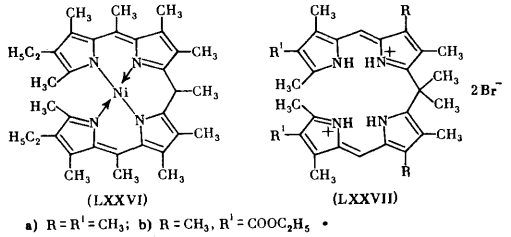
(LXXIII) (LXXII)

The nickel–octadehydrocorrin complex (LXXIV) containing methyl groups at the *meso*-positions 5 and 15 was obtained by aerating the 1,19-dideoxybiladiene-*ac* complex (LXXV):[33]



(LXXV) (LXXIV)

The nickel complex (LXXVI) of completely *meso*-substituted biladiene-*ac*,[33] like the 10,10-dimethylbiladiene (LXXVII),[18] could not be converted into the octadehydrocorrin complex.



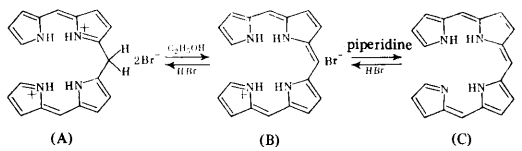
(LXXVI) (LXXVII)

a) R = R' = CH_3; b) R = CH_3, R' = $COOC_2H_5$.

An important condition for the cyclisation of biladienes-*ac* into octadehydrocorrins is the formation of metal complexes of 1,19-dideoxybiladienes (LIX). The first stage in the cyclisation[33] of the biladiene-*ac* dihydrobromide (LVIII) into the 1,19-disubstituted octadehydrocorrin consists in formation of the nickel–biladiene complex (LIX), which was isolated under controlled conditions, and in the presence of sodium acetate and air converted into the cyclic nickel–octadehydrocorrin complex (LVII).

In the absence of a metal it has proved impossible to achieve the cyclisation of biladienes into octadehydrocorrins [16,33], in contrast to the formation of corroles[10,16]. The initiating reaction is probably detachment of a proton from the central methylene group in the metal–biladiene complex (LIX). Involvement of the methylene group of 1,19-dideoxybiladienes is indicated by the absence of cyclisation when the two 10-hydrogen atoms have been replaced by two methyl groups[18], whereas the 10-methyl derivative (LXXIII) cyclises only slightly more slowly than does the unsubstituted compound. Yet the rate of cyclisation of the 5,15-dimethyl derivative (LXXV) is of the same order as that of the *meso*-unsubstituted compound.

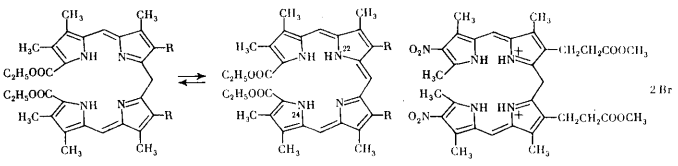
Data on the acidic properties of protons attached to carbon atom 10 in 1,19-dideoxybiladienes-*ac* have been obtained from a study of the visible absorption spectra[16]. Biladiene dihydrobromides (A) form red solutions in chloroform, benzene, and dichloromethane, but yellow solutions in methanol, ethanol, and dimethyl sulphoxide (DMSO); the solutions become green on addition of an organic base, e.g. piperidine. These colour changes are consistent with abstraction of a proton by polar solvents with formation of 1,19-dideoxybilatriene-*abc* monohydrobromides (B), which are converted by excess of piperidine into the corresponding free bilatriene bases (C):[6,19]



(A) (B) (C)

The monohydrobromides (B) are characterised by intense absorption at 420–450 and 750–800 nm, whereas the corresponding bases (C) have absorption bands at 400 and 650 to 750 nm. If a biladiene contains a 10-methyl group, its ethanolic solution does not absorb in the range 650–750 nm when piperidine is present, but the spectrum of a 10,10-dimethylbiladiene in fact remains unchanged with variation in the type of solvent[16].

Detachment of a 10-proton is faciliated by the presence of electron-accepting substituents in the biladiene-*ac*.[16,47,59–61] Yet biladienes containing alkyl, hydrogen, or iodine at positions 1 and 19 exist only as salts like the dihydrobromide (A),[59] and 1,19-diethoxycarbonylbiladienes are equilibrium mixtures of a biladiene salt of type (A) and bilatrienes of types (B) and (C).[59] For example, biladiene-*ac* (LXXVIIIa) is present in chloroform solution partly as a bilatriene salt of type (B),[16] but (LXXVIIIb) exists in dichloromethane solution partly as the tautomeric 22,24-dihydrobilatriene (LXXIX):[60]

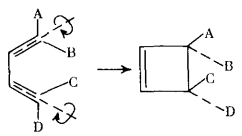


(LXXVIII) (LXXIX) (LXXX)

a) R = C_2H_5; b) R = CH_3.

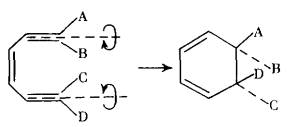
Dinitrobiladiene (LXXX) [61] is present in chloroform solution as a mixture of a neutral bilatriene of type (C) and a monocation of type (B), but the 2,18-dicyanobiladiene dihydrobromide (LVIIIe),[47] when dissolved in chloroform, passes into a 2,18-dicyanobilatriene hydrobromide of type (B), which is converted in methanol into the free 2,18-dicyanobilatriene base of type (C).

The action of a base on the intermediate nickel–biladiene complex (LIX) yields the anion (LXXXI), which is a 22-π-electron system (or an 18-π-electron system if the two cross-conjugated double bonds are neglected). Two further stages—electrocyclic formation of a direct 1,19-bond and an oxidation stage—are required to convert this anion into the nickel complex of octadehydro-1,19-dimethylcorrin (LVII). The sequence of these stages has been established from a determination of the stereochemistry of (LVII), which has a *trans*-configuration of the angular 1- and 19-alkyl substituents[5,62]. In electrocyclic processes[63] conjugated acyclic 4*n*-π-electron systems undergo cyclisation in a conrotatory manner, e.g.



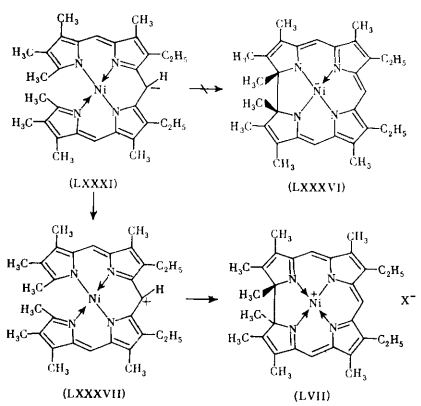
(LXXXII) (LXXXIII)

whereas (4*n* + 2)-π-electron systems cyclise in a disrotatory manner, e.g.



LXXXIV) (LXXXV)

The cyclisation of (LXXXI), which is of the second type, should also involve rotation of terminal groups in opposite sense with formation of the *cis*-isomer (LXXXV), which on oxidation may be converted into the *cis*-octadehydrocorrin–nickel complex. Since, however, the 1,19-disubstituted octadehydrocorrin (LVII) exists in the *trans*-form, the anion (LXXXI) probably undergoes initial two-electron oxidation to the cation (LXXXVII), which is a 4*n*-π-electron system, and on cyclisation is converted into the *trans*-compound (LVII):[8]



(LXXXI) (LXXXVI)

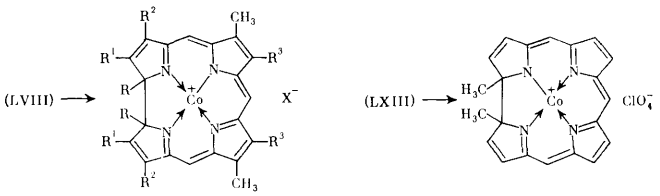
(LXXXVII) (LVII)

The action of several one-electron oxidants in DMSO was examined[54] in the search for milder methods of cyclising 1,19-disubstituted biladiene salts into octadehydrocorrin macrorings containing labile side-chains. Cyclisation of the nickel–biladiene-*ac* complex (LXXV) in the presence of ammonium cerium nitrate in DMSO yields the nickel–octadehydro-1,19-dimethylcorrin complex (LXXIV), which was isolated as the perchlorate in 39% yield.

Cyclisation of 1,19-dideoxybiladienes-*ac* into octadehydrocorrins in the presence of one-electron oxidants apparently occurs also by a free-radical mechanism with intermediate formation of bilatrienes-*abc*.

3. Synthesis of Cobalt and Palladium Complexes of 1,19-Disubstituted Octadehydrocorrins from Biladienes-*ac*

Cyclisation of the 1,19-disubstituted biladiene-*ac* (LVIIIa) is far more rapid in the presence of cobalt acetate than of nickel acetate. Aeration of a methanolic solution at room temperature gives the perchlorate (LXXXVIIIa) of the cobalt–octadehydrocorrin complex in 71% yield[33]:



(LVIII) (LXXXVIII) (LXIII) (LXXXIX)

LXXXVIII: a) R=R¹=R²=CH₃, R³=C₂H₅, X=ClO₄; b) R=R¹=R²=R³=CH₃, X=ClO₄;
c) R=COOC₂H₅, R¹=R²=CH₃, R³=C₂H₅, X=ClO₄;
d) R=R¹=R³=CH₃, R²=OCH₂C₆H₅, X=Br;
e) R=R¹=R³=CH₃, R²=(CH₂)₂COOH, X=ClO₄;
f) R=R²=CH₃, R¹=CH₂COOH, R³=(CH₂)₂COOH, X=ClO₄.

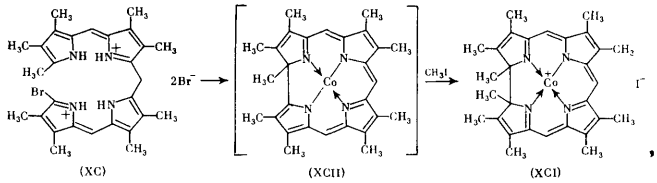
The decamethylated complex (LXXXVIIIb) has also been obtained as the perchlorate[44,45]. The 1,19-diethoxycarbonylbiladiene (LVIIIf) cyclises more rapidly in the presence of cobalt acetate than does the 1,19-dimethyl derivative (LVIIIa), and forms the complex (LXXXVIIIc) in 80% yield[33].

A cobalt–biladiene complex analogous to the nickel complex (LIX) could not be isolated[33]. Aeration of a suspension of the biladiene (LVIIIa) in methanol in the presence of cobalt acetate caused immediate separation of a small quantity of a green crystalline compound (XXXVb) containing two tetrahedral cobalt atoms and two quadridentate 1,19-dideoxybiladiene ligands[25,33]. Cyclisation of the biladiene-*ac* (LVIIIc) yields the cobalt–octadehydrocorrin bromide (LXXXVIIId) having benzyloxy-groups at positions 3 and 17.[46]

The cobalt–octadehydrocorrin complex (LXXXIX) with completely unsubstituted β-positions[36,53] was obtained from the biladiene-*ac* (LXIII) in 26% yield by the use of cobalt acetate in DMSO.[53] Cobalt complexes containing residues of acetic and propionic acids at β-positions are, like the nickel complexes, difficultly accessible because of the lability of the side-chains. However, octadehydrocorrins have been prepared containing residues of propionic esters in all the pyrrole rings[54] and residues of acetic and propionic esters at positions 2, 18 and 3, 17,[55] as well as those containing both acetic and propionic ester groups in all the pyrrole rings[56]. The cobalt complex (LXXXVIIIe) with propionic groups at positions 8 and 12, and (LXXXVIIIf) with acetic and propionic acid residues together at positions 2, 8, 12, and 18, are formed in lower yields than are the corresponding nickel complexes[47]. The cobalt complex (LXIX: M = Co) is obtained[57] similarly to the nickel complex (LXIX: M = Ni) from bilirubin (LXX).

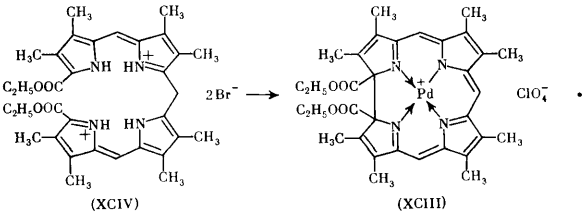
When 1-bromo-19-methylbiladiene-*ac* (XC) undergoes cyclisation in the presence of cobalt acetate in a degassed solvent, addition of iodomethane in the absence of oxygen leads to isolation of a crystalline iodide of the cobalt–octadehydro-1,19-dimethylcorrin complex (XCI), apparently an

alkylation product of the intermediate cobalt–octadehydro-1-methylcorrin complex (XCII):[64]



(XC) (XCII) (XCI)

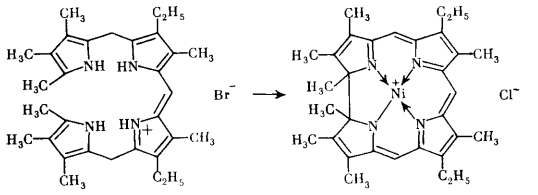
The palladium–octadehydrocorrin complex (XCIII) containing angular 1,19-ethoxycarbonyl substituents has been obtained by aeration of an alcoholic solution of the biladiene-*ac* (XCIV) (yield 35%):[65]



(XCIV) (XCIII)

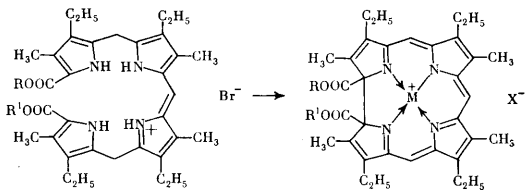
4. Synthesis of Nickel and Cobalt Complexes of 1,19-Disubstituted Octadehydrocorrrins from Bilenes-*b*

Johnson's oxidative cyclisation[33] can be applied not only to 1,19-dideoxybiladienes-*ac* but also to bilenes-*b* (XCV) to give metal complexes of octadehydrocorrins[43,66]. The cyclisation of 1,19-dimethylbilenes-*b* to nickel complexes of octadehydro-1,19-dimethylcorrins is accomplished under the same conditions as that of the corresponding salts of 1,19-dideoxy-1,19-dimethylbiladienes-*ac*.[43,66] For example, aeration of the bilene-*b* (XCV) in the presence of nickel and sodium acetates in boiling methanol followed by treatment with dilute hydrochloric acid gives the nickel–octadehydro-1,19-dimethylcorrin chloride (XCVI):[43]



(XCV) (XCVI)

Nickel and cobalt complexes of octadehydrocorrins with various substituents at positions 1 and 19 (XCVIII) have been obtained[66] from bilenes-*b* (XCVII):



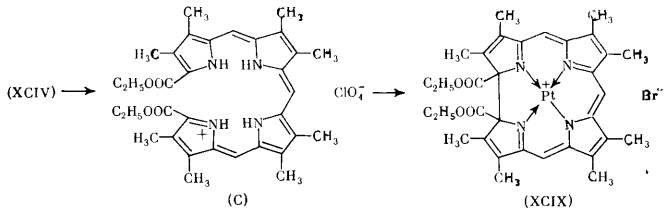
(XCVII) (XCVIII)

a) R = R' = C_2H_5; b) R = R' = $CH_2C_6H_5$; c) R = C_2H_5, R' = $CH_2C_6H_5$.

Far more severe conditions (DMF as solvent aerated at 70 °C for 4 h) are required[66] to obtain the cobalt–octadehydrocorrin complex (XCVIIIa: X = ClO_4) from bilene-*b* than to obtain a similar compound from the biladiene-*ac*.[33]

5. Synthesis of Platinum, Nickel, Cobalt, and Palladium Complexes of 1,19-Disubstituted Octadehydrocorrins from Bilatrienes-*abc*

Until 1977 octadehydrocorrins had been obtained only in the form of nickel[33,43], cobalt[33,67], and palladium complexes. Discovery of the antitumour activity of platinum complexes coordinated with nitrogen[68] led to the synthesis[69] of a platinum–octadehydrocorrin complex (XCIX), which was obtained only in insignificant quantities[69] by oxidative cyclisation[33,43] from the biladiene-*ac* dihydrobromide (XCIV). This complex was prepared in higher yields (15%) from the 1,19-dideoxybilatriene-*abc* hydroperchlorate (C),[16] which is formed when a methanolic solution of the biladiene-*ac* (XCIV) is heated with zinc perchlorate[69]. Boiling a suspension of platinum chloride, sodium acetate, and the bilatriene (C) in acetonitrile yields the platinum–octadehydrocorrin complex (XCIX):

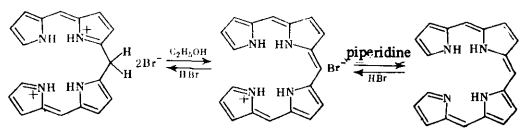


(XCIV) (C) (XCIX)

The synthesis of metal complexes of 1,19-diethoxycarbonyl derivatives of octadehydrocorrin from the bilatriene salt (C) gives better yields[69] of nickel, cobalt, and palladium complexes analogous to (XCIX) than those obtained from the biladiene-*ac* (XCIV). This applies especially to the palladium complex (yield 66%), previously obtained from the biladiene in 35% yield[65].

6. Nickel and Cobalt Complexes of 1,19-Disubstituted Octadehydrocorrins by Metal Exchange

A novel approach to the preparation of cobalt complexes of octadehydrocorrins, by the replacement of nickel using reductive fission of the macroring, was suggested[60] in 1974. When a metal–octadehydrocorrin complex, e.g. (CI: M = Ni), is treated with a reducing agent (hydrogen sulphide, sodium dithionite), it adds two electrons and passes into a negatively charged complex B, which after rupture of the $C_{(1)}$–$C_{(19)}$ bond is converted into the metal complex of 22,24-dihydrobilatriene (CII: M = Ni); protonation of the latter at $C_{(10)}$ converted it into the neutral biladiene complex (CIII):



(A) (B) (C)

At this stage nickel is easily replaced by cobalt. Thus the nickel complex (CIII) is readily demetallised by the action of such acids as trifluoroacetic and hydrochloric, and the resulting biladiene (LXXVIIIb) can be recyclised in the presence of atmospheric oxygen and nickel or cobalt acetate to form the corresponding metal complex, e.g. (CI).[60]

Cobalt complexes occupy a special position, since they undergo ring cleavage even under very mild conditions (hydrogen sulphide at room temperature)[60].

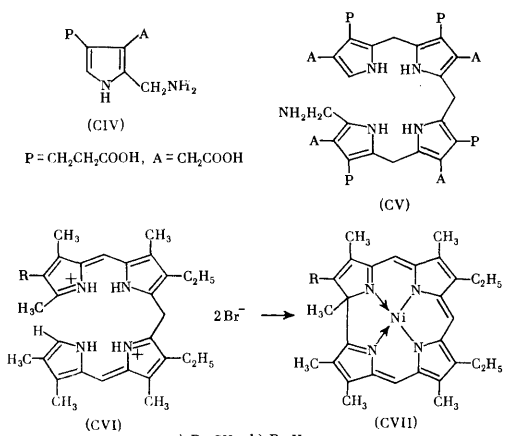
V. SYNTHESIS OF NICKEL COMPLEXES OF 1-SUBSTITUTED OCTADEHYDROCORRINS

1-Alkyloctadehydrocorrins are neutral complexes of bivalent nickel. The tetrapyrrole macroring contains only one angular substituent. Only nickel complexes of 1-alkyloctadehydrocorrins are known.

1. Synthesis of Nickel Complexes of 1-Substituted Octadehydrocorrins by the Oxidative Cyclisation of Biladienes-*ac*

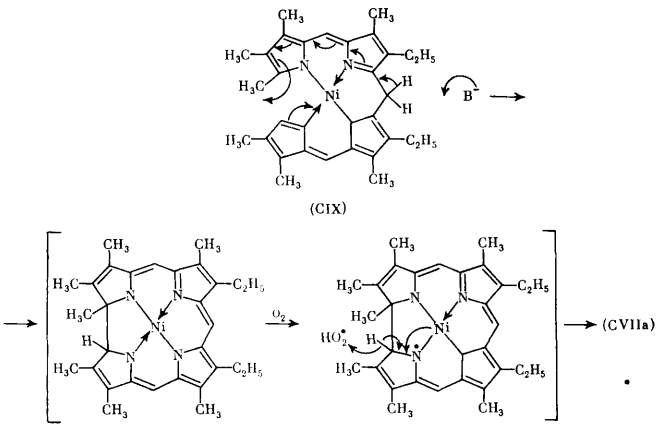
Nickel complexes of octadehydro-1-methylcorrin are formed[7] by the cyclisation of 1-methylbiladienes-*ac*[76] when alkaline solutions are aerated in the presence of nickel ions.

The biosynthesis of the corrin chromophore of vitamin B_{12} involves porphobilinogen (CIV), which is probably converted into a bilane derivative of the type (CV).[70–73] The cyclisation of 1,19-dideoxybiladienes containing an unsubstituted α-position (CVI) was examined[72] to ascertain whether a similarity exists in the mechanisms of the cyclisation of the bilane (CV) and biladienes-*ac*. Such cyclisation was effected[43,70] by heating the biladienes (CVIa,b) in methanol containing nickel acetate and piperidine, which in the presence of oxygen gave the octadehydro-1-methylcorrin–nickel complexes (CVIIa,b) in the respective yields 56% and 59%:

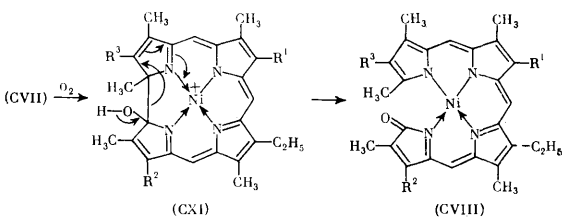


a) R = CH_3, b) R = H

Although cyclisation of α-unsubstituted biladienes (CVI) is caused by aeration with oxygen[43], conversion of (CVIa) into the complex (CVIIa) requires partial degasification of the methanolic solution of biladiene and nickel acetate containing piperidine (in contrast to the cylisation of metal complexes of 1,19-disubstituted octadehydrocorrins, which occurs in the presence of excess of atmospheric oxygen), but in such a way that the quantity of oxygen remaining is sufficient for cyclisation and insufficient to oxidise (CVIIa) to the lactam (CVIII).[32] Formation of octadehydro-1-methylcorrin apparently involves free-radical intermediate compounds resulting from the action of oxygen on a carbanion obtained by detachment of a proton from the metal–biladiene complex (CIX) under the influence of a base[43]:



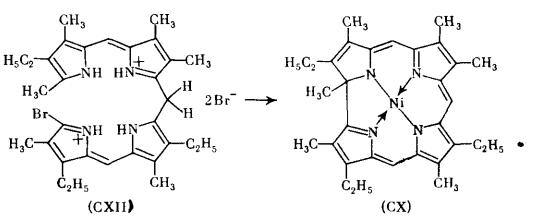
The mechanism of oxidation of the nickel complex (CVII) and (CX) to the lactam (CVIII) has not been established, although intermediate formation of octadehydro-1-hydroxy-19-methylcorrin (CXI) has been postulated[32,43]:



a) $R^1 = C_2H_5$, $R^2 = R^3 = CH_3$; b) $R^1 = CH_3$, $R^2 = R^3 = C_2H_5$.

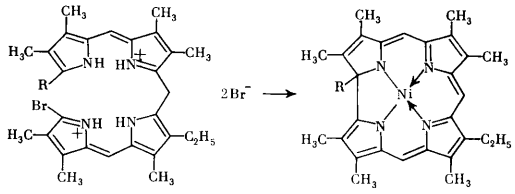
2. Synthesis of Nickel Complexes of 1-Substituted Octadehydrocorrins from Biladienes-*ac* by Non-oxidative Cyclisation

Nickel complexes of octadehydro-1-methylcorrins (CX) are formed by the cyclisation of dihydrobromides not only of 1-substituted biladienes-*ac* but also of 1-bromo-19-methylbiladienes-*ac* (CXII) in the presence of nickel ions and a base[5,32,33,74]:



This probably takes place in the absence of oxygen[32], which distinguishes it significantly from the cyclisation of dihydrobromides of 1,19-dimethyl- and 1-methyl-biladienes-*ac*, requiring an oxidation stage. When the reaction was conducted in the presence of oxygen, the lactam (CVIIIb) was isolated[32]. The cyclisation of (CXII) was extended to the

dihydrobromides of 1-bromo-19-ethyl(and isopropyl)biladienes-*ac* (CXIIIa,b), which gave the corresponding nickel octadehydro-1-alkylcorrins (CXIVa,b) in high yields[32]:



(CXIII) a) R = C_2H_5, b) R = $(CH_3)_2CH$ (CXIV)

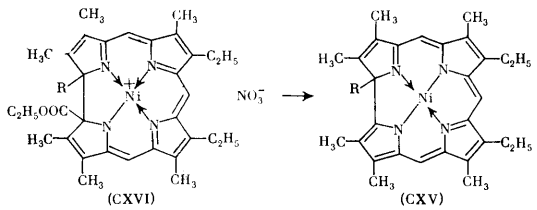
Nickel complexes of 1-alkyloctadehydrocorrins have been synthesised from 1-alkylbiladienes-*ac* containing various 19-substituents, e.g. alkoxy[75] and iodo[21], which are removed during the reaction, but the use of such initial compounds is less convenient than that of 19-bromobiladienes-*ac*.

Attempts to obtain cobalt complexes of octadehydro-1-methylcorrins by cyclisation of the corresponding biladienes in the presence of cobalt acetate in various solvents proved unsuccessful[32,64]. Such behaviour contrasts sharply with the ease of formation of cobalt complexes of 1,19-disubstituted octadehydrocorrins[33].

The attempted cyclisation of 1-bromo-19-methylbiladiene to the corresponding octadehydro-1-methylcorrin in the presence of copper acetate proved unsuccessful[32]. The reaction gives a low yield (8–25%) of a copper–porphyrin complex[42].

3. Synthesis of Nickel Complexes of 1-Substituted Octadehydrocorrins from 1,19-Disubstituted Octadehydrocorrins

Nickel complexes of 1-substituted octadehydrocorrins (CXVa,b) have been obtained from those of 1,19-disubstituted octadehydrocorrins (CXVIa,b) containing a 19-ethoxycarbonyl group[27,32]:



(CXVI) a) R = CH_3, b) R = $COOC_2H_5$ (CXV)

Hydrolysis and decarboxylation of the ethoxycarbonyl group in (CXVIa) gave a nickel complex of octadehydro-1-methylcorrin (CXVa) [32] identical with the compound obtained from the corresponding 19-bromo-1-methylbiladiene-*ac*. Rapid treatment of the octadehydro-1,19-diethoxycarbonylcorrin (CXVIb) [33] with aqueous caustic soda and rapid separation gives a good yield of the nickel complex of octadehydro-1-ethoxycarbonylcorrin (CXVb).[27]

---o0o---

Thus a great deal of experimental information has accumulated during the past decade on the synthesis of metal complexes of octadehydrocorrins and corroles. This opens up the possibility of a broad study of these interesting and complicated compounds, akin to porphyrins and corrins, and possessing biological activity.

REFERENCES

1. Biochemistry, **13**, 1555 (1974).
2. M.E.Vol'pin, V.M.Berezovskii, G.N.Novodarova, T.A.Melent'eva, E.M.Kolosova, N.S.Genokhova, and T.A.Lebedeva, Izv.Akad.Nauk SSSR, Ser.Khim., 2231 (1977).
3. A.I.Scott, Quart.Rev., **19**, 1 (1965).
4. R.L.N.Harris, A.W.Johnson, and I.T.Kay, Quart. Rev., **20**, 211 (1966).
5. A.W.Johnson, Pure Appl.Chem., **23**, 375 (1970).
6. K.M.Smith, Quart.Rev., **25**, 31 (1971).
7. K.M.Smith, Heterocycl.Comp., 319 (1973).
8. A.W.Johnson, Chem.Soc.Rev., **4**, 1 (1975).
9. T.A.Melent'eva, N.D.Pekel', and V.M.Berezovskii, Uspekhi Khim., **38**, 2016 (1969) [Russ.Chem.Rev., No.12 (1969)].
10. A.W.Johnson and I.T.Kay, J.Chem.Soc., 1620 (1965).
11. A.W.Johnson and I.T.Kay, Proc.Chem.Soc., 89 (1964).
12. G.Shelton, A.W.Johnson, M.J.Broadhurst, and R.Grigg, J.Chem.Soc., Perkin Trans.I, 143 (1972).
13. G.L.Closs and L.E.Closs, J.Amer.Chem.Soc., **85**, 818 (1963).
14. A.W.Johnson and I.T.Kay, Proc.Roy.Soc.A, **288**, 334 (1965).
15. R.Grigg, A.W.Johnson, and G.Shelton, J.Chem.Soc.C, 2287 (1971).
16. D.Dolphin, A.W.Johnson, J.Leng, and P.van den Broek, J.Chem.Soc.C, 880 (1966).
17. A.W.Johnson, Chem.in Britain, **3**, 253 (1967).
18. A.W.Johnson, I.T.Kay, D.Dolphin, R.L.N.Harris, J.L.Huppatz, and J.Leng, J.Chem.Soc.C, 98 (1966).
19. E.Bullock, R.E.Grigg, A.W.Johnson, and J.W.Wasley, J.Chem.Soc.C, 2326 (1963).
20. R.L.N.Harris, A.W.Johnson, and I.T.Kay, J.Chem. Soc.C, 22 (1966).
21. J.Engel and A.Gossauer, Chem.Comm., 713 (1975).
22. M.J.Broadhurst, R.Grigg, and A.W.Johnson, J.Chem. Soc., Perkin Trans.I, 1124 (1972).
23. R.Grigg, A.W.Johnson, and G.Shelton, Chem.Comm., 1151 (1968).
24. R.Grigg, A.W.Johnson, and G.Shelton, Annalen, **746**, 32 (1971).
25. Y.Murakami, Y.Matsuda, and Y.Kanaoka, Bull.Chem. Soc.Japan, **44**, 409 (1971).
26. D.Dolphin, R.L.N.Harris, A.W.Johnson, and I.T.Kay, Proc.Chem.Soc., 359 (1964).
27. R.Grigg, A.W.Johnson, K.Richardson, and M.J.Smith, J.Chem.Soc.C, 1289 (1970).
28. E.Billig, H.B.Gray, S.I.Shupack, J.H.Waters, and R.Williams, Proc.Chem.Soc., 110 (1964).
29. M.Gerlock, B.M.Higson, and E.D.McKenzie, Chem. Comm., 1149 (1971).
30. J.J.Bour, P.T.Beurskens, and J.J.Steggarda, Chem. Comm., 221 (1972).
31. J.M.Conlon, A.W.Johnson, W.R.Overend, D.Rajapaksa, and C.M.Elson, J.Chem.Soc., Perkin Trans.I, 2281 (1973).
32. D.A.Clarke, R.Grigg, R.L.N.Harris, A.W.Johnson, I.T.Kay, and K.W.Shelton, J.Chem.Soc.C, 1648 (1967).
33. D.Dolphin, R.L.N.Harris, J.L.Huppatz, A.W.Johnson, and I.T.Kay, J.Chem.Soc.C, 30 (1966).
34. Y.Murakami, Y.Kohno, and Y.Matsuda, Inorg.Chim. Acta, **3**, 671 (1971).
35. R.Chong, P.S.Clezy, A.J.Liepa, and A.W.Nichol, Austral.J.Chem., **22**, 229 (1969).
36. A.W.Johnson and W.R.Overend, J.Chem.Soc., Perkin Trans.I, 2681 (1972).

37. M.J.S.Dewar and T.Nakaya, J.Amer.Chem.Soc., **90**, 7134 (1968).
38. A.M.Abeysekera, R.Grigg, J.Trocha-Grimshaw, and V.Viswanatha, J.Chem.Soc., Perkin Trans.I, 36 (1977).
39. R.Grigg, J.Trocha-Grimshaw, and V.Viswanatha, Tetrahedron Letters, 289 (1976).
40. Y.Murakami, Y.Matsuda, and S.Yamada, Chem.Letters, 689 (1977).
41. W.A.Little, Phys.Rev., **A**, **134**, 1416 (1964).
42. A.W.Johnson and I.T.Kay, J.Chem.Soc., 2418 (1961).
43. I.D.Dicker, R.Grigg, A.W.Johnson, H.Pinnock, K.Richardson, and P.van den Broek, J.Chem.Soc., 536 (1971).
44. T.A.Melent'eva, N.D.Pekel', and V.M.Berezovskii, Zhur.Obshch.Khim., **40**, 165 (1970).
45. Y.Murakami, K.Sakata, Y.Tanaka, and T.Matsuo, Bull.Chem.Soc.Japan, **48**, 3622 (1975).
46. H.H.Inhoffen, N.Schwarz, and K.-P.Heise, Annalen, 146 (1973).
47. N.S.Genokhova, T.A.Melent'eva, and V.M.Berezovskii, Zhur.Obshch.Khim., **47**, 121 (1977).
48. A.Gossauer, D.Miehe, and H.H.Inhoffen, Annalen, 738, 31 (1970).
49. R.Grigg, A.W.Johnson, and P.van den Broek, Chem.Comm., 502 (1967).
50. T.A.Melent'eva, N.S.Genokhova, N.D.Pekel', T.A.Stetsko, and V.M.Berezovskii, Zhur.Obshch. Khim., **44**, 929 (1974).
51. T.A.Melent'eva, N.D.Pekel', and V.M.Berezovskii, Zhur.Obshch.Khim., **42**, 180 (1972).
52. H.H.Inhoffen, J.Ullrich, H.A.Hoffman, G.Klinzmann, and R.Scheu, Annalen, **738**, 1 (1970).
53. A.W.Johnson and W.R.Overend, Chem.Comm., 710 (1971).
54. R.Grigg, A.W.Johnson, P.Kenyon, V.B.Math, and K.Richardson, J.Chem.Soc., 176 (1969).
55. H.H.Inhoffen, F.Fattinger, and N.Schwarz, Annalen, 412 (1974).
56. J.Engel and A.Gossauer, Chem.Comm., 570 (1975).
57. H.H.Inhoffen, H.Maschler, and A.Gossauer, Annalen, 145 (1973).
58. A.W.Nichol and D.B.Morell, Biochim.Biophys.Acta, 177, 599 (1969).
59. J.Engel and A.Gossauer, Annalen, 1637 (1976).
60. H.H.Inhoffen and H.Maschler, Annalen, 1269 (1974).
61. P.S.Clezy, A.J.Liepa, and N.W.Webb, Austral.J. Chem., **25**, 2687 (1972).
62. R.Grigg, A.P.Johnson, A.W.Johnson, and M.J.Smith, J.Chem.Soc., 2457 (1971).
63. R.B.Woodward and R.Hoffmann, Angew.Chem.Internat. Edn., **8**, 781 (1969).
64. R.Grigg, A.W.Johnson, and K.W.Shelton, J.Chem.Soc., 1291 (1968).
65. A.Gossauer, H.Maschler, and H.H.Inhoffen, Tetrahedron Letters, 1277 (1974).
66. J.M.Conlon, J.A.Elix, G.I.Feutrill, A.W.Johnson, M.W.Roomi, and J.Whelan, J.Chem.Soc., Perkin Trans. I, 713 (1974).
67. C.M.Elson, A.Hamilton, and A.W.Johnson, J.Chem. Soc., 775 (1973).
68. B.Lippert, Machr.Chem.Tech., **21**, 115 (1973).
69. J.Engel and H.H.Inhoffen, Annalen, 767 (1977).
70. I.D.Dicker, D.Dolphin, R.Grigg, and A.W.Johnson, Chem.Comm., 560 (1967).
71. E.Bullock, A.W.Johnson, E.Markham, and K.B.Shaw, J.Chem.Soc., 1430 (1958).
72. R.Reichard, J.Biochem., **3**, 259 (1968) [sic].
73. J.H.Mathewson and A.H.Corwin, J.Amer.Chem.Soc., **83**, 155 (1961).
74. R.L.N.Harris, A.W.Johnson, and I.T.Kay, Chem. Comm., 355 (1965).
75. J.H.Atkinson, A.W.Johnson, and W.Raudenbusch, J.Chem.Soc., 1155 (1966).
76. A.F.Mironov and R.P.Evstigneeva, Khim.Geterotsikl. Soed., 291 (1976).

All-Union Vitamins Scientific
Research Institute, Moscow

Translated from *Uspekhi Khimii*, **49**, 2159 - 2187 (1980) U.D.C. 547.414.8

Chemistry of α-Halogenonitroalkanes

A.L.Fridman (deceased), V.D.Surkov, and S.S.Novikov (deceased)

Methods of preparation of α-halogenonitroalkanes and their functional derivatives are surveyed, together with the chief results obtained for the geometric parameters, electronic structure, and ultraviolet, infrared, and nuclear magnetic and quadrupole resonance spectroscopy, as well as acid - base properties. Reactions involving reduction, addition at multiple bonds, substitution of halogen atoms and the nitro-group, and interaction with diazoalkanes are analysed, and the most important mechanisms are discussed. Data are given on the toxicity, physiological activity, and practical use of these compounds. A list of 316 references is included.

CONTENTS

I. Introduction 1068
II. Methods of preparation 1068
III. Spectral properties and structure 1071
IV. Chemical properties 1073
V. Physiological activity and practical use 1077

I. INTRODUCTION

The chemistry of aliphatic nitro-compounds is now a well studied field. Aspects of the preparation, structure, and chemical behaviour of nitroalkanes and their many derivatives have been quite widely discussed in several reviews[1-10] and in a monograph[11]. However, α-halogenonitro-compounds either are not discussed at all in these publications[1-3,9] or are only partly covered[4-8,10,11]. Yet their unique properties merit a separate review. This unusual class of substances has long attracted the attention of chemists and other specialists, as is indicated by the large number of original peprs in this field. The possibility of the direct use of α-halogenonitro-compounds as agricultural chemicals, and also as intermediates in the production of novel biologically active compounds, explosives, and rocket fuel components, still maintains this interest even at the present time.

α-Halogenonitroalkanes are undoubtedly also of theoretical interest. The combination of a nitro-group and a halogen attached to the same carbon atom confers on the halogen special properties differing markedly from those in ordinary halogenated aliphatic compounds. This difference is especially characteristic of α-halogenopolynitroalkanes, which exhibit the properties of compounds having a "positively" polarised halogen atom[12]. The reactions of α-halogenonitroalkanes involve either homolytic or heterolytic fission of the carbon–halogen bond depending on the nature of the halogen and the conditions: the heterolytic process may release the halogen as either a cation or an anion, so that a wide range of reactions can be accomplished. Furthermore, reactions involving the nitro-group or an α-hydrogen atom can also occur.

The present Review summarises the literature up to 1977 on methods of preparation, structure, and characteristic reactions. Since the bibliography on these compounds comprises more than 500 sources, we considered it advisable to give references to the most recent work, from which the early primary sources can usually be found. The concluding Section gives information available to us on the biological activity and practical utilisation of α-halogenonitroalkanes.

II. METHODS OF PREPARATION

1. Replacement by Halogen of an α-Hydrogen Atom in Nitroalkanes and their Derivatives

Halogenation of nitroalkanes and their functional derivatives is usually accomplished in the presence of a base, the most common method for obtaining α-halogenonitro-compounds[11]. The process is applied to a solution of the nitroalkane in aqueous alkali[13-15]; sometimes organic solvents are used[14,15].

The action of chlorine and bromine on primary mononitroalkanes may form mono- and di-halogenated derivatives, but nitromethane can also give trihalogenitromethanes, when each succeeding hydrogen atom is replaced more easily than the previous one:

$$CH_3NO_2 \xrightarrow{Br_2,NaOH} CH_2BrNO_2 \xrightarrow{Br_2,NaOH} CHBr_2NO_2 \xrightarrow{Br_2,NaOH} CBr_3NO_2 .$$

Kinetic studies have been made of the bromination of nitromethane and nitroethane[16,17]. The rate constants of the formation of mono-, di- and tri-halogenonitromethanes are in the proportions 1 : 200 : 10 000.[16] Simultaneous chlorination and bromination of salts of nitroalkanes gives bromochloronitroalkanes[18].

Hydrolysis[19] and interaction with nitroalkane salts[20-22] have been observed as side reactions accompanying the halogenation of nitroalkanes:

$$RCH{=}NOO^-Na^+ + RCH(NO_2)Cl \rightarrow RCH_2NO_2 + RC(Cl){=}NOO^-Na^+ ,$$

$$RC(Cl){=}NOO^-Na^+ \begin{cases} \xrightarrow{H_2O} RC(OH){=}NOO^-Na^+ + HCl \rightarrow RCHO + HNO_2 + NaCl \\ \xrightarrow{RCH(NO_2)Cl} RCH(NO_2)CCl(NO_2)R + NaCl . \end{cases}$$

Halogenation is conducted with equimolecular quantities of reactants at low temperatures in order to suppress side reactions[23].

Halogenated 1,1-dinitroalkanes and trinitromethane are readily formed from alkali-metal salts of the nitro-compounds[25-27]:

$$RC(NO_2)_2^-M^+ + X_2 \rightarrow RC(NO_2)_2X + MX ,$$

$R{=}NO_2$, Alk; M=Na, K, NH_4; X=Cl, Br .

However, dinitromethane in aqueous alkali gives only dihalogenodinitromethanes[28,29]:

$$CH(NO_2)_2^-K^+ + 2X_2 + KOH \rightarrow C(NO_2)_2X_2 + 2KX + H_2O \quad X=Cl, Br .$$

Dichloro- and dibromo-dinitromethanes are easily converted by alkali into the corresponding salts of the monohalogenodinitromethanes[29,30]:

$$C(NO_2)_2X_2 + 2KOH \rightarrow XC(NO_2)_2^-K^+ + KOX + H_2O .$$

In an attempt to obtain monohalogenated derivatives of dinitromethane by acidifying their salts the dihalogenodinitromethanes were isolated[30]:

$$2XC(NO_2)_2^-K^+ + H_2SO_4 \rightarrow C(NO_2)_2X_2 + K_2SO_4 + N_2O + CO_2 + H_2O \quad X=Cl, Br, I .$$

Bromodinitromethane was reported[28] to be formed when the potassium salt of dinitromethane was treated with excess of bromine in a neutral medium.

The halogenation of nitroalkanes takes place by an ionic mechanism. The rate-determining stage is isomerisation of the true nitro-compound into the *aci*-form[16,17]. α-Halogenated polynitroalkanes are formed by halogenation of the anions of the latter, which result directly from the nitroalkane without intermediate formation of the *aci*-form[31].

Among other halogenating agents used are interhalogen compounds[28,32], sodium hypochlorite and hypobromite[33], *N*-chloro-*N*-nitroamines, *N*-bromo- and *N*-chloro-succinimide, and sodium *N*-chlorobenzenesulphonamide[34]. In several cases the selectivity is enhanced and the yield of required products increased[34]. Salts of nitro-compounds are smoothly chlorinated by chlorine fluorosulphate[35]:

$$RC(NO_2)_2^-M^+ + ClOSO_2F \rightarrow RC(NO_2)_2Cl + MOSO_2F ,$$
$$R=NO_2, CN; \quad M=Na, K .$$

Fluorination of salts of nitro-compounds is effected with elementary fluorine in water[36]. Secondary mononitroalkanes are converted into satisfactory yields of α-fluoromononitroalkanes[37], whereas the primary compounds give low (5–14%) yields of fluoro-derivatives[36]. The latter are obtained by replacing an α-hydrogen atom in the mononitroalkane by an alkoxycarbonyl group, which after fluorination is removed by alkaline hydrolysis[11]:

$$\begin{matrix} RC{=}NOO^- \\ | \\ COOC_2H_5 \end{matrix} \xrightarrow{F_2,\,N_2} \begin{matrix} RCFNO_2 \\ | \\ COOC_2H_5 \end{matrix} \xrightarrow{C_2H_5O^-} RCF{=}NOO^- \xrightarrow{H^+} RCHFNO_2 .$$

Fluorination with elementary fluorine in water is used to obtain α-fluoropolynitroalkanes[26,36,38–40]. Solid-phase fluorination of nitroform and its salts with elementary fluorine is accompanied by fluorolysis, difluorodinitromethane being formed with fluoronitroform[41].

α-Fluoromononitroalkanes have been prepared by fluorinating salts of the mononitroalkanes with elementary fluorine in methanol at −30 to −60 °C,[42] with yields of 58–73%. Another method for obtaining α-fluoronitroalkanes consists in the action of perchloryl fluoride on the sodium salts of secondary nitroalkanes and nitrocycloalkanes[43]:

$$RR'C{=}NOO^-Na^+ + FClO_3 \rightarrow RR'CFNO_2 + NaClO_3 .$$

Alkali-metal salts of 1,1-dinitroalkanes and trinitromethane are also readily converted by perchloryl fluoride into α-fluoropolynitroalkanes[44–47]:

$$RC(NO_2)_2^-M^+ + FClO_3 \rightarrow RC(NO_2)_2F + MClO_3 ,$$
$$R=NO_2, CH_3, C_6H_5, C_6H_5CH_2; \quad M=Na, K, NH_4 .$$

Undecafluoropiperidine fluorinates smoothly the sodium salt of 2-nitropropane in methanol[48].

Fluoro-chloro-, -bromo-, and -iodo-dinitromethanes are obtained by the halogenation of bisfluorodinitromethylmercury[49]:

$$Hg[C(NO_2)_2F]_2 + 2X_2 \rightarrow 2XC(NO_2)_2F + HgX_2 ,$$
$$X=Cl, Br, I .$$

In contrast to bromo-, chloro-, and fluoro-nitroalkanes, α-iodonitroalkanes have been inadequately studied, owing to the difficulty of preparing them and their instability. The action of iodine on alkali-metal salts of mononitroalkanes led to the isolation of dimeric products, formed by reaction between the nitroalkane anion and the iodonitroalkane[20–22]:

$$2C_6H_5CH{=}NOO^-Na^+ + I_2 \rightarrow C_6H_5CH(NO_2)CH(NO_2)C_6H_5 + 2NaI .$$

α-Iodopolynitroalkanes cannot be obtained in this way, because of occurrence of the reverse reaction[24]

$$RC(NO_2)_2I + KI \rightarrow RC(NO_2)_2^-K^+ + I_2 ,$$
$$R=NO_2, Hal, Alk .$$

They are formed by the action of iodine on silver salts of polynitroalkanes in organic solvents. Iodotrinitromethane has thus been prepared with ether as solvent[27,50]. Many α-iodonitro-derivatives have been obtained by iodinating anions of mono- and poly-nitroalkanes with iodine chloride[28,32,51].

Replacement of an α-hydrogen atom in a nitro-compound by halogen in the presence of a base is a general method for obtaining functional α-halogenonitro-compounds. The reaction is selective and is not complicated by the presence of a group such as keto[52,53], amino[54], ester[55–57], nitrile[57,58], amide[59], sulphonyl[59,60], hydrazino[61] or an unsaturated bond[62].

Chlorination and fluorination of potassium salts of 2,2-dinitroethyl ethers of oximes readily yield halogeno-derivatives without affecting the C=N bond[63]:

$$RR'C{=}NOCH_2C(NO_2)_2^-K^+ \begin{cases} \xrightarrow{FClO_3} RR'C{=}NOCH_2C(NO_2)_2F , \\ \xrightarrow{Cl_2} RR'C{=}NOCH_2C(NO_2)_2Cl . \end{cases}$$

Treatment of nitroalcohols with caustic alkalis[64] or alkali-metal alkoxides[65] forms salts, whose halogenation in water or in an organic solvent yields halogenonitroalcohols:

$$RCH(OH)C(NO_2)_2^-K^+ + X_2 \rightarrow RCH(OH)C(NO_2)_2X + KX ,$$
$$(HOCH_2)_2C{=}NOO^-Na^+ + X_2 \rightarrow (HOCH_2)_2C(NO_2)X + NaX ,$$
$$X=F, Cl, Br .$$

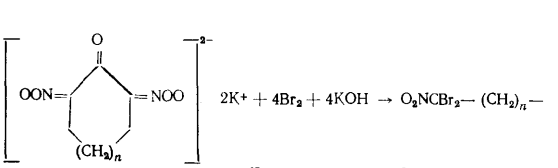
Fluoro-, chloro-, and bromo-derivatives of nitroalcohols and nitrodiols have been obtained in this way[37,39,44,65–69]. Similarly, salts of nitroalkyl ethers[70], sulphides[71], and sulphones[60] are halogenated to the corresponding halogenonitro-derivatives:

$$H_3COCH_2C(NO_2)_2^-K^+ + Br_2 \rightarrow H_3COCH_2C(NO_2)_2Br + KBr ,$$
$$RSO_2C(NO_2)_2^-Na^+ + Cl_2 \rightarrow RSO_2C(NO_2)_2Cl + NaCl .$$

Bis-1-nitroalkyl disulphides are converted by halogens into 1-halogeno-1-nitroalkylsulphenyl halides[72,73]:

$$RCH(NO_2)S{-}SCH(NO_2)R \xrightarrow{Cl_2} RCCl(NO_2)SCl .$$

Cyclic αα′-dinitro-ketones react with bromine in an alkaline medium with cleavage of the ring and formation of tetrabromodinitroalkanes[74]:



$$2K^+ + 4Br_2 + 4KOH \rightarrow O_2NCBr_2{-}(CH_2)_n{-}$$
$$-CBr_2NO_2 + K_2CO_3 + 4KBr \quad n=2–5 .$$

2-Nitrodimedone, 2-nitroindanedione, and analogous compounds are readily brominated and chlorinated in aqueous solution without preliminary conversion into their salts[75]. 2-Iodo-2-nitrodimedone has been obtained in 92% yield by iodinating 2-nitrodimedone with an iodine monochloride–dioxan complex in acetic acid[76].

The halogenation of mononitroalkanes, which are weak carbon–hydrogen acids, is quite rapid in acid media[16,17]. The first stage is assumed[77–79] to involve an acid-catalysed prototropic change with formation of a nitronic acid, which, passing through a stage of formation of the ion of the nitro-compound, readily adds a halogen or a hypohalic acid to form the 1-halogenonitroalkane:

$$\rangle CHNO_2 + H^+ \rightleftarrows \rangle CHNO_2H^+ \rightleftarrows \rangle C{=}NOOH + H^+$$
$$\rangle C{=}NOOH \rightleftarrows \rangle C{=}NOO^- + H^+$$
$$\rangle C{=}NOO^- + X_2 \rightarrow \rangle CXNO_2 + X^- .$$

The rate of the acid-catalysed halogenation of nitroalkanes is independent of either the nature of the concentration of the halogen, and the reaction is first order with respect to the nitro-compound[77,78].

Hydrogen can be replaced by halogen without preliminary conversion into a salt also in polynitroalkanes, which are strong carbon–hydrogen acids. This reaction was first observed by Shishkov[80], in the action of bromine on trinitromethane in sunlight:

$$CH(NO_2)_3 + Br_2 \xrightarrow{h\nu} C(NO_2)_3Br + HBr .$$

Treating polynitroalkanes with perchloryl fluoride in a solvating aprotic solvent yields the corresponding fluoro-derivatives[45]:

$$RCH(NO_2)_2 + FClO_3 \rightarrow RC(NO_2)_2F + HClO_3 ,$$
$$R{=}NO_2, F, CH_3 .$$

Fluorotrinitromethane has been prepared by the action of elementary fluorine on trinitromethane in water and in various organic solvents[26,38].

Chloro- and bromo-nitroforms are readily produced when nitroform is treated with the corresponding halogens or hydrohalic acids in a mixture of sulphuric and nitric acids[81].

2. Halogenation of Conjugated Nitroalkenes

In chloroform, tetrachloromethane, or carbon disulphide conjugated nitroalkenes readily add chlorine and bromine to form the *vic*-dihalogenated derivatives[82–85]:

$$-C{=}CNO_2 + X_2 \rightarrow -\overset{|}{\underset{X}{C}}-\overset{|}{\underset{X}{C}}-NO_2 ,$$
$$X{=}Cl, Br .$$

Bromine can be replaced by its pyridine complex to obtain dibromo-derivatives[86]. The reaction has a heterolytic mechanism, and the rate of electrophilic addition of halogen is greatly diminished by electron-accepting substituents. For example, halogens cannot be added to *vic*-dinitroalkenes under normal conditions. To obtain dichloro-derivatives a mixture of the dinitroalkene and liquid chlorine is exposed to sunlight for a long time[87]. 1,2-Dinitroethylene adds bromine in the presence of hydrobromic acid in acetic acid[88].

Addition of bromine and chlorine to nitroalkenes is hindered also by the presence of a halogen at the double bond. Trichloro- and tribromo-nitroethylenes are brominated only at high temperatures, with formation of 1,2-dibromo-1,2,2-trichloronitroethane and pentabromonitroethane respectively. Arylated 1-bromo-1-nitroalkenes are not brominated at the double bond[82].

Addition of chlorine and bromine is more difficult to 1,4-dinitrobuta-1,3-diene than to nitroalkenes: 1,2,3,4-tetrahalogeno-derivatives are formed at 56–61 °C.[85,89–91] On recrystallisation the tetrabromide is converted into 1,4-dibromo-1,4-dinitrobuta-1,3-diene[85]. Under normal conditions 2,3-dimethyl-1,4-dinitrobuta-1,3-diene reacts very slowly with bromine, forming 1,4-dibromo-2,3-dimethyl-1,4-dinitrobuta-1,3-diene. This reaction is accelerated by addition of a catalytic quantity of hydrobromic acid[85].

Phenyl substituents in dinitrobutadienes create considerable hindrance to bromination. 1,4-Dinitro-2,3-diphenylbuta-1,3-diene reacts slowly with bromine, but the 1,4-diphenyl isomer under normal conditions does not add bromine at the double bond[82].

The halogenation of conjugated nitroalkenes enables polyhalogenated nitroalkanes to be obtained that are difficult to prepare by other methods.

3. Nitration of Halogenated Alkenes and Other Halogenated Compounds

The nitration of chloro- and bromo-alkenes with nitrogen dioxide yields a complicated mixture of products including α-halogenonitroalkanes[92–94]. Addition of nitrogen dioxide at the double bond depends in considerable measure on the nature of the halogenoalkane and the reaction conditions; dinitro-derivatives and alkyl nitrites may be formed. Furthermore, the process is complicated by substitution of a nitro-group for halogen and by formation of nitrosyl halides, which add to the halogenoalkenes to give nitroso-compounds[95–97]. The action of nitrogen dioxide on vinyl, propenyl, isopropenyl, and isobutenyl bromides and on α- and β-bromostyrenes forms dinitro-derivatives only with the last three compounds, in the respective yields 33.0%, 14.5%, and 9.7%.[92,93]

When halogenoethylenes are heated with nitrogen dioxide, the corresponding 1,2-dinitro-derivatives are formed[94,98]:

$$X_2C{=}CX_2 + 2NO_2 \rightarrow X_2C(NO_2)C(NO_2)X_2 ,$$
$$X{=}Cl, Br .$$

The yields of dinitro-derivatives are increased by the presence of anhydrous aluminium chloride[94].

In 1948 the first results were published on the nitration of fluorinated ethylenes with nitrogen dioxide[99]. Subsequently this reaction was studied in greater detail[100–104]. It was accomplished in the gas phase[100], and in non-polar solvents[101] at room or elevated temperatures and pressures[102–104]. The resulting *vic*-dinitroalkanes were accompanied by alkyl nitrites[101].

On passing from perfluoroethylene to perfluoropropene and perfluoroisobutene, the first of which reacts explosively with nitrogen dioxide in the absence of a solvent, more severe conditions are required (100 and 180 °C respectively)[101–103].

The nitration of fluoroalkenes by nitrogen dioxide is assumed to have a radical mechanism[102,103]:

$$CF_3-CF{=}CF_2 \xrightarrow{\dot{O}NO} CF_3-\dot{C}F-CF_2NO_2 \xrightarrow{\dot{O}NO} CF_3-\overset{NO_2}{\overset{|}{C}}F-CF_2NO_2$$
$$\downarrow \dot{O}NO$$
$$CF_3-\underset{ONO}{\overset{|}{C}}F-CF_2NO_2 \xrightarrow{H_2O,H_2SO_4} CF_3-\underset{O}{\overset{\|}{C}}-CF_2NO_2 .$$

Hydrolysis of the halogenonitroalkyl nitrites yields the corresponding halogenated nitroalcohols[105–107] and nitrocarboxylic acids[100,102,107].

Nitrosyl chloride and bromide react with halogenoalkenes yielding the corresponding nitro-derivatives, which are formed by oxidation of the nitroso-derivatives by a second molecule of the nitrosyl halide. Addition of the nitrosyl halides takes place in conformity with the polarisation of the double bond[95,108,109].

Oxides of nitrogen react in hydrofluoric acid with halogenoalkenes to form the 1-halogeno-2-fluoronitroalkanes[110–112].

The nitration of halogenoalkenes by concentrated nitric acid is accompanied by degradation of the alkene molecule and yields halogenonitromethanes. Thus treatment of trichloroethylene and tetrabromoethylene leads to the isolation respectively of dichlorodinitromethane[113] and dibromodinitromethane[114]; but the main product of the degradative nitration of tetrachloroethylene is chlorodinitromethane, accompanied by small quantities of trichloronitromethane[114].

Chlorinated nitromethanes are obtained by nitrating chloroacetone with nitric acid, or by treating acetone with nitric acid saturated with chlorine[115] or in the presence of sodium chloride[116].

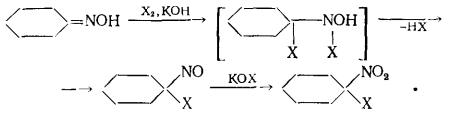
The nitration of halogenoalkenes and other halogenated compounds by nitric acid is accompanied by the oxidising action of oxides of nitrogen and halogens formed in the reaction, which results in complicated mixtures, so that this procedure is rarely used as a method of preparation.

4. α-Halogenonitro-compounds from Oximes

The halogenation of oximes in alkaline medium enables halogenated mononitroalkanes of diverse structure to be obtained[7,117,118]:

$$RR'C{=}NOH + 2X_2 + 3NaOH \rightarrow RR'C(NO_2)X + 3NaX + 2H_2O$$
$$X{=}Cl,\ Br\ .$$

Aliphatic and especially alicyclic ketoximes readily undergo this reaction[119,120]. It involves three stages—addition of halogen at the C=N bond in the oxime, formation of a halogenonitroso-derivative, and oxidation of the latter to the halogenonitro-derivative[117]:

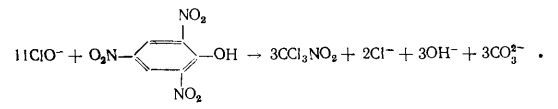


This mechanism is supported by the ease of oxidation of chloronitroso-compounds to the corresponding chloronitro-derivatives[118]. Bromonitroso-derivatives are readily formed by the action of *N*-bromosuccinimide on ketoximes[119,120]. The nitroso-group is smoothly oxidised to a nitro-group by nitric acid or its mixture with 30% hydrogen peroxide[121]. In this way 2-bromo-2-nitropropane, 2-bromo-2-nitrobutane, and 3-bromo-3-nitropentane have been obtained in yields of 18%, 46%, and 38% respectively[120], as well as other α-chloro- and α-bromo-nitroalkanes[121].

The use of oximes for the preparation of α-halogenonitro-compounds extends considerably the range of starting materials. This is important in cases in which the corresponding nitroalkanes are not available to the research worker.

5. Other Methods

When 2,4,6-trinitrophenol is treated with hypochlorite or hypobromite, the aromatic ring is cleaved to form the trihalogenonitromethanes[122]:



This method is used in industry to obtain trichloronitromethane. Picric acid, which is sparingly soluble in water, can be replaced by calcium picrate, and chlorine can be used instead of hypochlorite.

Hydrolytic cleavage of α-halogeno-α-nitro-ketones yields α-halogenonitroalkanes[123–126]:

$$CH_3\overset{\overset{O}{\|}}{C}CBr(NO_2)R \xrightarrow{H_2O} RCHBrNO_2 + CH_3COOH\ ,$$
$$CF_3\overset{\overset{O}{\|}}{C}F_2NO_2 \xrightarrow{H_2O(NaOH)} F_2CHNO_2 + CF_3COOH\ .$$

Halogenonitromethanes are formed also by the hydrolysis of halogenonitroacetyl chlorides[127].

Bromopolynitroethanes are obtained from tribromonitromethane and potassium cyanide. The resulting tetrabromo-1,2-dinitroethane is easily converted into 1,2-dibromotetranitroethane[128,129].

Several α-fluorodinitroalkanes are obtained by alkylating the silver salt of fluorodinitromethane[130]:

$$CF(NO_2)_2^-Ag^+ + RX \rightarrow RC(NO_2)_2F + AgX\ ,$$
$$R{=}CH_3,\ C_3H_7,\ C_3H_5CH_2,\ CH_2{=}CH{-}CH_2;\ X{=}Br,\ I\ .$$

It has recently been shown that α-halogenonitroalkanes are formed by halogenating α-nitroalkylsulphonium salts[131]:

$$(CH_3)_2\overset{+}{S}CH(NO_2)_2\ HSO_4^- \xrightarrow{X_2} CH(NO_2)_2X\ ,$$
$$X{=}Cl,\ Br\ .$$

The action of nitrogen dioxide on fluoro-carboxylic acids or their silver salts yields fluoronitroalkanes[132,133].

Fluoro- and chloro-trinitromethanes have been obtained by nitrating fluoro- and chloro-dinitromethanes respectively with nitryl fluoride[134]:

$$CH(NO_2)_2X + FNO_2 \rightarrow C(NO_2)_3X\ ,$$
$$X{=}F,\ Br\ .$$

Halogenotrinitromethanes are formed by reaction between tetranitromethane and chlorine, *NN*-dichlorobenzenesulphonamide[135], sodium *N*-chlorobenzenesulphonamide[136], or an alkali-metal halide[137–139].

Electrochemical methods of preparing α-halogenonitroalkanes have also been reported[140,141].

III. SPECTRAL PROPERTIES AND STRUCTURE

1. Geometrical Parameters and Electronic Structure

Structural investigations have been made only on the simplest α-halogenonitroalkanes. Gas-phase electron diffraction has been used to determine geometrical parameters for chloronitromethane[142,143], trihalogenonitromethanes[144–147], and halogenotrinitromethanes[143,148,149].

In chloronitromethane free rotation is observed about the carbon–nitrogen bond, which has the usual length for organic nitro-compounds. A conformational peculiarity of chloronitromethane is that the chlorine–carbon–nitrogen angle (114°) is considerably larger than the corresponding angle in trichloronitromethane.

The carbon–halogen distances in trifluoro-, trichloro-, and tribromo-nitromethanes are almost the same as in other similar molecules. The bond angles of the trihalogenomethyl group are close to the tetrahedral values. A conformational peculiarity of trihalogenonitromethanes is a considerable increase in the carbon–nitrogen bond length (1.56–1.59 Å) in comparison with ordinary nitroalkanes, and the presence of a barrier to internal rotation about this bond. Trifluoronitromethane vapour contains two rotational isomers—with staggered and eclipsed forms—in the proportions 2 : 1; the CNO_2 group is non-planar, and the angle between each of the nitrogen–oxygen bonds and the plane containing the carbon–nitrogen bond is $\gamma = 9°35'$.[144] Tribromonitromethane vapour contains only the rotational isomer having the staggered form; the CNO_2 group is non-planar, and $\gamma = 8°33'$.

Electron diffraction and microwave spectroscopy give considerably different results for carbon–nitrogen bond lengths and barriers to internal rotation in trihalogenonitromethanes. The latter method indicates free rotation about the carbon–nitrogen bond in trifluoronitromethane and the usual bond length for nitroalkanes[150]. The reasons for the discrepancy have not been elucidated.

Gas-phase electron diffraction shows C_3 conformations for trinitromethane and its chloro- and bromo-derivatives, with the HCNO, etc. dihedral angles respectively 26°, 49°, and 49°.[143] According to X-ray diffraction[151] the carbon atom in iodotrinitromethane is located at the centre of an almost regular tetrahedron, with mean angles of 71° between the planes of the nitro-groups.

Increasing use has recently been made of theoretical conformational analysis to examine the structure of nitro-compounds. Angles of rotation of the nitro-group and barriers to internal rotation about the carbon–nitrogen bond in halogenated mono-, di-, and tri-nitromethanes determined by this method[152–155] agree well with experiment. The electronic structures of several α-halogenonitroalkanes have been investigated by quantum-chemical methods[153–155]. Thus calculation shows a decrease in negative charge on the halogen atom and a shift in electron density to the trinitromethyl group on passing from fluoro- to iodo-trinitromethane. The negative charge on the oxygen atoms and the carbon–nitrogen bond order diminish, while the order of the nitrogen–oxygen bonds increases, on passing from mono- to di-nitro-compounds.

Valuable information on the electronic structure of α-halogenonitroalkanes has been obtained from studies of molecular dipole moments[156–158]. Interaction of the nitro-groups with the halogen atom leads to considerable changes in the electron shell of the molecules and is responsible for differences between calculated and experimental dipole moments. Additive resolution of the dipole moment among bonds in a molecule has yielded the values

$$\mu^{+}_{C-F} = 1.0^{156};\ \mu^{+}_{C-Cl} = 0.23;\ \mu^{+}_{C-Br} = 0.15;\ \mu^{+}_{C-I} = 1.39\ D^{157}$$

for the halogenotrinitromethanes. These dipole moments differ markedly from those of the same bonds in halogenoalkanes, owing to a mesomeric effect. Quantum-chemical calculations on halogenotrinitromethanes are consistent with this view[153].

2. Vibrational Spectra

Results obtained in the numerous investigations on the vibrational spectroscopy of nitro-compounds, including α-halogenonitroalkanes, have been surveyed in reviews[6,159] and in a monograph[11]. The antisymmetric and symmetric stretching frequencies of the nitro-group are important characteristics of the vibrational spectra of α-halogenonitroalkanes. In nitroalkanes they may lie in the respective ranges 1500–1600 and 1300–1370 cm^{-1}.[6] Replacement of hydrogen by halogen atoms in nitroalkanes raises the frequency of antisymmetric and lowers that of symmetric stretching vibrations of the nitro-group, as well as lowering the carbon–nitrogen stretching frequency. A similar pattern is observed with increase in the number of nitro-groups.

The position of the absorption band of antisymmetric nitro-stretching vibrations in the infrared spectra of α-halogenonitroalkanes is determined mainly by the inductive effect of substituents[160–163], and the frequency correlates quite well with the inductive constants of the latter[162,163]:

$$\nu_{as\,(NO_2)} = 1562 + 12\sigma^{*}.$$

Furthermore, the frequency is influenced by steric factors and the conjugation effect.

The position of symmetric nitro-stretching vibrations in a series of nitroalkanes is influenced mainly by the steric factor[159], the shifts caused by different substituents being additive. The shift depends on the bulk of the substituent and is independent of its electron-acceptor or electron-donor properties. The position of these vibrations is almost uninfluenced by inductive and conjugation effects.

The solvent has an insignificant effect on the position of absorption bands corresponding to nitro-stretching vibrations in the infrared spectra and on their integral intensity[159].

The mutual influence of nitro-group and halogen is clearly evident in the vibrational spectra of halogenotrinitromethanes. Their Raman and infrared spectra show a high intensity in bands corresponding to characteristic carbon–halogen vibrations and abnormally low frequencies—366 and 344 cm^{-1} for chloro- and bromo-trinitromethanes respectively[164], compared with the range 600–700 cm^{-1} for ordinary alkyl halides—the fall in frequency being so great that it cannot be attributed solely to the inductive effect of the trinitromethyl group. It is probably due to a mesomeric effect leading to a decrease in negative charge on the halogen and a redistribution of the carbon–nitrogen and nitrogen–oxygen bond orders.

3. Electron Spectra

Two absorption bands are usually observed in the ultraviolet spectra of mono- and poly-nitroalkanes: a strong band at 200–210 nm lies in a region that is marginal for the instruments used in practical spectroscopy, and is usually disregarded; most studies are devoted to a weak band at 270 to 280 nm attributed to an $n-\pi^{*}$ transition[165,166]. The latter has no fine structure, its intensity depends on the number of nitro-groups in the molecule, and its position varies with the solvent, increase in whose polarity shifts the band to shorter wavelengths[165]. The position of this band is influenced also by substituents[6]. The introduction of halogen atoms α to the nitro-group leads to a slight bathochromic displacement and an increase in intensity, which is explained by interaction of the electron shells of nitrogen–oxygen and carbon–halogen bonds[167].

The absorption coefficent increases with the accumulation of nitro-groups in the molecule, but not in proportion to their number[165].

Anions of halogenodinitroalkanes give an intense broad band ($\varepsilon > 10\,000$) with maximum absorption at 365–380 nm.

4. Microwave Spectroscopy

The chemical shift of protons in the nuclear magnetic resonance spectra of α-halogenonitro-compounds is determined mainly by the total inductive effect of the substituents[6,11]. The presence of such electronegative substituents as nitro, fluoro, chloro, bromo greatly diminishes the shielding of α- and β-protons and produces a downfield shift of signals in the n.m.r. spectra of α-halogenonitroalkanes. The variation in the chemical shift of a 1-proton in the spectra of nitroalkanes on the introduction of electronegative substituents other than a fluorine atom parallels the variation in the acid ionisation constants of these compounds[168].

During recent years the structure of α-halogenonitroalkanes has been increasingly investigated by n.m.r. not only with hydrogen but also on nitrogen-14, carbon-13, and oxygen-17 nuclei[169–173]. Chemical shifts of the nitrogen-14

signal in n.m.r. spectra of these compounds depend linearly on the total inductive effect of the substituents[169]:

$$\delta = -25.0 + 13.8\sigma^*.$$

Increase in the electronegativity of a substituent leads to a diamagnetic shift in the signal in the spectra of mono- and poly-nitroalkanes, which indicates displacement of electron density of the nitrogen–oxygen bond from the oxygen to the nitrogen atom.

The replacement of hydrogen atoms in a nitroalkane by halogen produces a diamagnetic shift of the oxygen-17 signal in the n.m.r. spectrum. Accumulation of nitro-groups in a molecule has little influence on this chemical shift. The tendency of the latter to vary in aliphatic nitro-compounds cannot be due to inductive effects as with nitrogen-14. Perhaps it is caused by the interaction of non-bonded atoms, and also by other effects.

The introduction of halogen or a nitro-group at carbon atom 1 causes a paramagnetic shift in the carbon-13 signal, which increases in the sequence Br < CH_3 < Cl < NO_2.

Fluorine-19 n.m.r. spectroscopy has provided information on the electronic structure of the fluorine atom in α-fluoronitroalkanes[174].

Nuclear quadrupole resonance on chlorine-35, bromine-79, and iodine-127 nuclei has been used to investigate the structure of α-halogenonitro-compounds. Chloronitroalkanes have been studied in greater detail[175,176], bromo- and iodo-nitroderivatives in less detail[174,177]. The n.q.r. spectra of α-halogenonitroalkanes exhibit displacement of the halogen signal to higher frequencies than in alkyl halides, which indicates a decrease in electron density on the halogen atom in the former.

A relation has been found between the ^{35}Cl n.q.r. frequencies and the induction constants of the substituents in a series of chloronitroalkanes[175]:

$$\nu^{35}_{Cl} = 34.68 + 1.63\sigma^*.$$

The frequencies $\nu_{^{35}Cl}$ for chlorodinitromethane and chlorofluorodinitromethane depart from the regression line, by 0.86 MHz to higher frequencies and 1.2 MHz to lower frequencies respectively. In the former case the departure is due to hydrogen bonding between chlorodinitromethane molecules; in the latter case it has been interpreted as resulting from conjugation of *p*-electrons of fluorine with the carbon–chlorine bond.

5. Acid–Base Properties

In polar solvents α-halogenonitroalkanes containing an α-hydrogen atom eliminate a proton and form a halogenonitroalkane anion. Deprotonation of the molecule and protonation of the anion occur by a mechanism of general acid–base catalysis[178–180]:

$$\mathrm{R{-}\underset{\mathrm{Hal}}{\underset{|}{C}}HNO_2} + B^- \rightleftarrows \mathrm{R{-}\underset{\mathrm{Hal}}{\underset{|}{C}}{=}NOO^-} + BH\ .$$

At ordinary temperatures they take place at a moderate rate, and kinetic measurements can easily be made. The rate constants correlate well with the pK_b values of the bases[179,181] and satisfactorily with the pK_a values of the α-halogenonitroalkanes[181–183].

The acid–base properties of α-halogenonitroalkanes vary over a wide range depending on the nature of the halogen and the structural parameters of the substituent. The dependence of the acidity on the total inductive effect of the substituents cannot be described by a single correlation equation[184,185]. Ionisation constants for compounds containing substituents having closely similar polar effects may differ substantially. Thus for difluoronitromethane pK_a = 12.4,[168] but the value for bromodinitromethane is 3.47.[185]

The complicated structural dependence of the acidity of α-halogenonitroalkanes is responsible for the diversity of views on this problem. Among factors determining the pK_a of nitroalkanes are inductive, steric, and mesomeric effects, $p-\pi$-electronic repulsion, solvation, and also purely formal features such as the numbers of α- and β-hydrogen atoms[186–190].

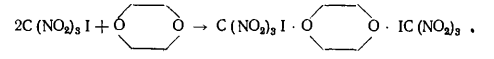
In view of the above considerations the results provided by physicochemical investigation of the structure of α-halogenonitroalkanes cannot be adequately explained in terms of the theory of the inductive effect, and most workers apply the concept of a mesomeric effect. The combination of a nitro-group and a halogen attached to the same carbon atom will obviously lead to electronic interaction between nitrogen–oxygen and carbon–halogen bonds. Such interaction affects primarily and mainly the latter bond, with the appearance of special properties in the halogen, differing substantially from the halogen in alkyl halides and constituting one reason for the peculiar chemical behaviour of α-halogenonitroalkanes.

IV. CHEMICAL PROPERTIES

1. Molecular Complexes

The specific chemical behaviour of α-halogenonitroalkanes is due primarily to the way in which the carbon–halogen bond is polarised. In ordinary alkyl halides—chlorides, bromides, and iodides—the halogen carries a strong negative charge: the dipole moments of the carbon–halogen bonds in chloro-, bromo-, and iodo-methanes lie between −1.55 and −1.17 D.[157] In the formation of complexes they usually act as *n*-donors. In α-halogenonitroalkanes the carbon–halogen bond is polarised differently: the dipole moments of such bonds in chloro-, bromo-, and iodo-trinitromethanes are resepctively −0.23, +0.15, and +1.39 D.[157] In contrast to alkyl halides these compounds act as electron-acceptors in complex formation, exhibiting the properties of pseudohalogens.

Iodo- and bromo-trinitromethanes readily form molecular complexes with various electron-donors (dioxan, *N*-, *S*-, and *P*-oxides, αα′-dioxodiazo-compounds, nitrosamines):[177,191,192]



Nuclear quadrupole resonance spectra indicate complex formation also by chlorotrinitromethane[177]. The chlorine-35, bromine-79, and iodine-127 signal frequencies in the spectra of halogenotrinitromethane complexes increase with the electron-donor power of the ligand and are higher than for these nuclei not combined in such complexes. Analogous signal shifts to higher frequencies are observed in the n.q.r. spectra of the iodine, iodine monochloride, and iodine monobromide complexes[193]. The regularity in the variation of the ^{35}Cl, ^{79}Br, and ^{127}I n.q.r. frequencies indicates an increase in the "positive" character of the halogen in the halogenotrinitromethane complexes.

Molecular complexes may play a definite part in effecting particular reactions of α-halogenonitroalkanes. A quantitative relation can apparently be expected between the frequency changes in the n.q.r. spectra of the complexes and their chemical activity in reactions involving rupture of the

carbon–halogen bond. This relation is readily seen qualitatively in the reaction with iodomethane[177]:

$$IC(NO_2)_3 + S \rightleftarrows S \cdot IC(NO_2)_3 ,$$
$$S \cdot IC(NO_2)_3 + CH_3I \rightleftarrows CH_3C(NO_2)_3 + I_2 + S ,$$

where S represents dimethyl sulphoxide, dioxan, etc. The ease of formation of 1,1,1-trinitroethane increases on passing from halogenotrinitromethanes to their complexes and with increase in the electron-donor power of the ligand[177,194–196].

2. Electrochemical Reduction

Assessment of the reactivity of α-halogenonitroalkanes can be approached by studying their electrochemical reduction. The first wave on a polarogram represents fission of the carbon–halogen bond, but subsequent waves are due to reduction of the nitro-group[197,198]. The half-wave potential $E_{1/2}$ serves as criterion of their chemical activity. These compounds are reduced at more positive potentials than are the corresponding halogenoalkanes, which indicates that the carbon–halogen bond is considerably weaker in the former.

When bromo- and chloro-nitromethanes are reduced, each gives a characteristic two-electron wave ($E_{1/2}$ = −0.05 and −0.45 V) and a wave corresponding to the reduction of nitromethane[199]:

$$CH_2(NO_2)X + 2e \rightarrow CH_2{=}NOO^- + X^- ,$$
$$CH_2{=}NOO^- + H^+ \rightarrow CH_3NO_2 ,$$
$$CH_3NO_2 + 4H^+ + 4e \rightarrow CH_3NHOH + H_2O ,$$

Polarograms obtained for dibromo- and dichloro-nitromethanes contain their own waves ($E_{1/2}$ = +0.03 and −0.12 V), waves due to CH_2NO_2Br (or CH_2NO_2Cl), and a wave due to CH_3NO_2. Trichloro- and tribromo-nitromethanes give their own waves (+0.01 and +0.02 V) and waves corresponding to the reduction of di- and mono-halogenonitromethanes, as well as a nitromethane wave. The reduction of halogenated derivatives of nitroethane[199] and 2-nitropropane[200] have been studied.

The ease of polarographic reduction of α-halogenonitroalkanes increases on passing from chloro- to iodo-derivatives and with increase in the number of nitro-groups. Chlorides are reduced with greater difficulty than are bromides, but this difference diminishes with the accumulation of nitro-groups, which facilitates also rupture of the carbon–nitrogen bond[201]. In α-fluoropolynitroalkanes the first stage of reduction corresponds to fission of this bond, not of the carbon–fluorine bond[202–204]:

$$FC(NO_2)_3 + 2H^+ + 2e \rightarrow CH(NO_2)F + HNO_2 .$$

Bromo- and iodo-trinitromethanes are reduced in the first stage to the trinitromethyl anion ($E_{1/2}$ = +0.036 and +0.42 V),[197] further reduction of which depends on the pH.[198,204] The reduction of chlorotrinitromethane takes place in two ways in the first stage—with rupture of the carbon–chlorine bond ($E_{1/2}$ = +0.248 V) and of a carbon–nitrogen bond[201].

Electron spin resonance indicates intermediate formation of radical-anions and -dianions in the electrochemical reduction of 1-halogenonitroalkanes[205–207].

3. Reactions with Nucleophilic Reagents

(a) Hydrolysis

α-Halogenonitroalkanes are slowly hydrolysed by water: the reaction goes to completion on heating in the presence of alkalis. Kinetic study of the hydrolysis of 1-chloro- and 1-bromo-1-nitroethanes showed that the reaction is preceded by a comparatively slow stage of isomerisation of the nitro- into the *aci*-form, and the latter is attacked by the solvent[180,208]:

$$CH_3CH(NO_2)Cl \xrightarrow{OH^-} CH_3C(Cl){=}NOO^- \xrightarrow[-Cl^-]{H_2O} CH_3C(OH){=}NOOH \rightarrow CH_3CHO + HNO_2 .$$

The action of bases on α-halogenopolynitroalkanes, in contrast to the mononitro-compounds, results in replacement of the halogen by the cation of the base[27,209]:

$$CH_3C(NO_2)_2X + 2KOH \rightarrow CH_3C(NO_2)_2^- K^+ + KOX + H_2O ,$$
$$3C(NO_2)_3X + 6KOH \rightarrow 3C(NO_2)_3^- K^+ + 2KX + KXO_3 + 3H_2O ,$$
$$X{=}Cl, Br, I .$$

Halogenotrinitromethanes are hydrolysed even by water[81,210]:

$$C(NO_2)_3X + H_2O \rightleftarrows HC(NO_2)_3 + HOX ,$$
$$X{=}Cl, Br, I ,$$

The equilibrium constants for the hydrolysis of chloro-, bromo-, and iodo-trinitromethanes are 8×10^{-12}, 3×10^{-11}, and 4×10^{-7} M^{-1} respectively[211].

Fluorotrinitromethane, unlike the other halogenotrinitromethanes, splits off a nitro-group on treatment with a base[44]. The action of alcoholic alkali breaks not only a carbon–nitrogen but also a carbon–fluorine bond[44,212].

(b) Action of reductants

Results obtained for the electrochemical reduction of α-halogenonitroalkanes provide evidence of the extraordinary ease of reduction of the halogen. In addition, the nitro-group is one of the functional groups most sensitive to reduction. Therefore reduction can occur in two directions depending on the nature of the α-halogenitroalkane and the selectivity of the reducing agent.

Chemical reduction of the halogen provides extremely interesting results. The action of reductants of basic character involves replacement of the halogen by the cation of the base with formation of a nitroalkane salt. The halogen that is eliminated behaves as an oxidant. Ease of reduction increases with the "positive" character of the halogen in the α-halogenonitroalkane, which can be explained by facilitation of nucleophilic attack by the reductant anion on the halogen atom.

More detailed research has been undertaken on the reaction with potassium iodide, which is widely used to characterise compounds having a "positively" polarised halogen atom[12]. α-Halogenopolynitroalkanes readily oxidise potassium iodide[24,210,213]:

$$RC(NO_2)_2X + 2KI \rightarrow RC(NO_2)_2^- K^+ + KX + I_2 ,$$
$$R{=}Alk, Hal, NO_2; \quad X{=}Cl, Br, I, NO_2 .$$

This reaction is used for the quantitative determination of halogen in iodo- and bromo-polynitroalkanes, as well as in chlorotrinitromethane[24]; chloro-derivatives of dinitroalkanes and halogenomononitroalkanes are less reactive[214]. The "positive" polarisation of the halogen atom diminishes in the same sequence of α-halogenonitroalkanes[156,157,174].

Various views are held on the mechanism of the reaction of α-halogenonitroalkanes with the iodide ion. From general considerations on the action of bases on α-halogenopolynitroalkanes it has been suggested[10] that the first stage involves formation of the polynitroalkyl anion (nucleophilic substitution at the halogen atom):

$$C(NO_2)_3X + I^- \xrightarrow{slow} C(NO_2)_3^- + XI ,$$
$$XI + I^- \xrightarrow{rapid} I_2 + X^- .$$

This hypothesis is supported by an investigation of the mechanism of the reaction of tetranitromethane with hydrogen peroxide and alkyl peroxide anions[215]:

$$ROO^- + C(NO_2)_4 \rightarrow \left[ROO^- \dashrightarrow O{=}N^+{-}C(NO_2)_3\right] \rightarrow ROOON \rightarrow O + C(NO_2)_3^-,$$

$$ROOON \rightarrow O \xrightarrow{H_2O} ROH + O_2 + HNO_2.$$

An alternative mechanism, based on kinetic data, involves a stage of bimolecular nucleophilic substitution of halogen by the iodide ion followed by reduction of the iodopolynitroalkane by a second molecule of potassium iodide[216–219]:

$$RC(NO_2)_2X + I^- \underset{\text{slow}}{\rightleftharpoons} RC(NO_2)_2I + X^-,$$

$$RC(NO_2)_2I + I^- \xrightarrow{\text{rapid}} RC(NO_2)_2^- + I_2.$$

The reaction is thus regarded as a particular case of nucleophilic substitution of the halogen attached to the carbon atom in the initial compound.

Fluorotrinitromethane undergoes denitration under the influence of the iodide or hydrogen peroxide ion[217,220]:

$$C(NO_2)_3F + 2KI \xrightarrow{H_2O} CH(NO_2)_2F + I_2 + KNO_2 + KOH.$$

Chlorotrinitromethane forms with the hydrogen peroxide ion a mixture of trinitromethane and chlorodinitromethane[10]. Tribromonitromethane reacts peculiarly with potassium iodide or cyanide in the presence of potassium nitrite[129]:

$$2CBr_3NO_2 + 6KI + 2KNO_2 \rightarrow K^+{}^-(O_2N)_2C{-}C(NO_2)_2^-K^+ + 6KBr + 3I_2.$$

The complex hydrides of alkali and alkaline-earth metals are extremely promising for the selective reduction of halogen in α-halogenonitroalkanes, because of the relative stability of nitro-groups to the action of hydride anions. A method was worked out for reducing aliphatic and alicyclic α-bromonitrocompounds with sodium tetrahydroborate in aqueous methanol to the corresponding nitroalkanes (in 15–80% yield).[119,121] This complex hydride was used also to reduce ααωω-tetrabromodinitro-compounds[74]:

$$CBr_2(NO_2)CH_2CH_2C(NO_2)Br_2 \xrightarrow{NaBH_4} CH_2(NO_2)CH_2CH_2CH_2NO_2.$$

Liquid ammonia[221] and hydrazine[222] reduce α-halogenonitroalkanes with evolution of nitrogen:

$$3C(NO_2)_2X_2 + 8NH_3 \rightarrow 3C(NO_2)_2X^-NH_4^+ + 3NH_4X + N_2,$$

$$2C(NO_2)_3X + H_2N{-}NH_2 + 4KOH \rightarrow 2C(NO_2)_3^-K^+ + 2KX + N_2 + 4H_2O.$$

Other reducing agents that are used are sodium thiosulphate, sulphide, and hydrogen sulphide[213], potassium cyanide and hexacyanoferrate(II),[223] and triphenylphosphine[224–226]. Other methods have been reported for the selective reduction of halogen in 1-halogenonitroalkanes, e.g. by the action of arsenic sesquioxide in caustic potash solution or of an aqueous–ammoniacal solution of hydrogen sulphide[227].

Still other methods reduce not only halogen but also the nitro-group. Among them are reduction with hydrogen in the presence of platinum-group metals, zinc, or iron and with tin(II) chloride in an acid medium[227].

(c) Relacement of halogen by the nucleophile

A most important property of α-halogenonitroalkanes is their ability to exchange the halogen atom for a nitro-group in the presence of alkaline potassium or sodium nitrite[11]:

$$RCH(NO_2)X + KNO_2 \xrightarrow{K_2CO_3} RC(NO_2)_2^-K^+ + KX,$$

X=Cl, Br.

This reaction, first described by ter Meer for 1-bromo-1-nitro-derivatives of ethane and propane, is now widely used to prepare *gem*-dinitroalkanes. It has been employed to obtain 1,1-dinitroethane[228–230], 1,1-dinitropropane[228,230], 1,1-dinitropentane[228], dinitromethane[231], and also ααωω-tetranitroalkanes[128].

The ter Meer reaction does not take place by the usual mechanism of nucleophilic substitution of the halogen in the *aci*-form of the α-halogenonitroalkane, as had previously been assumed[233], but is a radical-chain process[232]:

$$CH_3CH(NO_2)Cl \xrightarrow{e} CH_3CH(NO_2)Cl^{\cdot-} \xrightarrow{-Cl^-} CH_3\dot{C}HNO_2 \xrightarrow{NO_2^-} \rightarrow CH_3CH(NO_2)_2^{\cdot-} \xrightarrow{CH_3CH(NO_2)Cl} CH_3CH(NO_2)_2 + CH_3CH(NO_2)Cl^{\cdot-} \rightarrow \text{etc.}$$

Iodotrinitromethane is converted into tetranitromethane by the action of silver nitrite[27].

A typical reaction of 1-halogenonitroalkanes is detachment of the halogen by the anions of nitro-compounds with formation of a new carbon–carbon bond[20–22]. It has been examined in detail on salts of secondary nitroalkanes interacting with their halogeno-derivatives[234–236]:

$$(CH_3)_2C(NO_2)X + (CH_3)_2C{=}NOO^- \xrightarrow{-X^-} (CH_3)_2C(NO_2){-}C(NO_2)(CH_3)_2,$$

X=Cl, Br.

Dinitroalkenes are formed similarly[237,238]:

$$CH_3CH(NO_2)Cl + CH_3CCl{=}NOO^- \xrightarrow{-Cl^-} CH_3CH(NO_2){-}CClCH_3 \xrightarrow{-H^+} \rightarrow CH_3C(NOO^-){-}CClCH_3(NO_2) \xrightarrow{-Cl^-} CH_3C(NO_2){=}CCH_3(NO_2).$$

These reactions can occur either by normal nucleophilic substitution[239,240] or by a radical-anion mechanism[234–236].

Kornblum et al. have shown[241] that the reaction with alkali-metal sulphinates has the latter mechanism:

$$(CH_3)_2C(NO_2)I + PhSO_2^- \rightarrow (CH_3)_2C(NO_2)I^{\cdot-} + PhSO_2^{\cdot},$$

$$(CH_3)_2C(NO_2)I^{\cdot-} \rightarrow (CH_3)_2C\dot{N}O_2 + I^-,$$

$$(CH_3)_2C\dot{N}O_2 + PhSO_2^- \rightarrow [(CH_3)_2C(NO_2)SO_2Ph]^{\cdot-},$$

$$[(CH_3)_2C(NO_2)SO_2Ph]^{\cdot-} + (CH_3)_2C(NO_2)I \rightarrow (CH_3)_2C(NO_2)SO_2Ph + (CH_3)_2C(NO_2)I^{\cdot-}.$$

The action on halogenotrinitromethanes of aryl derivatives of magnesium, mercury, and tin involves a stage of electron transfer from the organometallic compound with formation of a radical-anion of the halogenotrinitromethane[242–244]:

$$PhMgCl + BrC(NO_2)_3 \rightarrow \left[\begin{matrix}BrC(NO_2)_3^{\cdot-}\\ PhMgCl^+\end{matrix}\right] \rightarrow Ph^{\cdot} + {}^1/_2Mg[C(NO_2)_3]_2 + {}^1/_2MgCl_2 + Br^{\cdot}.$$

The appearance of radical-anions in the action of nucleophilic reagents on difluorodinitromethane and fluorotrinitromethane has been confirmed by electron spin resonance[245–247]:

$$CF_2(NO_2)_2 + ArO^- \rightarrow CF_2(NO_2)_2^{\cdot-} + ArO^{\cdot}$$

The radical-anions can break down with fission of either a carbon–nitrogen or a carbon–halogen bond[248]:

$$C(NO_2)_3X^{\cdot-} \rightarrow \begin{cases} C(NO_2)_3^- + X^{\cdot} & (X{=}Cl, Br, NO_2),\\ C(NO_2)_2X^- + NO_2^{\cdot} & (X{=}F, Cl, Br, NO_2).\end{cases}$$

It has recently been established[138,139,249] that fluorotrinitromethane and tetranitromethane, under the influence of alkali-metal halides in anhydrous polar solvents, form products in which a nitro-group has been replaced by a halide ion; under these conditions chlorotrinitromethane forms both nitro-substitution and halogen-substitution products:

$$XC(NO_2)_3 + MY \rightarrow \begin{cases} XC(NO_2)_2Y & (X{=}F, NO_2),\\ XC(NO_2)_2Y + YC(NO_2)_3 & (X{=}Cl),\\ YC(NO_2)_3 & (X{=}Br),\end{cases}$$

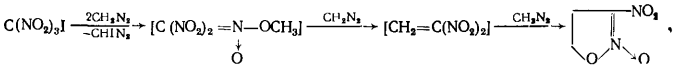
M=K, Li, Rb, Cs; Y=F, Cl, Br.

It is supposed that bimolecular nucleophilic substitution at the carbon atom is involved[216]. In electron-donor polar solvents intermolecular halogen exchange occurs in halogenated derivatives of di- and tri-nitromethanes[250]:

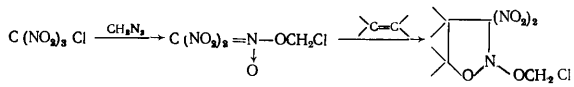
$$C(NO_2)_3Cl + C(NO_2)_2Br_2 \rightleftarrows C(NO_2)_3Br + BrC(NO_2)_2Cl\ ,$$
$$2BrC(NO_2)_2Cl \rightleftarrows C(NO_2)_2Br_2 + C(NO_2)_2Cl_2\ .$$

(d) Reaction with diazoalkanes

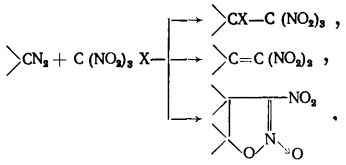
The action of diazomethane on chloro-, bromo-, and iodotrinitromethanes is accompanied by detachment of a nitro-group and of halogen, and yields 3-nitroisoxazoline *N*-oxide[251,252] with intermediate formation of *O*-alkyl esters of trinitromethane followed by 1,1-dinitroethylene[252]:



In the case of chlorotrinitromethane the *O*-chloromethyl ester of trinitromethane is formed as intermediate[252]:



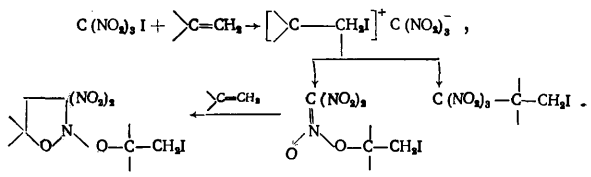
When halogenotrinitromethanes are treated with diazomethane derivatives—9-diazofluorene, diazoanthrone, diazoacetic ester—derivatives of 1-halogeno-2,2,2-trinitroethane, *gem*-dinitroalkenes, and 3-nitroisoxazoline *N*-oxide can be isolated depending on the nature of the reagents and the conditions[251]



(e) Reaction with alkenes

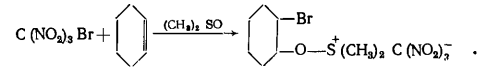
Electrophilic addition at the double bond occurs with iodo- and bromo-trinitromethanes, which is explained by the considerable "positive" character of the halogen. Chlorotrinitromethane does not undergo this reaction.

Iodotrinitromethane reacts exceptionally with alkenes[253–255], forming with ethylene *N*-2′-iodoethoxy-3,3-dinitroisoxazoline and 1-iodo-3,3,3-trinitropropane. Electrophilic attack at the double bond gives the corresponding carbocation and the ambident trinitromethyl anion, which is able to react with either the carbon or the oxygen centre depending on the cation and the solvent[253]:



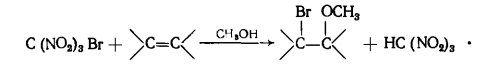
Only *O*-alkylated products are formed with cyclohexene[254] and with trimethylsilylethylene[255].

The reaction between bromonitroform and alkenes has been studied in detail[256–259]. Hardly any reaction occurs in non-polar or weakly polar solvents (benzene, chloroform), but in dimethyl sulphoxide it takes place even at room temperature. However, the products are not nitronic esters of trinitromethane, as had been supposed earlier[256,257], but sulphonium derivatives[258]:



Addition of bromonitroform is slowed down by the presence of electron-accepting substituents at the double bond: cinnamic acid, acrylic esters, and 2,3-dibromopropene do not form adducts even after an hour[256]. Addition of bromotrinitromethane to methyl vinyl ketone and to isopropyl vinyl ether gives *C*-alkylated products[260,261].

In alcoholic solution the reaction of bromotrinitromethane involves intermediate formation of an alkyl hypobromite, which with the alkene gives the final product[262]:



Aromatic hydrocarbons are brominated in the ring by bromotrinitromethane[259].

4. Nucleophilic Addition at Multiple Bonds

(a) Michaelis reaction

Primary α-halogenonitroalkanes are added at an activated double bond[263–266]. The activating influence of substituents diminishes in the sequence[267]

$$CHO > COR > CN > COOR > NO_2.$$

The reactivity of these compounds is determined by their acidity, with fluoro- and chloro-dinitromethanes reacting especially readily[53,263,265,266]:

$$CH(NO_2)_2X + CH_2{=}CHR \rightarrow XC(NO_2)_2CH_2CH_2R\ ,$$
R=CHO, COR′, $COOCH_3$, CN, NO_2; X=F, Cl, Br .

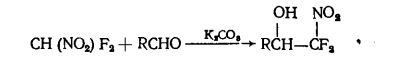
(b) Condensation with aldehydes and ketones (Henry's reaction)

1-Halogenonitroalkanes resemble other compounds containing a mobile hydrogen atom in undergoing condensation with aldehydes:

$$RCH(NO_2)X + R'CHO \rightarrow RC(NO_2)(X)CHR'(OH)\ ,$$
R=H, Alk; R′=H, CH_3; X=F, Cl, Br .

The reaction goes especially smoothly between the lower homologues[268–271]. It is assumed that an aldol-type condensation is involved. The rate depends on the nature of the reactants, the catalyst, the ionising power of the solvent, and other factors.

Alcohols and glycols can be obtained from monohalogenonitromethanes depending on the proportions of the reactants[271,272]. Difluoronitromethane condenses with aldehydes when heated (100–120 °C) in the presence of potassium carbonate[103,268]:



The condensation of α-halogenonitroalkanes with aldehydes may be accompanied by dehydration with formation of alkenes[273].

The action of formaldehyde on halogenodinitromethanes yields the corresponding halogenodinitroethanols[44,53,68], which readily break down to give the original α-halogenonitroalkane[185]:

$$XC(NO_2)_2CH_2OH + H_2O \rightleftarrows XCH(NO_2)_2 + CH_2(OH)_2 ,$$
$$X=F, Cl, Br .$$

Fluorodinitromethane condenses with acetaldehyde[270] and with glycollaldehyde[68] in the absence of a catalyst at room temperature. With dialdehydes fluorodinitromethane forms the corresponding tetranitro-diols[270]. With glyoxal at 45 °C it forms also β-fluoro-α-hydroxy-ββ-dinitropropionic acid[68]:

$$\begin{matrix}CHO\\|\\CHO\end{matrix} + FCH(NO_2)_2 \rightarrow FC(NO_2)_2-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-C(NO_2)_2F + FC(NO_2)_2\underset{\underset{OH}{|}}{CHCOOH} .$$

The reaction with pyruvaldehyde involves only the formyl group[68].

Less detailed study has been made of the condensation of α-halogenonitroalkanes with ketones[263,266,274,275]. With the lower ketones in the presence of potassium carbonate difluoronitromethane gives nitroalkanols[268,274]:

$$R-\underset{\underset{O}{\|}}{C}-R + F_2CHNO_2 \rightarrow RR\underset{\underset{OH}{|}}{C}C(NO_2)F_2 .$$

With unsaturated aldehydes and ketones the reaction involves primarily the carbon–carbon double bond, and only then is the carbonyl group affected[263,266].

An unusual method of obtaining *gem*-dinitro-alcohols is to boil 1-bromo-1,1-dinitro-compounds with aqueous formaldehyde[209,276]; the process is analogous to Henry's reaction:

$$RC(NO_2)_2Br + CH_2O \xrightarrow{H_2O} RC(NO_2)_2CH_2OH ,$$
$$R=CH_3, CH_2CH_2COOH .$$

Under these conditions dibromidinitromethane is converted into 2,2-dinitropropane-1,3-diol[277]. ββ-Dinitro- and βββ-trinitro-alcohols are formed by the action of formalin on halogenotrinitromethanes, when the course of the reaction varies[277–279]:

$$C(NO_2)_3X + CH_2O + H_2O \begin{cases} \rightarrow C(NO_2)_3CH_2OH & (X=Br, I) ,\\ \rightarrow XC(NO_2)_2CH_2OH & (X=Cl) ,\\ \rightarrow XC(NO_2)_2CH_2OH + (HOCH_2)_2C(NO_2)_2 & (X=F, NO_2) . \end{cases}$$

5. Radical Reactions

(*a*) Thermolysis

The gas-phase thermolysis of α-halogenopolynitroalkanes involves as first stage rupture of a carbon–nitrogen bond[280–284]:

$$RC(NO_2)_2X \rightarrow R\dot{C}(NO_2)X + NO_2^{\cdot} ,$$
$$R=CH_3, C_2H_5, NO_2, F, C(NO_2)_2F, C(NO_2)_3;$$
$$X=F, Cl, Br, I.$$

In all cases the reaction is predominantly homogeneous and unimolecular. Only 1-chloro-1,1-dinitroethane shows a surface effect, which is due to loss of resulting chlorine atoms on the walls of the reaction vessel[281]. Loss of the halogenonitroalkyl radical in systems containing nitric oxide and nitrogen dioxide occurs broadly similarly in all the α-halogenonitroalkanes investigated, and can be represented by the scheme

$$CH_3\dot{C}(NO_2)X \begin{cases} \xrightarrow{NO_2} CH_3-\underset{\underset{NO_2}{|}}{\overset{X}{\overset{|}{C}}}-ONO \rightarrow CH_3C\overset{O}{\underset{X}{<}} + NO + NO_2 ,\\ \xrightarrow{NO} CH_3-\underset{\underset{NO_2}{|}}{\overset{X}{\overset{|}{C}}}-NO \rightarrow CH_3\dot{C}(NO)X + NO_2 \rightarrow CH_3CN + XO^{\cdot} . \end{cases}$$

The rate of the gas-phase thermal decomposition of trichloronitromethane depends on the initial pressure and on additions of inhibitors (toluene, formaldehyde)[285].

The dependence of the carbon–nitrogen bond dissociation energy on α-substituents has been established. Chlorine, bromine, and iodine atoms lower this energy in α-halogenonitroalkanes, but a fluorine atom has an insignificant effect comparable with that of hydrogen. The rate of decomposition increases in the sequence of substituents from nitro through chloro and bromo to iodo[281–284]. This dissociation energy is closely similar in magnitude to the activation energy of thermolysis, which is evidence of a radical mechanism of decomposition with initial rupture of a carbon–nitrogen bond in α-halogenonitroalkanes.

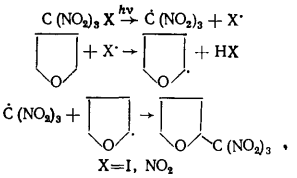
Products of the thermal breakdown of the potassium salts of chloro- and bromo-dinitromethanes in aprotic solvents have been studied[286,287]. The reaction probably involves intermediate formation of dinitro- and halogenonitro-carbenes[287].

(*b*) Other reactions

The possibility of homolytic fission of a carbon–halogen bond in an α-halogenonitroalkane was first shown in the oxidation of tetralin catalysed by bromo- and chloro-trinitromethanes[288], and was later demonstrated in the polymerisation of methyl acrylate in the presence of an α-halogenonitroalkane[289].

It has recently been found that iodotrinitromethane and tetranitromethane react with cyclic ethers (oxolan, oxan) by a non-chain radical mechanism with intermediate formation of the trinitromethyl radical[290–294]:

$$C(NO_2)_3X \xrightarrow{h\nu} \dot{C}(NO_2)_3 + X^{\cdot}$$



$$X=I, NO_2$$

However, the photolysis of tetranitromethane and of fluoro- and chloro-trinitromethanes in dimethylformamide and in hydroxylated solvents involves decomposition of the polynitroalkanes to give only anions of the latter[295].

Radical addition of tribromonitromethane at a double bond has been reported[296].

V. PHYSIOLOGICAL ACTIVITY AND PRACTICAL USE

Halogenonitro-compounds are of interest as a consequence of their great physiological activity. Accumulation of nitro-groups at the same carbon atom in α-halogenonitroalkanes leads to an increase in acute toxicity, and a similar effect is observed with increase in the number of halogen atoms. Dihalogenodinitromethanes are the most toxic. Bromonitroalkanes are usually more toxic than their chlorinated analogues[297]. The majority of α-halogenonitroalkanes (but not 1,1-dichloro-1-nitroethane) have a lachrymatory action, which diminishes with increase in molecular weight[298,299].

The antibacterial activity of α-halogenonitroalkanes has been studied[297,300]. Derivatives of nitroethane are more active than those of nitromethane towards *Escherichia coli* and *Staphylococcus aureus pyogenes*[297]. The accumulation of bromine atoms in nitroalkanes leads to an increase in antibacterial activity. The bactericidal activity of α-halogenonitroalkanes is usually attributed to their oxidising power[300].

α-Halogenonitroalkanes exhibit a broad spectrum of activity and possess insecticidal[298–301], fungicidal[302–306], herbicidal[307], bactericidal[308], and nematocidal[302,308,309] properties. Trichloronitromethane and 1,1-dichloro-1-nitroethane are used as insecticides and fungicides either alone or mixed with other compounds[305,310]. "Mixed" α-halogenonitroalkanes, which possess greater activity, have been proposed as fumigants. Thus it is recommended that bromodifluoronitromethane should be used in amounts of 0.15–0.30 g m^{-3} to combat granary pests, and at doses below 448 kg per hectare to treat soil against nematodes[302]. Bromochloronitroalkanes containing 1–5 carbon atoms possess insecticidal and fungicidal activity[302,303].

α-Halogenonitroalkanes can be used also an antibacterial additives in diesel fuels, lubricating oils, and hydraulic fluids[311,312]. They have been recommended for combination with tetraethyl-lead in antiknock compositions, for the thinning and dispersion of oils[313], and for the deparaffination of diesel fuels and oils[314].

1-Chloro-1-nitroethane is an excellent agent for preventing the gelling of rubber additives[315].

α-Halogenonitroalkanes are used also as intermediates in the production of biologically active compounds[316], explosives, and rocket fuel components[137,224].

REFERENCES

1. G.A.Shvekhgeimer, V.A.Smirnyagin, R.A.Sadykov, and S.S.Novikov, Uspekhi Khim., 37, 816 (1968) [Russ.Chem.Rev., No.5 (1968)].
2. S.L.Ioffe, L.M.Leont'eva, and V.A.Tartakovskii, Uspekhi Khim., **46**, 1658 (1977) [Russ.Chem.Rev., No.9 (1977)].
3. G.A.Shvekhgeimer, N.F.Pyatakov, and S.S.Novikov, Uspekhi Khim., **28**, 485 (1959).
4. G.M.Nazin, G.B.Manelis, and F.I.Dubovitskii, Uspekhi Khim., **37**, 1443 (1968) [Russ.Chem.Rev., No.8 (1968)].
5. R.Noble, F.Borgardt, and W.Reed, Chem.Rev., **64**, 19 (1964).
6. C.N.R.Rao, in "Chemistry of the Nitro- and Nitroso-groups" (Edited by H.Feuer) (Translated into Russian), Mir, Moscow, 1972, Part 1, p.60.
7. G.O.Larson, in "Chemistry of the Nitro- and Nitroso-groups" (Edited by H.Feuer) (Translated into Russian), Mir, Moscow, 1972, Part 1, p.224.
8. A.T.Nielson, in "Chemistry of the Nitro- and Nitroso-groups" (Edited by H.Feuer) (Translated into Russian), Mir, Moscow, 1972, Part 1, p.260.
9. H.H.Baer and L.Urbas, in "Chemistry of the Nitro- and Nitroso-groups" (Edited by H.Feuer) (Translated into Russian), Mir, Moscow, 1973, Part 2, p.63.
10. L.A.Kaplan, in "Chemistry of the Nitro- and Nitroso-groups (Edited by H.Feuer) (Translated into Russian), Mir, Moscow, 1973, Part 2, p.221.
11. S.S.Novikov, G.A.Shvekhgeimer, V.V.Sevost'yanova, and V.A.Shlyapochnikov, "Khimiya Alifaticheskikh i Alitsiklicheskikh Nitrosoedinenii" (Chemistry of Aliphatic and Alicyclic Nitro-compounds), Khimiya, Moscow, 1974.
12. S.S.Novikov, V.V.Sevost'yanova, and A.A.Fainzil'berg, Uspekhi Khim., **31**, 1417 (1962) [Russ.Chem.Rev., No.12 (1962)].
13. K.Namba, J.Ind.Expl.Soc.Japan, **25**, 206 (1967).
14. C.A.Buehler and D.E.Pearson, "Survey of Organic Syntheses" (Translated into Russian), Mir, Moscow, 1973, p.436.
15. S.Trippett and D.Walker, J.Chem.Soc., 2976 (1960).
16. R.Junell, Z.phys.Chem., **141**, 71 (1929).
17. R.Junell, Arkiv Mineral.Geol., **11**, B1 (1934).
18. US P.3 159 868 (1964).
19. M.Hawthorne and R.Strahm, J.Amer.Chem.Soc., **79**, 3471 (1957).
20. C.Dale and R.Shriner, J.Amer.Chem.Soc., **58**, 1502 (1936).
21. G.Brown and R.Shriner, J.Org.Chem., **2**, 376 (1937).
22. L.Seigle and H.Hass, J.Org.Chem., **5**, 100 (1940).
23. D.Levering, J.Org.Chem., **27**, 2930 (1962).
24. S.S.Novikov, A.A.Fainzil'berg, V.V.Gulevskaya, and V.V.Sevost'yanova, Izv.Akad.Nauk SSSR, Otd.Khim. Nauk, 672 (1961).
25. L.V.Okhlobystina, V.M.Khutoretskii, and A.A.Fainzil'berg, Izv.Akad.Nauk SSSR, Ser.Khim., 1487 (1971).
26. A.V.Fokin, L.T.Eremenko, V.S.Galakhov, A.V.Davydov, and F.Ya.Natsibullin, Izv.Akad.Nauk SSSR, Ser. Khim., 656 (1968).
27. A.Hantzsch, Ber., **39**, 2478 (1906).
28. R.Scholl and A.Schmidt, Ber., **35**, 4288 (1902).
29. V.I.Erashko, S.A.Shevelev, and A.A.Fainzil'berg, Izv.Akad.Nauk SSSR, Ser.Khim., 2060 (1965).
30. R.Gotts and L.Hunter, J.Chem.Soc., **125**, 442 (1924).
31. V.I.Slovetskii, A.I.Ivanov, A.A.Fainzil'berg, S.A.Shevelev, and S.S.Novikov, Zhur.Org.Khim., **2**, 937 (1966).
32. M.Hawthorne, J.Amer.Chem.Soc., **79**, 2510 (1957).
33. C.Kimura, K.Kashigata, and T.Asahara, J.Chem.Soc. Japan, Ind.Chem.Sect., **63**, 585 (1960).
34. A.L.Fridman, T.N.Ivshina, V.P.Ivshin, and S.S.Novikov, Izv.Akad.Nauk SSSR, Ser.Khim., 2617 (1969).
35. A.V.Fokin, Yu.N.Studnev, A.I.Rankin, D.D.Kuznetsov, and V.A.Komarov, Izv.Akad.Nauk SSSR, Ser. Khim., 489 (1976).
36. V.Grakauskas and K.Baum, J.Org.Chem., **33**, 3080 (1968).
37. K.Baum, J.Org.Chem., **35**, 846 (1970).
38. L.T.Eremenko and F.Ya.Natsibullin, Izv.Akad.Nauk SSSR, Ser.Khim., 676 (1968).
39. L.T.Eremenko, F.Ya.Natsibullin, G.V.Oreshko, and G.N.Nesterenko, Izv.Akad.Nauk SSSR, Ser.Khim., 2556 (1970).
40. L.T.Eremenko, F.Ya.Natsibullin, I.P.Borovinskaya, and N.D.Karpova, Izv.Akad.Nauk SSSR, Ser.Khim., 431 (1968).
41. L.T.Eremenko, F.Ya.Natsibullin, and I.P.Borovinskaya, Izv.Akad.Nauk SSSR, Ser.Khim., 429 (1968).
42. F.Ya.Natsibullin, G.B.Oreshko, and L.T.Eremenko, Izv.Akad.Nauk SSSR, Ser.Khim., 2344 (1971).
43. H.Shechter and E.Roberson, J.Org.Chem., **25**, 175 (1960).
44. M.Kamlet and H.Adolph, J.Org.Chem., **33**, 3073 (1968).
45. L.V.Okhlobystina, V.M.Khutoretskii, and A.A.Fainzil'berg, Izv.Akad.Nauk SSSR, Ser.Khim., 476 (1969).
46. V.M.Khutoretskii, L.V.Okhlobystina, and A.A.Fainzil'berg, Izv.Akad.Nauk SSSR, Ser.Khim., 387 (1970).
47. L.V.Okhlobystina, V.M.Khutoretskii, and A.A.Fainzil'berg, Izv.Akad.Nauk SSSR, Ser.Khim., 1487 (1971).
48. R.Banks and G.Williamson, Chem.and Ind., 1864 (1964).
49. L.V.Okhlobystina, G.Ya.Legin, and A.A.Fainzil'berg, Izv.Akad.Nauk SSSR, Ser.Khim., 708 (1969).
50. J.Meisenheimer and M.Swarz, Ber., **39**, 2543 (1906).
51. A.L.Fridman, F.A.Gabitov, G.S.Ismagilova, V.A.Zakharov, and S.S.Novikov, "VI Vsesoyuznoe Soveshchanie po Khimii Nitrosoedinenii" (Sixth All-Union Conference on the Chemistry of Nitro-compounds—Abstracts), Moscow, 1977, p.102.

52. H.Feuer and R.Harmetz, J.Org.Chem., **26**, 1061 (1961).
53. L.T.Eremenko and F.Ya.Natsibullin, Izv.Akad.Nauk SSSR, Ser.Khim., 1331 (1969).
54. M.Kamlet and J.Dacons, J.Org.Chem., **26**, 3005 (1961).
55. H.Feuer and F.Vincent, J.Org.Chem., **29**, 939 (1964).
56. S.Trilalat and M.Grall, Compt.rend., **269C**, 83 (1969).
57. H.Feuer and C.Savides, J.Amer.Chem.Soc., **81**, 5830 (1959).
58. C.Parker, M.Emmons, H.Rolewicz, and K.McCallum, Tetrahedron, **17**, 79 (1962).
59. W.E.Truce and L.W.Christensen, Tetrahedron, **25**, 181 (1969).
60. A.V.Sultanov, V.I.Erashko, S.A.Shevelev, and A.A.Fainzil'berg, Izv.Akad.Nauk SSSR, Ser.Khim., 2750 (1975).
61. V.I.Markovskii, G.A.Marchenko, S.S.Novikov, and V.I.Slovetskii, Izv.Akad.Nauk SSSR, Ser.Khim., 2838 (1975).
62. E.Witucki, G.Rowley, M.Warther, and M.Frankel, J.Org.Chem., **37**, 152 (1972).
63. A.D.Nikolaeva, L.B.Zamirova, and N.M.Lyapin, Zhur. Org.Khim., **10**, 2304 (1974).
64. L.M.Kozlov and V.I.Burmistrov, "Nitrospirty i ikh Proizvodnye" (Nitroalcohols and their Derivatives), Kazan, 1960, p.181.
65. L.T.Eremenko and G.V.Oreshko, Izv.Akad.Nauk SSSR, Ser.Khim., 380 (1960).
66. F.Borgardt, A.Seeler, and P.Noble, J.Org.Chem., **31**, 2806 (1966).
67. H.Adolph and M.Kamlet, J.Org.Chem., **34**, 45 (1969).
68. L.T.Eremenko and G.V.Oreshko, Izv.Akad.Nauk SSSR, Ser.Khim., 1765 (1969).
69. L.T.Eremenko, G.V.Oreshko, and L.I.Berezina, Izv. Akad.Nauk SSSR, Ser.Khim., 2268 (1970).
70. V.Grakauskas, J.Org.Chem., **38**, 2999 (1973).
71. V.I.Erashko, A.V.Sultanov, S.A.Shevelev, and A.A.Fainzil'berg, Izv.Akad.Nauk SSSR, Ser.Khim., 350 (1973).
72. B.P.1 094 250 (1967); Chem.Abs., **68**, 105 227 (1968).
73. US P.3 479 413 (1969); Chem.Abs., **72**, 12 093 (1970).
74. K.Klager, J.Org.Chem., **20**, 646 (1955).
75. E.Yu.Gudrinietse, O.Ya.Neiland, and G.Ya.Vanag, Zhur.Obshch.Khim., **24**, 1863 (1954).
76. O.Ya.Neiland, E.Yu.Gudrinietse, and G.Ya.Vanag, Zhur.Obshch.Khim., **26**, 3139 (1956).
77. R.Junell, Z.phys.Chem., **A141**, 71 (1929).
78. H.Feuer and A.Nielsen, J.Amer.Chem.Soc., **84**, 688 (1962).
79. R.Cundall and A.Locke, J.Chem.Soc.B, 98 (1968).
80. L.M.Schischkow, Annalen, **119**, 247 (1861).
81. A.Macbeth and D.Pratt, J.Chem.Soc., **119**, 354 (1921).
82. V.V.Perekalin and A.S.Sopova, "Nepredel'nye Nitrosoedineniya" (Unsaturated Nitro-compounds), Khimiya, Moscow and Leningrad, 1966.
83. H.Hass, A.Susie, and R.Heider, J.Org.Chem., **15**, 8 (1950).
84. A.I.Vil'dovskaya, K.B.Rall', and A.A.Petrov, Zhur. Org.Khim., **3**, 434 (1967).
85. E.S.Lipina and V.V.Perekalin, Zhur.Obshch.Khim., **34**, 3644 (1964).
86. K.Rosenmund and W.Kuhnhem, Ber., **56**, 1262 (1923).
87. L.Clapp, J.Brown, and L.Zefteb, J.Org.Chem., **15**, 1043 (1950).
88. E.S.Lipina, Z.F.Pavlova, and V.V.Perekalin, Zhur. Org.Khim., **5**, 1312 (1969).
89. F.Carroll, S.Kerbow, and M.Wall, Canad.J.Chem., **44**, 2115 (1966).
90. J.Durden, D.Heywood, A.Sousa, and H.Spurr, J.Agric.Food Chem., **18**, 50 (1970).
91. E.S.Lipina, V.V.Perekalin, and Ya.S.Bobovich, Dokl.Akad.Nauk SSSR, **163**, 894 (1965).
92. S.V.Vasil'ev and O.T.Burdelev, Zhur.Org.Khim., **2**, 1542 (1966).
93. S.V.Vasil'ev and O.T.Burdelev, Zhur.Org.Khim., **2**, 1961–1965 (1966).
94. I.V.Martynov, Yu.L.Kruglyak, and G.A.Leibovskaya, Zhur.Vses.Khim.Obshch.Mendeleeva, **10**, 591 (1965).
95. D.Barr and R.Haszeldine, J.Chem.Soc., 1151 (1960).
96. J.Park, A.Stefani, and J.Lacher, J.Org.Chem., **26**, 4017 (1961).
97. D.Cook, O.Pierce, and E.McBee, J.Amer.Chem.Soc., **76**, 83 (1954).
98. S.Andreades, J.Org.Chem., **27**, 4163 (1962).
99. US P.2 447 504 (1948); Chem.Abs., **43**, 3024 (1949).
100. E.Bissell, J.Org.Chem., **26**, 5100 (1961).
101. I.L.Knunyants and A.V.Fokin, Dokl.Akad.Nauk SSSR, 111, 1035 (1956).
102. I.L.Knunyants, V.L.Dyatkin, A.V.Fokin, and V.A.Komarov, Izv.Akad.Nauk SSSR, Ser.Khim., 1425 (1964).
103. I.L.Knunyants, A.V.Fokin, and V.A.Komarov, Izv. Akad.Nauk SSSR, Ser.Khim., 466 (1966).
104. J.Park, A.Stefani, G.Crawford, and J.Lacher, J.Org. Chem., **26**, 3316 (1961).
105. M.Hauptschein and R.E.Oesterling, J.Org.Chem., **28**, 1279 (1963).
106. Yu.V.Baskakov and V.V.Perekalin, Dokl.Akad.Nauk SSSR, **136**, 1075 (1961).
107. I.L.Knunyants, A.V.Fokin, Yu.M.Kosyrev, I.N.Sorokin, and K.V.Frosina, Izv.Akad.Nauk SSSR, Ser. Khim., 1772 (1963).
108. A.Ya.Yakubovich, V.A.Shpanskii, and A.L.Lemke, Dokl.Akad.Nauk SSSR, **96**, 773 (1954).
109. A.Ya.Yakubovich, V.A.Shpanskii, and A.L.Lemke, Zhur.Obshch.Khim., **24**, 2257 (1954).
110. A.I.Titov, Dokl.Akad.Nauk SSSR, **149**, 330 (1963).
111. I.V.Martynov, N.F.Privezentseva, Yu.L.Kruglyak, Z.I.Khromova, G.A.Leibovskaya, and I.L.Knunyants, Zhur.Vses.Khim.Obshch.Mendeleeva, **11**, 479 (1966).
112. L.German and I.Knunyantz, Angew.Chem., **81**, 321 (1969).
113. US P.3 054 828 (1960).
114. R.Burrows and L.Hunter, J.Chem.Soc., 1357 (1932).
115. French P.1 315 009 (1962).
116. W.Boyd, J.Soc.Chem.Ind., **44**, 2227 (1925).
117. E.M.Cherkasova and N.N.Mel'nikov, Zhur.Obshch. Khim., **19**, 321 (1949).
118. H.Rheinboit and M.Dewald, Annalen, **455**, 300 (1927).
119. D.Iffland and G.Criner, J.Amer.Chem.Soc., **75**, 4047 (1953).
120. D.Iffland, G.Criner, M.Koral, F.Lotspeich, Z.Papanastassion, and S.White, J.Amer.Chem.Soc., **75**, 4044 (1953).
121. D.Iffland and T.-F.Ven, J.Amer.Chem.Soc., **76**, 4083 (1954).
122. S.Franke, "Analysis of Chemical Warfare Agents" (Translated into Russian), Khimiya, Moscow, 1973, Part 1.
123. C.Hurd and M.Nilson, J.Org.Chem., **20**, 927 (1955).
124. A.V.Fokin, A.T.Uzun, and V.A.Khekhnev, Zhur. Obshch.Khim., **38**, 669 (1968).
125. A.V.Fokin and A.T.Uzun, Zhur.Obshch.Khim., **39**, 1340 (1969).
126. E.Bagley, J.Birchall, and R.Haszeldine, J.Chem. Soc.C, 1232 (1966).
127. I.V.Martynov and Yu.L.Kruglyak, Zhur.Obshch.Khim., **35**, 248 (1965).

128. H.Feuer, C.Colwell, G.Leston, and A.Nielsen, J.Org. Chem., **27**, 3598 (1962).
129. W.Will, Ber., **47**, 961 (1914).
130. C.Coon and R.Simon, Synthesis, 605 (1953).
131. S.A.Shevelev, V.V.Semenov, and A.A.Fainzil'berg, Izv.Akad.Nauk SSSR, Ser.Khim., 2621 (1975).
132. R.Haszeldine and J.Jander, J.Chem.Soc., 4172 (1953).
133. R.Scribner, J.Org.Chem., **29**, 284 (1964).
134. B.S.Fedorov, R.G.Gafurov, and L.T.Eremenko, Izv. Akad.Nauk SSSR, Ser.Khim., 915 (1974).
135. A.L.Fridman, V.D.Surkov, and F.M.Mukhametshin, Zhur.Org.Khim., **7**, 2003 (1971).
136. A.L.Fridman, V.P.Ivshin, and S.S.Novikov, Zhur. Org.Khim., **5**, 1317 (1969).
137. US P.3 127 736 (1964); Chem.Abs., **61**, 5445 (1964).
138. G.Kh.Khisamutdinov, V.I.Slovetskii, M.Sh.L'vova, O.G.Ustynyuk, M.A.Besprozvannyi, and A.A.Fainzil'berg, Izv.Akad.Nauk SSSR, Ser.Khim., 2553 (1970).
139. G.Kh.Khisamutdinov, V.I.Slovetskii, A.A.Fainzil'berg, and M.Sh.L'vova, Izv.Akad.Nauk SSSR, Ser. Khim., 1073 (1971).
140. V.A.Petrosyan, V.M.Khutoretskii, L.V.Okhlobystina, V.I.Slovetskii, and A.A.Fainzil'berg, Izv.Akad.Nauk SSSR, Ser.Khim., 1544 (1973).
141. A.V.Bukhtiarov, I.N.Rozhkov, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 2190 (1970).
142. N.I.Sadova, L.V.Vilkov, and T.M.Anfimova, Zhur. Strukt.Khim., **13**, 763 (1972).
143. L.V.Vilkov, N.I.Sadova, N.I.Popik, Yu.A.Pankrushev, V.A.Shlyapochnikov, E.G.Slepnev, and N.A.Tarasenko, "II Vsesoyuznyi Simpozium po Molekulyarnomu Vzaimodeistviyu i Konformatsiyam Molekul. Tezisy" (Second All-Union Symposium on Molecular Interaction and the Conformations of Molecules—Abstracts), Volgograd, 1974, p.39.
144. J.L.Karle and J.J.Karle, J.Chem.Phys., **36**, 1969 (1962).
145. W.Barrs, J.Chem.Phys., **27**, 1260 (1957).
146. R.Knudsen, C.George, and J.Karle, J.Chem.Phys., **44**, 2334 (1966).
147. A.Castelli, A.Palm, and C.Alexander, J.Chem.Phys., **44**, 1577 (1966).
148. N.Sadova, N.Popik, L.Vilkov, Ju.Pankrushev, and V.Shlyapochnikov, Chem.Comm., 708 (1973).
149. I.L.Vilkov, N.I.Sadova, N.I.Popik, G.E.Slepnev, Yu.A.Pankrushev, and V.A.Shlyapochnikov, "V Vsesoyuznoe Soveshchanie po Khimii Nitrosoedinenii" (Fifth All-Union Conference on the Chemistry of Nitro-compounds—Abstracts), Moscow, 1974, p.15.
150. W.Tolles, E.Handelman, and D.G.Gwinn, J.Chem.Phys., **43**, 3019 (1965).
151. N.I.Golovina and L.O.Atovmyan, Zhur.Strukt.Khim., **7**, 235 (1966).
152. M.Dakhis, A.Levin, and V.Shlyapochnikov, J.Mol. Structure, **14**, 321 (1972).
153. M.I.Dakhis, A.A.Levin, and V.A.Shlyapochnikov, Zhur.Strukt.Khim., **14**, 162 (1973).
154. M.I.Dakhis, A.A.Levin, and V.A.Shlyapochnikov, "IV Vsesoyuznoe Soveshchanie po Khimii Nitrosoedinenii" (Fourth All-Union Conference on the Chemistry of Nitro-compounds—Abstracts), Moscow, 1971, p.48.
155. A.A.Levin, M.I.Dakhis, V.A.Shlyapochnikov, and S.S.Novikov, "Materialy III Vsesoyuznoi Konferentsii po Issledovaniyu Stroeniya Organicheskikh Soedinenii Fizicheskimi Metodami" (Proceedings of the Third All-Union Conference on the Investigation of Physical Methods of the Structure of Organic Compounds), Kazan, 1971, p.133.
156. V.G.Osipov, V.M.Khutoretskii, L.V.Okhlobystina, and V.A.Shlyapochnikov, Izv.Akad.Nauk SSSR, Ser.Khim., 688 (1976).
157. A.N.Shidlovskaya, Ya.K.Syrkin, S.S.Novikov, A.S.Fainzil'berg, V.V.Sevost'yanova, and V.I.Gulevskaya, Dokl.Akad.Nauk SSSR, **132**, 1376 (1960).
158. S.Soundararajan, Tetrahedron, **19**, 2171 (1963).
159. V.I.Slovetskii, Uspekhi Khim., **40**, 740 (1971) [Russ. Chem.Rev., No.4 (1971)].
160. M.Hauptschein, R.Oesterling, M.Braid, E.Tyczkowski, and D.Gardner, J.Org.Chem., **28**, 1281 (1963).
161. H.Shecher and E.Roberson, J.Org.Chem., **25**, 175 (1960).
162. V.I.Slovetskii, A.A.Fainzil'berg, and S.S.Novikov, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 989 (1962).
163. S.S.Novikov, A.A.Fainzil'berg, and V.I.Slovetskii, "Trudy Konferentsii po Probleme Korrelyatsionnykh Uravnenii v Organicheskoi Khimii" (Proceedings of a Conference on the Problem of Correlation Equations in Organic Chemistry), Tartu, 1963, p.109.
164. V.A.Shlyapochnikov, A.A.Fainzil'berg, and S.S.Novikov, Izv.Akad.Nauk SSSR, Ser.Khim., 519 (1962).
165. V.I.Slovetskii, A.A.Fainzil'berg, V.I.Gulevskaya, and S.S.Novikov, Izv.Akad.Nauk SSSR, Ser.Khim., 683 (1961).
166. V.I.Slovetskii, V.A.Shlyapochnikov, S.A.Shevelev, A.A.Fainzil'berg, and S.S.Novikov, Izv.Akad.Nauk SSSR, Ser.Khim., 330 (1961).
167. V.A.Shlyapochnikov, A.A.Fainzil'berg, V.I.Slovetskii, and S.S.Novikov, "Trudy Konferenstii po Voprosam Stroeniya i Reaktsionnoi Sposobnosti Atsetalei (1961)" (Proceedings of a Conference on Aspects of the Structure and Reactivity of Acetals 1961), Frunze, 1963, p.78.
168. I.L.Knunyants, L.S.German, and I.N.Rozhkov, Izv. Akad.Nauk SSSR, Ser.Khim., 1062 (1966).
169. L.T.Eremenko and A.A.Borisenko, Izv.Akad.Nauk SSSR, Ser.Khim., 675 (1968).
170. E.T.Lippmaa, M.Ya.Myagi, Ya.O.Past, S.A.Shevelev, V.I.Erashko, and A.A.Fainzil'berg, Izv.Akad.Nauk SSSR, Ser.Khim., 1006, 1012 (1971).
171. L.T.Eremenko, A.A.Borisenko, S.I.Petrov, and V.F.Andrianov, Izv.Akad.Nauk SSSR, Ser.Khim., 428 (1968).
172. M.Ya.Myagi, V.I.Erashko, S.A.Shevelev, and A.A.Fainzil'berg, Izv.Akad.Nauk Est.SSR, Ser.Khim., Geol., 297 (1971).
173. M.Witanowski, T.Urbanski, and L.Stefaniak, J.Amer. Chem.Soc., **86**, 2569 (1964).
174. A.V.Kessenikh, L.V.Okhlobystina, V.M.Khutoretskii, A.A.Fainzil'berg, T.A.Babushkina, and G.K.Semin, Teor.Eksper.Khim., **5**, 426 (1969).
175. L.V.Okhlobystina, T.A.Babushkina, V.M.Khutoretskii, and G.K.Semin, Izv.Akad.Nauk SSSR, Ser.Khim., 1899 (1970).
176. T.A.Babushkina, V.I.Robas, I.A.Safin, and G.K.Semin, Fiz.Tverd.Tela, **7**, 924 (1965).
177. A.L.Fridman, V.D.Surkov, F.A.Gabitov, S.I.Gushchin, S.A.Petukhov, and F.M.Mukhametshin, Zhur.Org. Khim., **10**, 2003 (1974).
178. V.M.Belikov, S.G.Mairanovskii, T.B.Korchemnaya, and S.S.Novikov, Izv.Akad.Nauk SSSR, Ser.Khim., 605 (1962).
179. A.G.Bazanov, S.V.Alekseeva, I.V.Tselinskii, and B.V.Gidaspov, Reakts.Sposobn.Org.Soed., **9**, 367 (1972).
180. R.Pearson and D.Dillon, J.Amer.Chem.Soc., **75**, 2439 (1958 [1953?]).

181. A.G.Bazanov, M.V.Chistyakova, M.F.Kozlova, I.V.Tselinskii, and B.V.Gidaspov, Reakts.Sposobn. Org.Soed., **10**, 807 (1973).
182. A.G.Bazanov, I.V.Tselinskii, N.V.Nikol'skaya, M.F.Kozlova, and B.V.Gidaspov, Reakts.Sposobn. Org.Soed., **10**, 817 (1973).
183. A.G.Baznov, M.F.Kozlova, I.V.Tselinskii, B.V.Gidaspov, and S.M.Dzyubenko, Reakts.Sposobn.Org.Soed., **12**, 37 (1975).
184. V.I.Slovetskii, S.A.Shevelev, V.I.Erashko, L.I.Biryukova, A.A.Fainzil'berg, and S.S.Novikov, Izv.Akad.Nauk SSSR, Ser.Khim., 655 (1966).
185. T.N.Hall, J.Org.Chem., **29**, 3587 (1964).
186. A.I.Ivanov, V.I.Slovetskii, S.A.Shevelev, V.I.Erashko, A.A.Fainzil'berg, and S.S.Novikov, Zhur.Fiz.Khim., **40**, 2298 (1966) [Russ.J.Phys.Chem., No.9 (1966)].
187. V.M.Belikov, A.I.Tal'vik, and T.B.Korchemnaya, Reakts.Sposobn.Org.Soed., **2**, 10 (1965).
188. V.I.Slovetskii, L.V.Okhlobystina, A.A.Fainzil'berg, A.I.Ivanov, L.I.Biryukova, and S.S.Novikov, Izv. Akad.Nauk SSSR, Ser.Khim., 2063 (1965).
189. H.Adolph and M.Kamlet, J.Amer.Chem.Soc., **88**, 4761 (1966).
190. I.V.Tselinskii and V.N.Dronov, Reakts.Sposobn.Org. Soed., **10**, 797 (1973).
191. V.D.Surkov, A.L.Fridman, and M.I.Vakhrin, Zhur. Fiz.Khim., **49**, 1014 (1975) [Russ.J.Phys.Chem., No.4 (1975)].
192. A.L.Fridman, F.A.Gabitov, V.D.Surkov, Yu.S.Andreichikov, and S.S.Novikov, USSR P.493 464 (1972); Byull.Izobr., No.44, 56 (1975).
193. G.K.Semin, T.A.Babushkina, and G.G.Yakobson, "Primenenie Yadernogo Kvadrupol'nogo Rezonansa v Khimii" (Application of Nuclear Quadrupole Resonance to Chemistry), Khimiya, Leningrad, 1972.
194. V.D.Surkov, A.L.Fridman, and F.A.Gabitov, see Ref.149, p.9.
195. A.L.Fridman, V.D.Surkov, and F.M.Mukhametshin, Zhur.Org.Khim., **7**, 1840 (1971).
196. F.M.Mikhametshin, V.D.Surkov, A.L.Fridman, and F.A.Gabitov, USSR P.515 738 (1974); Byull.Izobr., No.20, 64 (1976).
197. S.G.Mairanovskii, A.A.Fainzil'berg, S.S.Novikov, and V.A.Klimova, Dokl.Akad.Nauk SSSR, **125**, 351 (1959).
198. Yu.P.Kitaev and I.M.Skrebkova, Dokl.Akad.Nauk SSSR, **149**, 1080 (1963).
199. J.Armand and P.Souchay, Compt.rend., **255C**, 2112 (1962).
200. J.Armand, Compt.rend., **254C**, 2777 (1962).
201. V.A.Petrosyan, V.I.Slovetskii, and A.A.Fainzil'berg, Izv.Akad.Nauk SSSR, Ser.Khim., 2027 (1973).
202. V.A.Petrosyan, S.G.Mairanovskii, L.V.Okhlobystina, V.I.Slovetskii, and A.A.Fainzil'berg, Izv.Akad.Nauk SSSR, Ser.Khim., 1690 (1971).
203. V.A.Petrosyan, V.M.Khutoretskii, V.I.Slovetskii, L.V.Okhlobystina, and A.A.Fainzil'berg, Izv.Akad. Nauk SSSR, Ser.Khim., 229 (1973).
204. V.A.Petrosyan, S.G.Mairanovskii, V.I.Slovetskii, A.A.Fainzil'berg, and S.I.Kvachenok, Izv.Akad.Nauk SSSR, Ser.Khim., 1721 (1968).
205. V.V.Bukhtiyarov and N.N.Bubnov, Teor.Eksper. Khim., **4**, 267 (1968).
206. V.I.Shapiro, M.V.Kazakov, Ya.K.Syrkin, M.V.Khutoretskii, and L.V.Okhlobystina, Teor.Eksper.Khim., 458 (1969).
207. D.Bartak and M.Hawlay, J.Electroanalyt.Chem., **33**, 13 (1971).
208. M.Simonetta, G.Farrini, and S.Carra, Atti.Accad.naz. Lincei, **17**, 375 (1954).
209. L.Zeldin and H.Shechter, J.Amer.Chem.Soc., **79**, 4708 (1957).
210. K.Klager, Analyt.Chem., **23**, 534 (1951).
211. L.Birkenbach, K.Huttner, and W.Stein, Ber., **62**, 2065 (1929).
212. A.L.Fridman, Yu.N.Senichev, F.A.Gabitov, and E.A.Ponomareva, Zhur.Obshch.Khim., **38**, 1902 (1968).
213. A.E.Kretov and N.N.Mel'nikov, Zhur.Obshch.Khim., **2**, 202 (1932).
214. M.Sh.L'vova, V.I.Slovetskii, and A.A.Fainzil'berg, Izv.Akad.Nauk SSSR, Ser.Khim., 323 (1968).
215. W.Sager and J.Hoffsommer, J.Phys.Chem., **73**, 4155 (1969).
216. V.I.Slovetskii, G.Kh.Khisamutdinov, and A.A.Fainzil'berg, Izv.Akad.Nauk SSSR, Ser.Khim., 1721 (1972).
217. V.I.Slovetskii, M.Sh.L'vova, A.A.Fainzil'berg, and T.I.Chaeva, Izv.Akad.Nauk SSSR, Ser.Khim., 2690 (1970).
218. V.I.Slovetskii, G.Kh.Khisamutdinov, V.A.Petrosyan, E.K.Orlova, and A.A.Fainzil'berg, Izv.Akad.Nauk SSSR, Ser.Khim., 1725 (1972).
219. M.Sh.L'vova, V.I.Slovetskii, L.V.Okhlobystina, V.M.Khutoretskii, and A.A.Fainzil'berg, Izv.Akad. Nauk SSSR, Ser.Khim., 95 (1971).
220. L.V.Okhlobystina, G.Ya.Legin, and A.A.Fainzil'berg, Izv.Akad.Nauk SSSR, Ser.Khim., 2318 (1969).
221. E.Schulz, S.Meisel, and F.Schmidt, J.Amer.Chem. Soc., **73**, 2962 (1961 [1951?]).
222. A.Macbeth and D.Pratt, J.Chem.Soc., **119**, 1356 (1921).
223. T.Henderson and A.Macbeth, J.Chem.Soc., **121**, 892 (1922).
224. T.Trippett, D.Walker, and H.Hoffman, J.Chem.Soc., 7140 (1965).
225. C.Grundman and H.Frommeld, J.Org.Chem., **30**, 2077 (1965).
226. A.Speziale and L.Smith, J.Amer.Chem.Soc., **84**, 1868 (1962).
227. S.L.Ioffe, V.A.Tartakovskii, and S.S.Novikov, Uspekhi Khim., **35**, 43 (1966) [Russ.Chem.Rev., No.1 (1966)].
228. H.Ungnade and L.Kissinger, J.Org.Chem., **22**, 1088 (1957).
229. E.Hamel, J.Dehn, J.Love, J.Seigliano, and A.Swift, Ind.Eng.Chem., **1**, 108 (1962).
230. J.Belew and L.Hepler, J.Amer.Chem.Soc., **78**, 4005 (1956).
231. H.Feuer, G.Bachman, and J.Kispersky, J.Amer.Chem. Soc., **73**, 1360 (1951).
232. B.V.Gidaspov, I.V.Tselinskii, and A.G.Bazanov, Zhur. Org.Khim., **7**, 1303 (1971).
233. M.Hawthorn, J.Amer.Chem.Soc., **78**, 4980 (1956).
234. G.Russell and W.Danen, J.Amer.Chem.Soc., **90**, 347 (1968).
235. G.Russell and W.Danen, J.Amer.Chem.Soc., **88**, 5663 (1966).
236. G.Russell, R.Norris, and E.Panek, J.Amer.Chem.Soc., **93**, 5839 (1971).
237. T.Mead and C.Leallyu, J.Org.Chem., **23**, 921 (1958).
238. US P.2 396 282 (1946); Chem.Abs., **40**, 3126 (1946).
239. C.Nenitzescu and D.Isacescu, Ber., **63**, 2484 (1930).
240. E.Tamelen and G.Zyl, J.Amer.Chem.Soc., **72**, 2979 (1950).
241. N.Kornblum, M.Kestner, S.Boyd, and L.Cattran, J.Amer.Chem.Soc., **95**, 3356 (1973).

242. S.A.Shevelev, R.V.Kolesnikov, A.A.Fainzil'berg, and I.P.Beletskaya, Izv.Akad.Nauk SSSR, Ser.Khim., 2824 (1973).
243. S.A.Shevelev, R.V.Kolesnikov, and I.P.Beletskaya, Zhur.Org.Khim., **10**, 1793 (1974).
244. S.A.Shevelev, R.V.Kolesnikov, A.A.Fainzil'berg, and I.P.Beletskaya, Izv.Akad.Nauk SSSR, Ser.Khim., 1368 (1975).
245. B.I.Shapiro, L.V.Okhlobystina, V.M.Khutoretskii, A.A.Fainzil'berg, and Ya.K.Syrkin, Dokl.Akad.Nauk SSSR, **190**, 151 (1970).
246. Ya.K.Syrkin, B.I.Shapiro, V.M.Kazakova, A.A.Fainzil'berg, V.M.Khutoretskii, and L.V.Okhlobystina, Dokl.Akad.Nauk SSSR, **181**, 621 (1968).
247. L.V.Okhlobystina, Izv.Akad.Nauk SSSR, Ser.Khim., 2339 (1969).
248. L.V.Okhlobystina and T.I.Cherkasova, Izv.Akad.Nauk SSSR, Ser.Khim., 2381 (1975).
249. V.I.Slovetskii, G.Kh.Khisamutdinov, and A.A.Fainzil'berg, Izv.Akad.Nauk SSSR, Ser.Khim., 728 (1970).
250. A.L.Fridman, V.D.Surkov, and F.A.Gabitov, Zhur. Org.Khim., **12**, 239 (1976).
251. A.L.Fridman, F.A.Gabitov, and V.D.Surkov, Zhur. Org.Khim., **8**, 2457 (1972).
252. A.A.Onishchenko, I.E.Chlenov, L.M.Makarenkova, and V.A.Tartakovskii, Izv.Akad.Nauk SSSR, Ser.Khim., 1516 (1971).
253. V.A.Tartakovskii, A.A.Fainzil'berg, V.I.Gulevskaya, and S.S.Novikov, Izv.Akad.Nauk SSSR, Ser.Khim., 621 (1968).
254. V.A.Tartakovskii, L.A.Nikonova, and S.S.Novikov, Izv.Akad.Nauk SSSR, Ser.Khim., 1290 (1966).
255. V.A.Tartakovskii, G.A.Shveikhgeimer, N.I.Skobtseva, and S.S.Novikov, Zhur.Obshch.Khim., **37**, 1163 (1967).
256. K.Torssel, Arkiv Kemi, **23**, 543 (1965).
257. K.Torssel, Arkiv Kemi, **23**, 537 (1965).
258. K.Torssel, Acta Chem.Scand., **21**, 1 (1967).
259. K.Torssel, Acta Chem.Scand., **21**, 1392 (1967).
260. H.Anspon, US P.3 041 379 (1962); Chem.Abs., **57**, 13 618 (1962).
261. H.Anspon, US P.3 038 946 (1962); Chem.Abs., **57**, 12 322 (1962).
262. E.Schmidt, A.Ascheri, and W.Knilling, Ber., **59**, 1876 (1926).
263. M.Graff and W.G.Gilligan, J.Org.Chem., **33**, 1247 (1968).
264. K.Klager, J.Org.Chem., **20**, 1348 (1955).
265. L.Kaplan and H.Pickard, Chem.Comm., 1500 (1969).
266. G.V.Strukov, R.G.Gafurov, and L.T.Eremenko, Izv. Akad.Nauk SSSR, Ser.Khim., 1054 (1971).
267. E.Bergman, D.G.Ginsburg, and R.Pappo, Org. Reactions, **10**, 179 (1959).
268. A.V.Fokin, V.A.Komarov, K.V.Frosina, and Kh.A.Abdulganieva, Zhur.Obshch.Khim., **37**, 152 (1967).
269. I.L.Knunyants, L.S.German, and I.N.Rozhkov, Izv. Akad.Nauk SSSR, Ser.Khim., 1630 (1964).
270. H.Adolph, J.Org.Chem., **35**, 3188 (1970).
271. T.Urbanski, Z.Eckstein, and H.Wojnowska, Roczniki Chem., **31**, 93 (1957).
272. R.Wilkendorf and M.Trenel, Ber., **57**, 306 (1924).
273. B.P.544 158 (1942); Chem.Abs., **36**, 6171 (1942).
274. A.V.Fokin, V.A.Komarov, S.M.Davydov, K.V.Frosina, and Kh.A.Abdulganieva, Zhur.Org.Khim., **7**, 1165 (1971).
275. T.N.Hall, Tetrahedron, **19**, Suppl.1, 115 (1963).
276. K.Klager, J.Org.Chem., **16**, 161 (1951).
277. A.L.Fridman, V.P.Ivshin, and T.N.Ivshina, Zhur.Org. Khim., **3**, 1529 (1967).
278. A.L.Fridman, T.N.Ivshina, V.P.Ivshin, and Yu.N.Senichev, Zhur.Obshch.Khim., **39**, 1181 (1969).
279. A.L.Fridman, V.P.Ivshin, and T.N.Ivshina, Zhur. Org.Khim., **4**, 917 (1968).
280. G.M.Nazin, G.N.Nichiporenko, F.I.Dubovitskii, G.B.Manelis, and D.N.Sokolov, Izv.Akad.Nauk SSSR, Ser.Khim., 315 (1968).
281. G.M.Nazin, G.B.Manelis, and F.I.Dubovitskii, Izv. Akad.Nauk SSSR, Ser.Khim., 1239 (1971).
282. G.M.Nazin, G.B.Manelis, and F.I.Dubovitskii, Izv. Akad.Nauk SSSR, Ser.Khim., 2631 (1968).
283. G.M.Nazin, G.B.Manelis, and F.I.Dubovitskii, Izv. Akad.Nauk SSSR, Ser.Khim., 2801 (1968).
284. G.M.Nazin, G.B.Manelis, and F.I.Dubovitskii, Dokl. Akad.Nauk SSSR, **177**, 1387 (1967).
285. V.V.Dubinin, G.M.Nazin, and G.B.Manelis, Izv.Akad. Nauk SSSR, Ser.Khim., 1338 (1971).
286. K.Torssel and R.Ryhage, Arkiv Kemi, **23**, 525 (1965).
287. A.L.Fridman, V.D.Surkov, F.A.Gabitov, Yu.S.Andreichikov, and A.I.Sitkin, Sbornik Nauch. Trudov Kuzbassk.Politekh.Inst., No.69, 163 (1974).
288. A.Robertson and W.Waters, J.Chem.Soc., 492 (1947).
289. T.Fukuto and J.Kispersky, Tetrahedron, **19**, Suppl.1, 105 (1963).
290. O.P.Shitov, S.L.Ioffe, V.A.Tartakovskii, and S.S.Novikov, Izv.Akad.Nauk SSSR, Ser.Khim., 490 (1972).
291. V.A.Kokorekina, O.P.Shitov, L.G.Feoktistov, S.L.Ioffe, V.A.Tartakovskii, and S.S.Novikov, Izv. Akad.Nauk SSSR, Ser.Khim., 2603 (1972).
292. O.P.Shitov, S.L.Ioffe, V.A.Tartakovskii, S.S.Novikov, N.N.Rozhdestvenskaya, and G.V.Isagulyants, Izv. Akad.Nauk SSSR, Ser.Khim., 122 (1973).
293. O.P.Shitov, S.L.Ioffe, T.N.Golovina, V.A.Tartakovskii, S.S.Novikov, N.N.Rozhdestvenskaya, and G.V.Isagulyants, Izv.Akad.Nauk SSSR, Ser.Khim., 124 (1973).
294. I.A.Leenson, G.B.Sergeev, O.P.Shitov, S.L.Ioffe, and V.A.Tartakovskii, Izv.Akad.Nauk SSSR, Ser. Khim., 1149 (1973).
295. E.M.Maksyutov and V.I.Slovetskii, "VI Vsesoyuznoe Soveshchanie po Khimii Nitrosoedinenii, Tezisy" (Sixth All-Union Conference on the Chemistry of Nitro-compounds—Abstracts), Moscow, 1976, p.181.
296. Yu.A.Baskakov and N.N.Mel'nikov, Zhur.Obshch. Khim., **29**, 1233 (1959).
297. A.L.Fridman, V.S.Zalesov, V.D.Surkov, L.V.Kratynskaya, and A.N.Plaksina, Khim.Farm.Zhur., **10**, No.6, 53 (1976).
298. H.Richardson and A.Casanges, J.Econ.Entomol., **35**, 664 (1942).
299. H.Young and R.Cotton, J.Econ.Entomol., **36**, 125 (1943).
300. Yu.E.Bartoshevich, V.N.Kopranenkov, O.T.Burdelev, and B.V.Unkovskii, Khim.Farm.Zhur., **6**, No.1, 13 (1972).
301. A.Bates, D.Spencer, and R.Wain, Ann.Appl.Biol., **51**, 153 (1963).
302. US P.3 445 576 (1969).
303. Jap.P.1299 (1966).
304. Jap.P.9876 (1963).
305. V.F.Ratanova, E.A.Levchenko, and S.A.Zheltova, Trudy Vses.Nauch.-issled.Inst.Zerna Produkt. Pererabotki, No.52, 141 (1964).
306. O.P.Pod'yapol'skaya, Trudy Vses.Nauch.issled.Inst. Zerna Produkt.Pererabotki, No.43, 69 (1963).
307. US P.2 591 589 (1952); Chem.Abs., **48**, 11 485 (1954).
308. Jap.P.19 772 (1964).

309. D.Kaktynya, "Sbornik Dokladov Nauchnoi Konferentsii po Zashchite Rastenii (1960)" (Collected Papers of a Scientific Conference on Plant Protection 1960), Tartu, 1962, p.267.
310. N.Hickin, Chem.Prod., **24**, 205 (1961).
311. US P.2 844 538 (1958); Chem.Abs., **52**, 19 115 (1958).
312. US P.2 987 479 (1961); Chem.Abs., **55**, 26 430 (1961).
313. US P.2 822 252 (1958); Chem.Abs., **52**, 7680 (1958).
314. S.V.Bondarev and L.M.Kozlov, Trudy Kazansk.Khim.-tekhnol.Inst.Kirova, Part 2, No.40, 222 (1969).
315. A.Campbell, Ind.Eng.Chem., **33**, 809 (1941).
316. L.S.Pupko, G.A.Lanchuk, and A.I.Dychenko, Ukrain. Khim.Zhur., **29**, 609 (1963).

Perm State Pharmaceutical Institute

Translated from *Uspekhi Khimii*, 49, 2188-2212 (1980) U.D.C. 547.431

Studies in the Field of Boron-substituted Functional Derivatives of Carbaboranes(12)

V.N.Kalinin

The advances in the synthesis and chemical reactions of boron-substituted functional derivatives of carbaboranes are described. The qualitative and quantitative differences between the reactivities of the functional groups linked to the hexacoordinate boron atom in carbaboranes and the functional groups in the corresponding derivatives of tri-coordinate boron are demonstrated.
The bibliography includes 115 references.

CONTENTS

I. Introduction 1084
II. The synthesis and properties of boron-substitued carbaboranes 1084
III. The electronic effects of *B*-carbaboranyl groups 1093

I. INTRODUCTION

One of the most important and interesting fields in the chemistry of carbaborane systems involves the study of the properties of boron-substituted carbaboranes. The increased coordination number of boron atoms in carbaboranes(12), which is 6, alters radically the properties of the functional groups linked to them compared with the compounds of tri-coordinate boron. The presence of an incomplete electron octet in the boron atom in the latter in many respects determines the high reactivity of compounds of this class, since attack by a given reagent is directed primarily to the central atom and this is responsible for the easy cleavage of the boron–element bonds. Boron-substituted carbaboranes exhibit a high chemical stability as regards the rupture of the boron–element bond and resemble chemically the corresponding aliphatic and aromatic derivatives. The lack of convenient methods for the introduction of functional groups at the boron atoms of the carbaborane nuclei retarded for a long time the development of this promising field and only the discovery in 1967 of the reaction involving the introduction of an amino-group into the carbaborane nucleus made it possible to develop extensively the chemistry of boron-substituted carbaboranes and to discover the characteristics and specific features of the behaviour of compounds of this class.

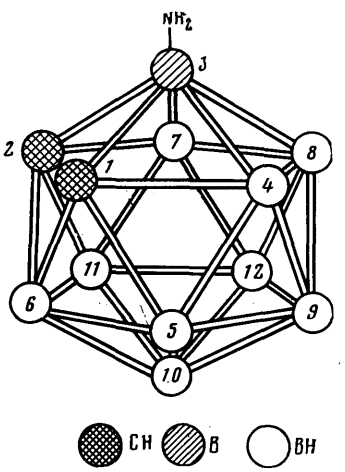
This review reflects the advances in the chemistry of boron-substituted functional derivatives of carbaboranes containing B–N, B–O, B–S, B–C, and B–element (element = metal or non-metal) bonds. The fundamental characteristics of the electrophilic and radical halogenation of carbaboranes will not be considered, since this problem has been described in detail in Grimes's monograph[1] and in dissertations[2–4]. One should only note that the method involving the use of *B*-halogenocarbaboranes for the synthesis of a wide variety of boron-substituted derivatives, which was at first sight seemingly extremely promising, did not justify the hopes associated with it because of the extremely low reactivity of the halogen in *B*-halogenocarbaboranes[5–7].

II. THE SYNTHESIS AND PROPERTIES OF BORON-SUBSTITUTED CARBABORANES

1. Carbaboranes with a B–N Bond

In 1967 Zakharkin and Kalinin found[8] that the dicarbadodecaborate(14) dianions, obtained as a result of the addition of two electrons to carbaboranes, react with liquid ammonia at a low temperature with liberation of hydrogen and the formation of *B*-aminated dianions. On oxidation with $KMnO_4$ or $CuCl_2$ in liquid ammonia, the latter are selectively converted into *o*-carbaborane derivatives containing the amino-group in the 3-position (see Figure):

$$RC{-}CR' \xrightarrow[NH_3(liq.)]{2Na} \left(RC{-}CR'\right)^{2-} \xrightarrow[-H_2]{NH_3(liq.)} \left(RC{-}CR'\right)^{2-} \xrightarrow[NH_3(liq.)]{KMnO_4(CuCl_2)} RC{-}CR'$$
$$B_{10}H_{10} \qquad B_{10}H_{10} \qquad B_{10}H_9NH_2 \qquad B_{10}H_9NH_2$$



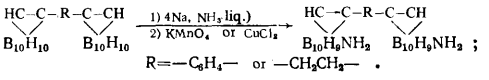
The structure of 3-amino-*o*-carbaborane.

The amination of the dicarbadodecaborate(14) dianion represents nucleophilic substitution at the boron atom linked to the hydrogen atom exhibiting the greatest hydride mobility[8,9]. It has been shown[10] that, in the amination of the dianions, the attacking species is the amide ion. We believe[11] that the possibility of using catalytic amounts of sodium amide in the amination of the dianions apparently arises because the NH_2 group in the amino-derivative of the dianion is less acidic than ammonia. The mechanism of the amination of the dianions remains obscure since final data on the structure of the dicarbadodecaborate(14) dianions have not as yet been obtained.

On the basis of general considerations, one can assume that, when the dicarbadodecaborane(14) dianion is acted upon by ammonia, its *closo*-structure is opened (in the case of a closed structure of the dianion) and the amide ion attacks a specific boron atom, which differs from all others. In the case of an open structure of the dianion the amide ion also attacks only a specific boron atom, linked to the hydrogen atom exhibiting the greatest hydride mobility. On treatment with oxidants, a transition from the *nido*- to the *closo*-structure and the formation of *B*-amino-*o*-carbaborane are observed. This is supported also by the finding that only the monoamino-*o*-carbaborane is formed on amination, while derivatives of *o*-carbaborane with more than one NH_2 group cannot be obtained. Nor was the formation of isomeric *B*-amino-*o*-carbaboranes observed; the reaction product is always only 3-amino-*o*-carbaborane(11).

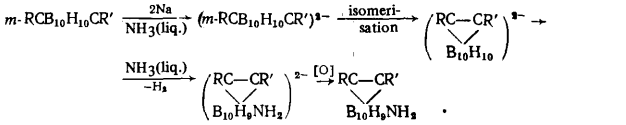
The reaction of dicarbadodecaborate(14) dianions with ammonia is influenced significantly by substituents at the carbon atoms. Whereas the dianion obtained from 1,2-dimethyl-*o*-carbaborane is aminated smoothly with formation of a *B*-amino-derivative, the dianion obtained from 1,2-diphenyl-*o*-carbaborane does not undergo the amination reaction. This is apparently associated with the large bulk of the phenyl groups compared with the methyl groups, which gives rise to steric hindrance to amination. The dianion derived from 1,1′-bis-*o*-carbaborane also does not undergo the amination reaction. *o*-Carbaboranes containing only one substituent at the carbon atom, i.e. 1-substituted *o*-carbaboranes, form dianions which readily undergo the amination reaction.

The application of this reaction to derivatives of *o*-carbaboranes containing two carbaborane nuclei proved to be of interest. It was found that *p*-bis-(*o*-carbaboranyl)benzene and 1,2-bis-(*o*-carbaboranyl)ethane combine with 4 equivalents of sodium to form bisdianions, which interact with ammonia and after oxidation give rise to *p*-bis-(3-amino-*o*-carbaboranyl)benzene and 1,2-bis-(3-amino-*o*-carbaboranyl)-ethane respectively[12,13]:

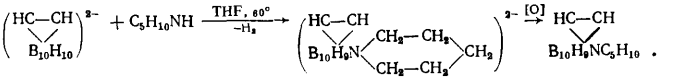


Polyamides[14] and polyureas[15] have been obtained from bis-(aminocarbaboranyl)ethane.

When an attempt is made to obtain *B*-amino-*m*-carbaborane by the reaction of the dianion derived from *m*-carbaborane with ammonia, only 3-amino-*o*-carbaborane is always formed[9]. As shown for the first time by Zakharkin et al.,[16] this is because the dianion obtained from *m*-carbaborane isomerises to the *o*-carbaborane dianion, which subsequently reacts with ammonia:

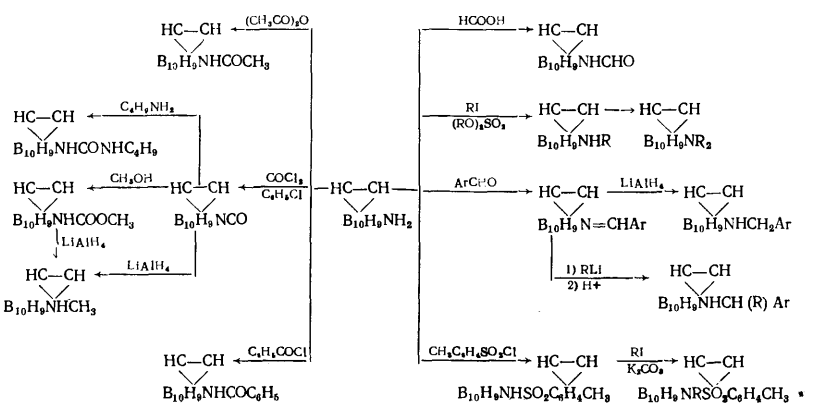


It was found that the dicarbadodecaborate(14) dianion can react with amines to form, after oxidation, derivatives with a B–N bond. Thus, on heating the dicarbadodecaborate(14) dianion in tetrahydrofuran (THF) with piperidine and subsequent oxidation with potassium permanganate in liquid ammonia, *N*-(3-*o*-carbaboranyl)piperidine was obtained[9]:

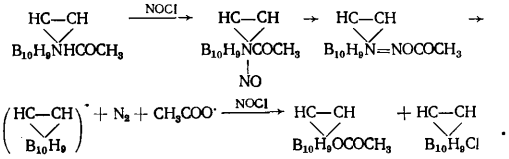


3-Amino-*o*-carbaboranes are colourless readily crystallisable substances resistant to the action of water, aqueous solutions of acids and alkalies, atmospheric oxygen, and heat. They undergo reactions characteristic of aliphatic and aromatic primary amines and are readily acylated by formic acid, acetic anhydride, benzoyl chloride, and *p*-toluenesulphonyl chloride to form the corresponding 3-acylamino-*o*-carbaboranes (Scheme 1).

Scheme 1



3-*o*-Carbaboranylamides of *p*-toluenesulphonic acid have NH groups exhibiting a considerable acidity and are readily alkylated by alkyl halides in acetone solution in the presence of potassium carbonate. When an attempt was made to obtain 3-(*N*-acetamido-*N*-nitroso)-*o*-carbaborane by treating 3-acetamido-*o*-carbaborane with nitrosyl chloride in a mixture of acetic acid and acetic anhydrides in the presence of sodium acetate, the reaction products were 3-acetoxy- and 3-chloro-*o*-carbaboranes[17]. The formation of these two compounds suggests that the decomposition of 3-(*N*-acetamido-*N*-nitroso)-*o*-carbaborane apparently proceeds similarly to the decomposition of *N*-acetyl-*N*-nitrosoarylamines, via a rearrangement to diazoacetate and radical cleavage of the latter. The 3-*o*-carbaboranyl radical formed on decomposition readily reacts with the acetoxy-radical to form 3-acetoxy-*o*-carbaborane, while on interaction with an excess of NOCl it abstracts the chlorine atom and is converted into 3-chloro-*o*-carbaborane:



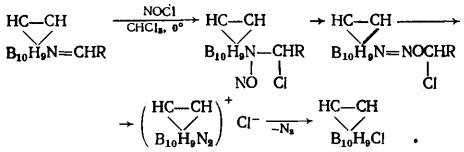
When phosgene is passed into a boiling solution of 3-amino-*o*-carbaborane in chlorobenzene, 3-*o*-carbaboranyl isocyanate is formed readily (Scheme 1). 3-*o*-Carbaboranyl isocyanates exhibit properties characteristic of aliphatic and aromatic isocyanates. For example, they readily react with alcohols and amines to form urethanes and asymmetrically substituted ureas respectively (Scheme 1). However, one should note the high hydrolytic stability of 3-*o*-carbaboranyl isocyanates, which are not hydrolysed on prolonged storage in a moist atmosphere.

The reduction of 3-*o*-carbaboranyl isocyanate with lithium tetrahydroaluminate in ethereal solution yields 3-methylamino-*o*-carbaborane, which is also formed on treatment of methyl 3-*o*-carbaboranyl-carbamate with lithium tetrahydroaluminate.

Like aliphatic and aromatic amines, 3-amino-*o*-carbaboranes condense with aromatic aldehydes to form analogues of Schiff bases containing a B—N bond[17]. *o*-Carbaborane Schiff bases can be readily reduced with lithium tetrahydroaluminate in ethereal solution to the corresponding *N*-arylalkylamines of the 3-*o*-carbaborane series.

o-Carbaborane Schiff bases readily react with organolithium compounds to form products of addition to the C=N double bond; on subsequent hydrolysis, 3-(*N*-alkyl-*N*-arylamino)-*o*-carbaboranes were obtained. *o*-Carbaborane azomethines are readily cleaved to the initial 3-amino-*o*-carbaborane and the aldehyde when they are chromatographed on alumina, which is an effective catalyst of the hydrolysis of azomethines.

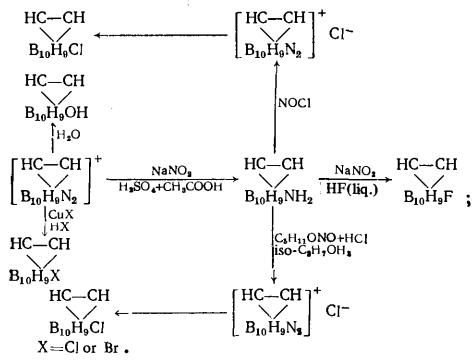
Nitrosyl chloride also cleaves *o*-carbaborane Schiff bases in chloroform, giving rise to *o*-carbaboranyldiazonium chloride, unstable at 0 °C, which decomposes with the liberation of nitrogen and the formation of 3-chloro-*o*-carbaborane[17]:



It is noteworthy that the 3-amino-*o*-carbaboranes themselves readily react with nitrosyl chloride to form 3-chloro-*o*-carbaboranes.

3-Amino-*o*-carbaboranes proved to be capable of being diazotised on treatment with various nitrosating agents with formation of 3-halogeno- and 3-hydroxy-*o*-carbaboranes (Scheme 2).

Scheme 2

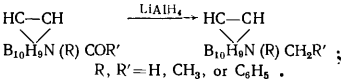


When the diazonium salt obtained by the diazotisation of 3-amino-*o*-carbaborane with nitrosylsulphuric acid in acetic acid is decomposed, the product is 3-hydroxy-*o*-carbaborane[9,18,19]. However, rapid addition of a solution of the diazonium salt to a solution of a copper(I) salt in hydrochloric acid leads readily to the corresponding 3-halogeno-*o*-carbaboranes.

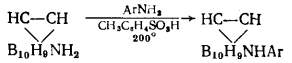
3-Amino-*o*-carbaboranes are also diazotised on treatment with pentyl nitrite in isopropyl alcohol saturated with hydrogen chloride. On subsequent increase of temperature, 3-chloro-*o*-carbaborane is formed[9]. 3-Amino-*o*-carbaboranes readily undergo the Schiemann reaction—the NH_2 groups is substituted by fluorine in liquid HF under the influence of sodium nitrite[9,20].

The decomposition of diazonium salts of the 3-*o*-carbaborane series in polar media apparently proceeds via the intermediate formation of the 3-*o*-carbaboranyl cation, which readily combines with a negative species (OH^-, Cl^-, Br^-, F^-) to form hydroxy- or halogeno-derivatives of the 3-*o*-carbaborane series.

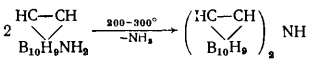
3-Amino-*o*-carbaboranes are alkylated by alkyl sulphates or halides to form secondary and tertiary alkylaminocarbaboranes. The reduction of the corresponding acyl derivatives constitutes a method of synthesis of alkylated aminocarbaboranes which is preparatively more convenient[17]:



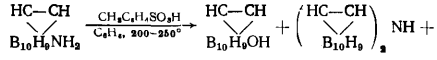
The arylation of 3-amino-*o*-carbaborane, which occurs readily when it is refluxed in an aromatic amine, for example, aniline or *p*-toluidine, in the presence of *p*-toluenesulphonic acid, is an interesting reaction[21,22]:



When 3-amino-*o*-carbaborane is heated to 200–300 °C in benzene under pressure, bis-(*o*-carbaboran-3-yl)amine is formed and NH_3 is evolved:



However, in the presence of an equimolar amount of *p*-toluenesulphonic acid, the unusual reaction involving the substitution of the NH_2 group in the *o*-carbaboranyl nucleus by the OH group takes place; the main product is 3-hydroxy-*o*-carbaborane. At the same time bis(carbaboranyl)amine and bis-(*o*-carbaboranyl) ether were isolated from the reaction products[22]:



The method involving the insertion-synthesis of dicarbollide ions with dialkyldiarylaminoboron dichlorides can be used to synthesise tertiary amines of the carbaborane series[23,24]:

$$7,8\text{-}C_2B_9H_{11}^{2-}2Na^+ + R_2NBCl_2 \rightarrow \begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9NR_2\end{matrix};$$
$$R = C_2H_5 \text{ or } C_6H_5 .$$

Primary and secondary amines of the 3-*o*-carbaboranes series readily interact with phenyl isocyanate to form asymmetrically substituted ureas[17]:

$$\begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9NHR\end{matrix} \xrightarrow{C_6H_5NCO} \begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9NRCONHC_6H_5\end{matrix} .$$

Secondary amino-*o*-carbaboranes are readily nitrosated on treatment with sodium nitrite in acetic acid to form stable *N*-nitroso-derivatives. When 3-methylamino-*o*-carbaborane was treated with the nitrating mixture, 3-(*N*-alkylamino-*N*-nitro)-*o*-carbaborane was obtained:

$$\begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9N(NO_2)R\end{matrix} \xleftarrow[H_2SO_4]{HNO_3} \begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9NHR\end{matrix} \xrightarrow[CH_3COOH]{NaNO_2} \begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9N(NO)R\end{matrix} .$$

Treatment of 3-dimethylamino-*o*-carbaborane with methyl iodide in nitromethane leads to the formation of a quaternary salt—3-*o*-carbaboranyltrimethylammonium iodide; thermal decomposition of the salt gives rise to the initial tertiary amine only[17]:

$$\begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9N(CH_3)_2\end{matrix} \xrightarrow[CH_3NO_2]{CH_3I} \left[\begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9N(CH_3)_3\end{matrix}\right]^+ I^- \xrightarrow{200^\circ} \begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9N(CH_3)_2\end{matrix} .$$

This mode of thermal cleavage of the quaternary salt indicates a greater stability of the B—N bond compared with the C—N bond in this compound.

When an attempt is made to obtain 3-*o*-carbaboranyltrimethylammonium hydroxide by treating 3-*o*-carbaboranyltrimethylammonium iodide with moist silver oxide, the carbaborane nucleus is cleaved to the dicarbaundecaborate(13) anion with formation of an inner salt[17]:

$$\left[\begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9N(CH_3)_3\end{matrix}\right]^+ I^- \xrightarrow{Ag_2O} \begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_9H_9^-{-}\overset{+}{N}(CH_3)_3\end{matrix} \xleftarrow[K_2CO_3]{CH_3I} \begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9N(CH_3)_2\end{matrix} .$$

The powerful electron-accepting effect of the trimethylammonium group in the 3-position in the *o*-carbaborane nucleus apparently destabilises the *o*-carbaborane system with respect to the action of bases. When tertiary amines of the *o*-carbaboranes series are synthesised by the direct alkylation of 3-amino-*o*-carbaborane with alkyl halides or dialkyl sulphates in the presence of potassium carbonate, the yield of the tertiary amine is apparently low and the main product is the inner salt of dicarbadodecahydro-*nido*-undecaborate(13). An interesting property of the inner salt is its ability to sublime *in vacuo* without decomposition.

Like aliphatic and aromatic formamides[25], the formyl derivatives of 3-amino-*o*-carbaboranes react with phosphoryl chloride in pyridine to form 3-*o*-carbaboranylisonitriles, which are capable of rearranging, after brief heating in boiling dodecane, to the corresponding 3-cyano-*o*-carbaboranes[26,27]:

$$\begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9NHCHO\end{matrix} \xrightarrow[C_5H_5N]{POCl_3} \begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9NC\end{matrix} \xrightarrow{220^\circ} \begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9CN\end{matrix} .$$

This rearrangement is the first example of the migration of the carbaboranyl group with dissociation of the B—N bond and the formation of a B—C bond. The migration of the C≡N group in the carbaborane nucleus was not observed under these conditions.

m-Carbaboranes containing amino-groups attached to boron atoms are now known. They can be synthesised by several methods. The reaction of *N*-diphenylaminoboron dichloride with the 7,9-dicarbollide ion led to the synthesis of 2-diphenylamino-*m*-carbaborane[24]:

$$7,9\text{-}C_2B_9H_{11}^{2-}2Li^+ + (C_6H_5)_2NBCl_2 \rightarrow m\text{-}HCB_{10}H_9[2\text{-}N(C_6H_5)_2]CH .$$

Treatment of 2-carboxy-*m*-carbaborane (see Section III) with hydrazoic acid in H_2SO_4 (the Schmidt reaction) leads to the migration of the 2-*m*-carbaboranyl group with an excess of electrons towards the nitrogen atom, which has an electron sextet, and after hydrolysis the product is 2-amino-*m*-carbaborane[28,29]:

$$m\text{-}HCB_{10}H_9(2\text{-}COOH)CH \xrightarrow[H_2SO_4]{HN_3} m\text{-}HCB_{10}H_9(2\text{-}CONH{-}\overset{+}{N}{=}N)CH \xrightarrow{-N_2}$$
$$\rightarrow m\text{-}HCB_{10}H_9\left(2\text{-}\begin{matrix}C\\ \|\\ O\end{matrix}{-}\overset{+}{N}H\right)CH \xrightarrow{-H^+} m\text{-}HCB_{10}H_9(2\text{-}N{=}C{=}O)CH \xrightarrow{H^+}$$
$$\rightarrow m\text{-}HCB_{10}H_9(2\text{-}NH_2)CH .$$

A novel method of synthesising *B*-amino-*m*-carbaboranes involves the thermal isomerisation of 3-amino-*o*-carbaborane[22]. It was found that, when 3-amino-*o*-carbaborane is passed through a quartz tube at 550—600 °C *in vacuo*, equal amounts of 2- and 4-amino-*m*-carbaboranes are formed in high yields:

$$\begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9NH_2\text{-}3\end{matrix} \xrightarrow{550\text{-}600^\circ} m\text{-}HCB_{10}H_9(2\text{-}NH_2)CH + m\text{-}HCB_{10}H_9(4\text{-}NH_2)CH .$$

An interesting method for the synthesis of 3-alkyl-2-amino-*m*-carbaboranes consists in the treatment with alkyl iodides in liquid ammonia of the dianion derived from *o*-carbaborane subjected to preliminary amination[30,31]:

$$\left(\begin{matrix}RC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_{10}\end{matrix}\right)^{2-} \xrightarrow[-H_2]{NH_3(liq.)} \left(\begin{matrix}RC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9NH_2\end{matrix}\right)^{2-} \xrightarrow{Alkl} \begin{matrix}RC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_8(NH_2)(Alk)\end{matrix} .$$
$$R = H, CH_3$$

The structure of the compounds obtained was demonstrated by X-ray diffraction of their reaction products—3-alkyl-2-chloro-9-iodo-*m*-carbaboranes—obtained as a result of the replacement of the amino-group by chlorine with subsequent monoiodination[32].

It has been found[22] that 2- and 4-amino-*m*-carbaboranes exhibit properties typical for organic amines and differ little in their chemical behaviour from 3-amino-*o*-carbaborane.

Thus it has been shown in relation to the reactions of aminocarbaboranes that the behaviour of the NH_2 group in these compounds differs little from that of the behaviour of the same group in aliphatic and aromatic amines. In contrast to the readily hydrolysable and oxidisable classical aminoboranes, aminocarbaboranes are stable organoelemental compounds capable of undergoing a wide variety of reactions via the NH_2 group. This is true also of other carbaborane derivatives containing the B—N bond, which were examined in this section.

2. Carbaboranes with a B—C Bond

A number of *B*-alkyl and *B*-aryl derivatives of carbaboranes have been obtained. A patent[33] reports the alkylation of *o*-carbaborane with methyl iodide in the presence of $AlCl_3$, which results in the formation of a mixture of different polymethylated carbaboranes, none of which have been isolated in a pure form:

$$\begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_{10}\end{matrix} + CH_3I \xrightarrow{AlCl_3} \begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_{10-n}(CH_3)_n\end{matrix};$$
$$n = 1\text{—}8 .$$

o-Carbaboranes and *m*-carbaboranes are alkylated in exactly the same way under the conditions of the Friedel—Crafts reaction with ethyl bromide and isopropyl bromide[34].

Up to eight ethyl groups can be introduced into the *o*- and *m*-carbaborane molecules, but in the case of isopropyl bromide the main products are mono- and di-substituted derivatives. The rate of electrophilic alkylation of *m*-carbaborane is lower than that of *o*-carbaborane.

The reaction of a mixture of 1- and 2-ethyldecaboranes with acetylene in acetonitrile yields a mixture of 8- and 9-ethyl-*o*-carbaboranes[35]:

$$HC{\equiv}CH + 1\text{- и } 2\text{-}B_{10}H_{13}C_2H_5 \xrightarrow[-H_2]{CH_3CN} \begin{matrix} HC{-}CH \\ \diagdown\diagup \\ B_{10}H_9C_2H_5 \end{matrix}\text{-(8 and 9)}.$$

A convenient method for the synthesis of alkyl and aryl derivatives of *o*-carbaboranes is based on insertion synthesis with 7,8-dicarbollide ion to form the icosahedral structure with alkyl- and aryl-boron dihalides, discovered by Hawthorne and Wegner in 1965[36,37]:

$$7,8\text{-}C_2B_9H_{11}^{2-}2Na^+ + RBCl_2 \rightarrow \begin{matrix} HC{-}CH \\ \diagdown\diagup \\ B_{10}H_9R\text{-}3 \end{matrix}.$$

The structure is formed in such a way that the substituent is bound to the boron atom in the 3-position of the *o*-carbaborane nucleus. 3-Methyl-,[29] 3-ethyl-,[37] 3-propyl-,[38] 3-butyl-,[38] 3-vinyl-,[39] and 3-phenyl-*o*-carbaboranes[36,37] as well as various 3-aryl-*o*-carbaboranes substituted in the benzene ring, and *p*- and *m*-tolyl and *p*- and *m*-fluorophenyl-*o*-carbaboranes[40-44] have been synthesised in this way.

It is of interest to note that 3,6-diethyl- and 3,6-diphenyl-*o*-carbaboranes have been synthesised by this method[37]:

$$C_2B_9H_{11}^{2-} + RBCl_2 \rightarrow \begin{matrix} HC{-}CH \\ \diagdown\diagup \\ B_{10}H_9R \end{matrix} \xrightarrow[2)\ NaH]{1)\ C_2H_5ONa} C_2B_9(R)H_{10}^{2-} \xrightarrow{RBCl_2} \begin{matrix} HC{-}CH \\ \diagdown\diagup \\ B_{10}H_8R_2 \end{matrix};$$
$$R = C_2H_5 \text{ or } C_6H_5.$$

The preparation of 1,4-bis-(3-*o*-carbaboranyl)butane containing two 3-*o*-carbaboranyl groups in the molecule has been reported[38]:

$$2C_2B_9H_{11}^{2-} + Cl_2B(CH_2)_4BCl_2 \rightarrow \begin{matrix} HC{-}CH \\ \diagdown\diagup \\ B_{10}H_9(CH_2)_4B_{10}H_9 \end{matrix} \quad \begin{matrix} HC{-}CH \\ \diagdown\diagup \end{matrix}.$$

Insertion synthesis of structures with the aid of alkyl(aryl)-boron dihalides has been extended to the 7,9-dicarbollide ion and 2-vinyl-[28,29] and 2-aryl-*m*-carbaboranes[45] have been obtained by this procedure:

$$7,9\text{-}C_2B_9H_{11}^{2-}2Li^+ + RBCl_2 \rightarrow m\text{-}HCB_{10}H_9(2\text{-}R)CH;$$
$$R = CH_2{=}CH,\ C_6H_5,\ FC_6H_4 \text{ or } CH_3C_6H_4.$$

A general method of synthesis of substituted *o*-carbaboranes containing a B–C bond consist in the interaction of the dicarbadodecaborate(14) dianions with organolithium and organomagnesium compounds, resulting in the formation of *B*-alkyl(alkenyl, aryl) dianions, which give rise to *B*-alkyl-(alkenyl, aryl)-*o*-carbaboranes after oxidation with $CuCl_2$[46-48]:

$$(HCB_{10}H_{10}CH)^{2-} + RM \xrightarrow[20^\circ]{THF} (HCB_{10}H_9RCH)^{2-} \xrightarrow{CuCl_2} \begin{matrix} HC{-}CH \\ \diagdown\diagup \\ B_{10}H_9R \end{matrix};$$
$$M = Li \text{ or } MgX;\ R = CH_3,\ C_4H_9,\ CH_2{=}CH,\ C_6H_5CH{=}CH,$$
$$C_6H_5,\ CH_3C_6H_4, \text{ or } FC_6H_4.$$

The reaction is not selective—a mixture of *B*-substituted carbaboranes containing the substituent in the 3-, 4-, 8-, and 9-positions in the *o*-carbaborane nucleus is always formed. X-Ray diffraction analysis of 1,2-dimethyl-9-phenyl-*o*-carbaborane and 4-(*p*-tolyl)-*o*-carbaborane has been carried out[48].

The reaction of the dianions with organometallic compounds is influenced significantly by the acidity of the hydrocarbon conjugate acid of the carbanion of the organometallic compound. For example, this reaction is not undergone by indenyl-lithium, fluorenyl-lithium, phenylethynyl-lithium, carboranyl-lithium, and cyclopentadienyl-lithium[46].

When the dicarbadodecaborate(14) dianion, obtained from *p*-carbaborane, interacts with arylmagnesium halides and the product is then oxidised, mainly a mixture of *B*-aryl-*m*-carbaboranes is obtained[47,48]:

$$p\text{-}HCB_{10}H_{10}CH \xrightarrow[THF]{2Na} (HCB_{10}H_{10}CH)^{2-} + ArMgX \rightarrow (HCB_{10}H_9ArCH)^{2-} \xrightarrow{CuCl_2} m\text{-}HCB_{10}H_9ArCH.$$

Apart from insertion syntheses of the 7,9-dicarbollide ion, high-temperature gas-phase isomerisation of 3-aryl-*o*-carbaboranes *in vacuo*, leading to 2- and 4-aryl-*m*-carbaboranes, has been proposed as a method of synthesis of aryl-*m*-carbaboranes[49,50]:

$$\begin{matrix} HC{-}CH \\ \diagdown\diagup \\ B_{10}H_9Ar \end{matrix} \xrightarrow{550-600^\circ} m\text{-}HCB_{10}H_9(2\text{-}Ar)CH + m\text{-}HCB_{10}H_9(4\text{-}Ar)CH.$$

Mironov and coworkers found[51-55] that trichlorovinylsilane alkylates *o*-, *m*-, and *p*-carbaboranes and their derivatives under the conditions of the Friedel–Crafts reaction via the B–H bonds of the carbaborane nuclei:

$$HCB_{10}H_{10}CH + CH_2{=}CHSiCl_3 \xrightarrow{AlCl_3} HCB_{10}H_{10-n}(CH_2CH_2SiCl_3)_nCH;$$
$$n = 1-3.$$

Chloromethylvinylsilanes also alkylate carbaboranes under analogous conditions, but, in view of the lower reactivity, the yields of the corresponding products are sharply reduced[55]:

$$HCB_{10}H_{10}CH + CH_2{=}CHSi(CH_3)_xCl_{3-x} \xrightarrow{AlCl_3} HCB_{10}H_{10-n}[CH_2CH_2Si(CH_3)_xCl_{3-x}]_nCH.$$

The mechanism of the silylalkylation of carbaboranes is analogous to the mechanism of the Friedel–Crafts reaction, the sites of the highest electron density in the nuclei being attacked; the trichlorosilylethyl group is therefore located at the boron atoms in the 9(12)-positions in *o*-carbaborane, the 9(10)-positions in *m*-carbaborane, and the 2-position in *p*-carbaborane. The structure of 1,7-bis(trimethylstannyl)-9-[β-(trimethylsilyl)ethyl]-*m*-carbaborane has been confirmed by X-ray diffraction[56].

Studies of the infrared and mass spectra of *B*-substituted carbaboranes have been carried out[57-59].

The formation of aminated *B*-alkyl-*m*-carbaboranes was mentioned above. The special case of the reaction of methyl iodide with the dianion derived from 1,2-di-methyl-*o*-carbaborane in liquid ammonia, resulting in the formation of a mixture of alkylated isomers of *o*- and *m*-carbaboranes[31], is noteworthy:

$$\left(\begin{matrix} CH_3C{-}CCH_3 \\ \diagdown\diagup \\ B_{10}H_{10} \end{matrix}\right)^{2-} \xrightarrow[2)\ CH_3I]{1)\ Ni(NH_3)_6\ (ж)} \underset{(2\text{-isomers})}{CH_3CB_{10}H_9(CH_3)CCH_3} + \underset{(2\text{-isomers})}{CH_3CB_{10}H_8(CH_3)_2CCH_3}.$$

One of the isomers is 1,2,3,6-tetramethyl-*o*-carbaborane[31].

The first functional derivative in the series of carbaboranes, containing a B–C bond, was obtained by Zakharkin and Kalinin in 1968.[39] Oxidation of 3-vinyl-*o*-carbaborane with chromium trioxide in a mixture of acetic and sulphuric acids gives a high yield of 3-carboxy-*o*-carbaborane:

$$\begin{matrix} HC{-}CH \\ \diagdown\diagup \\ B_{10}H_9CH{=}CH_2 \end{matrix} \xrightarrow{CrO_3} \begin{matrix} HC{-}CH \\ \diagdown\diagup \\ B_{10}H_9COOH \end{matrix}.$$

2-Carboxy-*m*-carbaborane has been obtained by an analogous mechanism from 2-vinyl-*m*-carbaborane[28,29].

o-Carbaborane- and *m*-carbaborane-carboxylic acids have been synthesised by the hydrolysis of 3-cyano-*o*-, 2-cyano-*m*-, and 4-cyano-*m*-carbaboranes[27,60]. Owing to the considerable bulk of the carbaborane nuclei, *B*-cyanocarbaboranes can be hydrolysed only by a two-stage method: in the first stage hydrolysis with sulphuric acid results in the formation of an amide, which is converted into the acid on subsequent treatment with sodium nitrite:

$$HCB_{10}H_9(CN)CH \xrightarrow[CH_3COOH,\ 110^\circ]{H_2SO_4} HCB_{10}H_9(CONH_2)CH \xrightarrow[10^\circ]{NaNO_2} HCB_{10}H_9(COOH)CH.$$

The oxidation of *B*-trimethylsilylethylcarbaboranes with chromium trioxide in a mixture of acetic and sulphuric acids gave 9-carboxy-*o*- and 9-carboxy-*m*-carbaboranes[61,62]:

$$HCB_{10}H_9[9\text{-}CH_2CH_2Si(CH_3)_3]CH \xrightarrow{CrO_3} HCB_{10}H_9(9\text{-}COOH)CH .$$

3-Carboxy-*o*-carbaboranes have the properties of the usual organic acids. They are soluble in aqueous solutions of alkalies and form 3-methoxycarbonyl-*o*-carbaboranes on reaction with diazomethane in ether. In contrast to 1-carboxy-*o*-carbaboranes, 3-carboxy-*o*-carbaboranes are esterified with methanol in the presence of H_2SO_4:

$$\underset{B_{10}H_9COOH}{HC-CH} \xrightarrow[\text{or } CH_3OH,\ H_2SO_4]{CH_2N_2,\ (C_2H_5)_2O} \underset{B_{10}H_9COOCH_3}{HC-CH} .$$

Treatment of 3-carboxy-*o*-carbaboranes with PCl_5 in benzene or with $SOCl_2$ leads to the formation of acid chlorides whose properties are similar to those of the usual carboxylic acid chlorides:

$$\underset{B_{10}H_9COOH}{HC-CH} \xrightarrow[\text{or } SOCl_2]{PCl_5,\ C_6H_6} \underset{B_{10}H_9COCl}{HC-CH} \begin{cases} \xrightarrow{LiAlH_4} \underset{B_{10}H_9CH_2OH}{HC-CH} \\ \xrightarrow[AlCl_3]{C_6H_6} \underset{B_{10}H_9COC_6H_5}{HC-CH} \end{cases} .$$

The reduction of the acid chloride with lithium tetrahydroaluminate in ether leads smoothly to the formation of 3-hydroxymethyl-*o*-carbaborane, while its refluxing in benzene in the presence of $AlCl_3$ gave 3-benzoyl-*o*-carbaborane via the Friedel–Crafts reaction[63].

The reduction of 3-benzoyl-*o*-carbaborane with lithium tetrahydroaluminate in ether led to the formation of a secondary alcohol, while the reaction with CH_3MgI gave a tertiary alcohol[63]:

$$\underset{\substack{B_{10}H_9C(OH)(CH_3)(C_6H_5)}}{HC-CH} \xleftarrow{CH_3MgI} \underset{B_{10}H_9COC_6H_5}{HC-CH} \xrightarrow{LiAlH_4} \underset{B_{10}H_9CH(OH)C_6H_5}{HC-CH} .$$

The large bulk of the *o*-carbaboranyl group influences the state of the OH group in primary, secondary, and tertiary alcohols of the type $B_{10}H_9\underset{}{\overset{HC-CH}{}}CRR'OH$. Whereas the infrared spectrum of 3-hydroxymethyl-*o*-carbaborane exhibits a broad absorption band at 3200–3500 cm^{-1} due to the OH group of the associated alcohol, the infrared spectrum of (3-*o*-carbaboranyl)phenylmethanol has two absorption bands due to the OH group: a broad band at 3200–3500 cm^{-1}, characteristic of associated alcohols, and a narrow band at 3550–3580 cm^{-1}, characteristic of unassociated alcohols. The infrared spectrum of the tertiary alcohol shows a single narrow band at 3550–3580 cm^{-1}, which indicates the existence of this alcohol solely in the unassociated state. A similar behaviour has been observed for primary, secondary, and tertiary alcohols, where the substituent was the 1-*o*-carbaboranyl group[64].

The hydroxy-group in 3-hydroxymethyl-*o*-carbaborane is readily substituted by chlorine on refluxing with PCl_5 or $SOCl_2$ in benzene:

$$\underset{B_{10}H_9CH_2OH}{HC-CH} \xrightarrow[\text{or } SOCl_2]{PCl_5,\ C_6H_6} \underset{B_{10}H_9CH_2Cl}{HC-CH} .$$

3-Chloromethyl-*o*-carbaborane formed a Grignard reagent in ethereal solution, the carboxylation of which led to the formation of 3-*o*-carbaboranylacetic acid[63]:

$$\underset{B_{10}H_9CH_2Cl}{HC-CH} \xrightarrow[(C_2H_5)_2O]{Mg} \underset{B_{10}H_9CH_2MgCl}{HC-CH} \begin{cases} \xrightarrow[2)\ H^+]{1)\ CO_2} \underset{B_{10}H_9CH_2COOH}{HC-CH} \\ \xrightarrow{H^+} \underset{B_{10}H_9CH_3}{HC-CH} \xleftarrow{7,8\text{-}C_2B_9H_{11}^{2-}} +CH_3BCl_2 . \end{cases}$$

The hydrolysis of 3-*o*-carbaboranylmethylmagnesium chloride yielded 3-methyl-*o*-carbaborane, which is also formed when the disodium salt of the 7,8-dicarbollide ion reacts with methylboron dichloride in THF.[29,65]

3-Carboxy-*o*-carbaborane can interact with four equivalents of methyl-lithium in ether and after hydrolysis the product is 3-acetyl-*o*-carbaborane. A ketone can also be obtained when three equivalents of methyl-lithium react with 3-cyano-*o*-carbaborane:

$$\underset{B_{10}H_9COOH}{HC-CH} \xrightarrow{4CH_3Li} \underset{\substack{B_{10}H_9C(OLi)(CH_3)(OLi)}}{LiC-CLi} \xrightarrow{H^+} \underset{B_{10}H_9COCH_3}{HC-CH} \xrightarrow{H^+}$$

$$\underset{B_{10}H_9CN}{HC-CH} \xleftarrow{3CH_3Li} \underset{\substack{B_{10}H_9C(NLi)(CH_3)}}{LiC-CLi} .$$

The chemical properties of 3-carboxy-*o*-carbaborane examined above are also characteristic of other representatives of carbaboranecarboxylic acids—2- and 4-carboxy-*m*-carbaboranes[60] and 9-carboxy-*o*- and 9-carboxy-*m*-carbaboranes[55,61,62].

Silyl and stannyl derivatives of these acids have been obtained from 9-carboxy-*o*-carbaborane and hexamethyldisilazane or hexaethyldistannoxane[62]:

$$\underset{B_{10}H_9COOSi(CH_3)_3}{HC-CH} \xleftarrow[-NH_3]{(CH_3)_3SiNHSi(CH_3)_3} \underset{B_{10}H_9COOH}{HC-CH} \xrightarrow{(C_2H_5)_3SnOSn(C_2H_5)_3} \underset{B_{10}H_9COOSn(C_2H_5)_3}{HC-CH} .$$

A remarkable feature of *B*-carboxycarbaboranes and their derivatives is the possibility of nucleophilic molecular rearrangements accompanied by the dissociation of the B–C bond and the migration of the carbaboranyl group with an electron pair to an electron-deficient reaction centre[63]. The carbaboranyl group migrates to a carbenoid carbon atom (the Wolff rearrangement), a nitrene (the Hofmann, Curtius, and Beckmann rearrangements and the Schmidt reaction), or an oxygen atom with a positive charge (the Baeyer–Villiger reaction) (Scheme 3):

It has been established that these rearrangements proceed intramolecularly, the electron pair does not migrate to other boron atoms in the carbaborane nuclei, and the new B–C, B–N, and B–O bonds are formed with the same boron atom to which the functional group had been linked initially.

Analysis of the literature data for the Curtius rearrangement[66] and the Baeyer–Villiger reaction[67] in the series of polyhedral ions $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ suggests that molecular nucleophilic rearrangements typical for organic chemistry are applicable to the dissociation of the B–C bond when the boron atom forms part of polyhedral borane anions or carbaboranes.

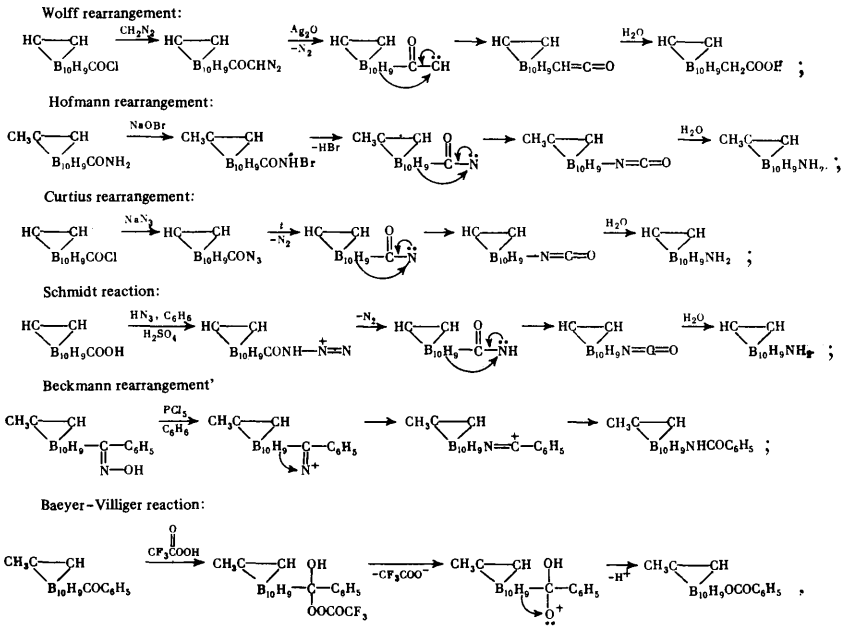
B-Alkenylcarbaboranes undergo the usual reactions characteristic of double bonds. For example, treatment of 3-vinyl-*o*-carbaborane with ozone yields 3-formyl-*o*-carbaborane[39] and hydrostannylation of 2-vinyl-*m*-carbaborane leads to a high yield of 2-triethylstannyl-*m*-carbaborane[68]:

$$\underset{B_{10}H_9CH=CH_2}{HC-CH} \xrightarrow{O_3} \underset{B_{10}H_9CHO}{HC-CH} ;$$

$$м\text{-}HCB_{10}H_9(-CH=CH_2)CH \xrightarrow{(C_2H_5)_2SnH} м\text{-}HCB_{10}H_9[-CH_2CH_2Sn(C_2H_5)_3]CH .$$

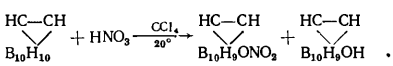
The study of the chemical properties of carbaborane derivatives containing a B–C bond and with functional groups attached to boron atoms, namely carboxy-*o*-carbaboranes and their derivatives, acyl derivatives of carbaboranes, and hydroxy- and chloromethyl-carbaboranes, showed that their chemical properties are similar to those of the corresponding aliphatic and aromatic organic derivatives with *C*-functional groups.

Scheme 3



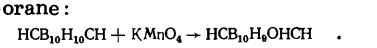
3. Carbaboranes with a B–O Bond

Historically *B*-hydroxycarbaboranes have been the first known type of compounds containing a functional group attached to a boron atom. In 1965 it was noted[69,70] that prolonged oxidation of *o*-carbaboranes with 100% nitric acid in CCl_4 results in the formation of *B*-hydroxycarbaboranes and the corresponding nitrates:



The sites with the highest electron density in the carbaborane nucleus are the first to be oxidised by nitric acid, i.e. the *B*-hydroxycarbaboranes obtained are largely 9-substituted isomers.

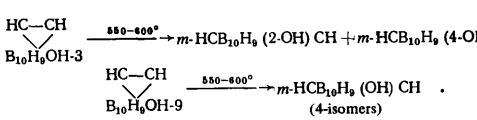
It was found subsequently[71,72] that *o*-, *m*-, and *p*-carbaboranes undergo oxidative hydroxylation on treatment with $KMnO_4$ in acetic acid with formation of all possible isomers: four in the case of *o*- and *m*-carbaboranes and one in the case of *p*-carbaborane:



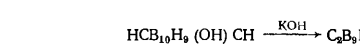
The oxidation of carbaboranes by treatment with CrO_3 is more selective and in this case the formation of mainly 9-substituted products was observed for *o*- and *m*-carbaboranes[72].

The diazotisation of *B*-amino-*o*-carbaborane with nitrosylsulphuric acid is a convenient method for the synthesis of 3-hydroxy-*o*-carbaboranes[18,19].

Thermal isomerisation of 3-hydroxy-*o*-carbaborane in a flow system at 550–600 °C leads to the formation of 2- and 4-hydroxy-*m*-carbaboranes only, while the isomerisation of 9-hydroxy-*o*-carbaborane gives rise to a mixture of all possible isomeric *B*-hydroxy-*m*-carbaboranes[60]:



3-Hydroxy-*o*- and 2-hydroxy-*m*-carbaboranes readily undergo intramolecular and nucleophilic cleavage in an alkaline medium, forming the corresponding dicarbaundecaborate(13) anions[73]:

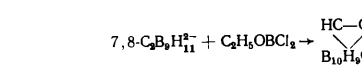


B-Hydroxycarbaboranes have the properties of the usual organic hydroxy-derivatives. We shall consider their chemical behaviour in relation to the most thoroughly investigated 3-hydroxy-*o*-carbaboranes. They readily react with acylating agents, such as acetic anhydride, benzoyl chloride and *p*-toluenesulphonyl chloride, forming the corresponding acyloxy-derivatives[19] (Scheme 4):

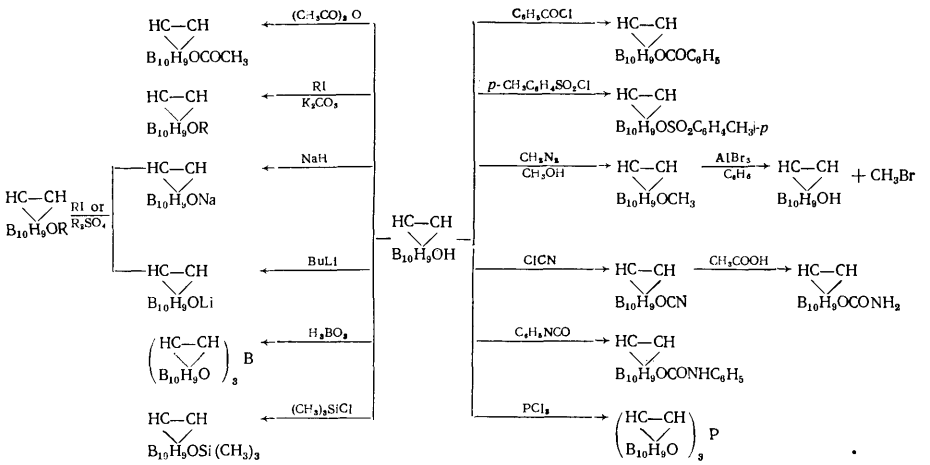
3-*o*-Carbaboranyl tosylates proved to be relatively unreactive in nucleophilic substitution reactions. When 3-*o*-carbaboranyl tosylate was heated with NaI in acetone at 140 °C for 10 h, no substitution products were observed. This result is consistent with the low reactivity of *B*-halogeno-*o*-carbaboranes in nucleophilic substitution reactions[11].

The following procedures can be used to synthesise 3-alkoxycarbaboranes (Scheme 4): (a) treatment of 3-hydroxy-*o*-carbaborane with diazomethane in methanol solution; (b) heating of an acetone solution of 3-hydroxy-*o*-carbaborane with an alkyl iodide in the presence of potassium carbonate; (c) treatment with alkyl iodides or dialkyl sulphates of lithium or sodium 3-*o*-carbaboranoxides prepared by the reaction of butyl-lithium or sodium hydride with 3-hydroxy-*o*-carbaboranes.

3-Ethoxy-*o*-carbaborane has been obtained by the insertion synthesis reaction of the 7,8-dicarbollide ion with ethoxyboron dichloride[23]:



Scheme 4



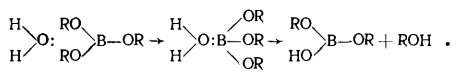
In contrast to boric acid esters, carbaborane ethers are resistant to hydrolysis but, on heating of 3-methoxy-*o*-carbaborane with $AlBr_3$ in benzene, the C–O bond is cleaved with exclusive formation of 3-hydroxy-*o*-carbaborane, while the B–O bond remains unaffected[19].

In this respect 3-methoxy-*o*-carbaboranes behave similarly to mixed aliphatic-aromatic ethers, the 3-*o*-carbaboranyl group playing the role of an aromatic group.

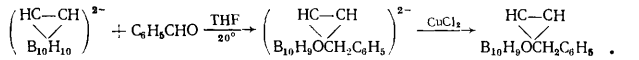
3-Hydroxy-*o*-carbaboranes react smoothly with boric acid, chlorotrimethylsilane, and phosphorus trichloride to form the corresponding ester or ether (Scheme 4).[19]

When 3-hydroxy-*o*-carbaborane reacts with chlorocyanogen in acetone in the presence of triethylamine, 3-*o*-carbaboranyl cyanate is formed smoothly. 3-Carbaboranyl cyanates are solid crystalline substances, which are stable in air. In contrast to aliphatic cyanates, they do not tend to isomerise and trimerise even in the presence of an active catalyst such as $AlCl_3$. 3-*o*-Carbaboranyl cyanates react with acetic acid to form carbamates. The reaction of 3-hydroxy-*o*-carbaborane with phenyl isocyanate leads to the corresponding urethane[11].

In contrast to alkyl(aryl)boronic acids and dialkyl(diaryl)-borinic acids, *B*-hydroxy-*o*-carbaboranes have chemical properties similar to those of aliphatic and aromatic hydroxy-derivatives. The unusually high hydrolytic stability of tris-(3-*o*-carbaboranyl) borate, which is not decomposed by water to boric acid and 3-hydroxy-*o*-carbaborane, in contrast to the readily hydrolysable alkyl and aryl borates[74], proved to be of interest. In the light of the mechanism proposed for the hydrolysis of borate esters[74], the hydrolytic stability can apparently be accounted for by the large bulk of the carbaborane nuclei, which hinders the formation of an intermediate complex with water:



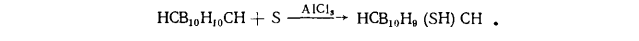
Kalinin and Zakharkin[75,76] discovered an interesting reaction involving the formation of the B–O bond in carbaboranes, which consists in the interaction of the dicarbadodecaborate(14) dianions with aromatic aldehydes and subsequent oxidation of the intermediates to neutral carbaboranes. It was found that the dicarbadodecaborate(14) dianion, obtained from *o*-carbaborane, resembles in terms of some of its properties the tetrahydroborate anion BH_4^-. This is reflected in the ability of the dianion derived from *o*-carbaborane to add to the carbonyl group of benzaldehyde, as a result of the dissociation of the B–H bond with formation of *B*-benzyloxy-dianions, the oxidation of which with copper(II) chloride in THF leads to *B*-benzyloxy-*o*-carbaboranes in high yields:



Although the structure of the dicarbadodecaborate(14) dianions has not been elucidated, there is no doubt that their addition to the carbonyl group of benzaldehyde should proceed via the B–H bonds exhibiting the highest hydride mobility. The main products of the oxidation of benzyloxy-dianions are 3-benzyloxy-*o*-carbaborane (75–80% yield) and 4-benzyloxy-*o*-carbaborane (20–25% yield). 4-Benzyloxy-*o*-carbaborane has been investigated by X-ray diffraction[77].

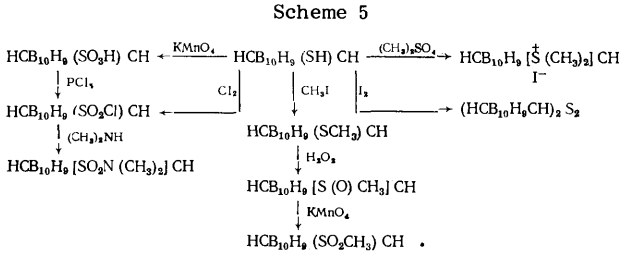
4. Carbaboranes with a B–S Bond

A general method of synthesis of *B*-mercaptocarbaboranes, consisting of the treatment of carbaboranes with elemental sulphur in the presence of $AlCl_3$, has been developed[78,79]:



The sulphur atom in *B*-mercaptocarbaboranes is linked to the boron atom in the 9-position in *o*- and *m*-carbaboranes and in the 2-position in *p*-carbaborane. The chemical properties of 9-mercapto-*o*- and 9-mercapto-*m*-carbaboranes, the main transformation cycle of which is illustrated in Scheme 5, have been investigated in detail[80,81]:

Scheme 5



The oxidation of mercaptans with $KMnO_4$ leads to sulphonic acids, which can be readily converted into sulphonyl chlorides and dimethylamides. In an alkaline medium mercaptans are readily *S*-alkylated by virtually any alkylating agents with formation of, for example, methylthiocarbaborane and carbaboranyldimethylsulphonium iodide. The oxidation of methylthiocarbaborane yields either carbaboranyl methyl sulphoxide or the corresponding sulphone, depending on the oxidation potential of the reactant. When mercaptocarbaboranes are treated with iodine, biscarbaboranyl disulphides are formed smoothly and can be reduced in their turn with zinc in acetic acid to mercaptans[78,80,81].

One may conclude that the sulphur derivatives of carbaboranes containing a B–S σ-bond have properties analogous to those of sulphur derivatives with a C–S bond.

5. Carbaboranes with a B–Metal Bond

A number of carbaborane derivatives containing a bond between boron and a transition or non-transition metal are known. It now appears that there are favourable prospects for the development of the chemistry of this extremely interesting class of compounds.

o-Carbaborane derivatives containing a σ-bond between boron and a transition metal were first obtained[82] via acyl derivatives. The reaction of the chloride of 3-*o*-carbaboranecarboxylic acid with $NaFe(CO)_2C_5H_5$-π leads to σ-(*o*-carbaboranyl-3-carbonyl)-π-cyclopentadienyliron dicarbonyl, the decarbonylation of which yields σ-(*o*-carbaboran-3-yl)-π-cyclopentadienyliron dicarbonyl (I):

$$\mathrm{HC{-}CH}\ (\mathrm{B_{10}H_9COCl}) + \mathrm{NaFe(CO)_2C_5H_5}\text{-}\pi \xrightarrow[\mathrm{THF}]{-70^\circ} \mathrm{HC{-}CH}\ (\mathrm{B_{10}H_9COFe(CO)_2C_5H_5}\text{-}\pi) \xrightarrow[-\mathrm{CO}]{170^\circ} \mathrm{HC{-}CH}\ (\mathrm{B_{10}H_9Fe(CO)_2C_5H_5}\text{-}\pi)\ (\mathrm{I})\ .$$

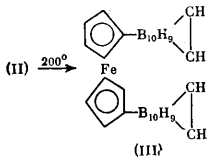
The rhenium derivative has been obtained via a similar mechanism[83]:

$$\mathrm{HC{-}CH}\ (\mathrm{B_{10}H_9COCl}) + \mathrm{NaRe(CO)_5} \xrightarrow[\mathrm{THF}]{-70^\circ} \mathrm{HC{-}CH}\ (\mathrm{B_{10}H_9CORe(CO)_5}) \xrightarrow{t^\circ} \mathrm{HC{-}CH}\ (\mathrm{B_{10}H_9Re(CO)_5})\ .$$

The reaction of halogens with a complex containing a B–Fe bond is of interest. The reaction of compound (I) with chlorine or bromine entails a rearrangement accompanied by the dissociation of the B–Fe bond and the migration of the carbaboranyl group to the cyclopentadienyl ring with formation of π-[(*o*-carbaboran-3-yl)cyclopentadienyl]dicarbonyliron halide (II)[84,85]:

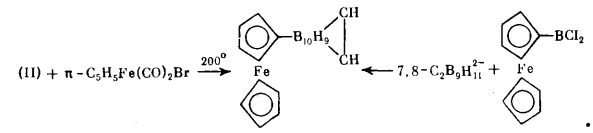
$$(\mathrm{I}) \xrightarrow[\mathrm{CCl_4}]{\mathrm{X_2}} \pi\text{-}\left(\mathrm{HC{-}CH}\ (\mathrm{B_{10}H_9C_5H_4})\right)\mathrm{Fe(CO)_2X}\ ;\quad \mathrm{X = Cl\ or\ Br}\ (\mathrm{II})\ .$$

Heating of compound (II, X = Br) at 200 °C in decalin leads to 1,1′-bis-(*o*-carbaboran-3-yl)ferrocene (III)[85,86]:



(III)

If complex (II) is heated in the presence of $\pi\text{-}C_5H_5Fe(CO)_2.Br$, then (*o*-carbaboran-3-yl)ferrocene is obtained together with ferrocene and compound (III); (*o*-carbaboran-3-yl)-ferrocene has also been obtained by specific synthesis from ferrocenylboron dichloride and the 7,8-dicarbollide ion[85,86]:



The polarographic reduction of carbaborane complexes with a B–Fe σ-bond proceeds in the same way as for the usual σ-alkyl derivatives and the primary products are the anions $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ and $[RCB_{10}H_9CR]^-$.[87]

In contrast to reactions with the halogens, complex (I) interacts with mercury(II) chloride in the normal manner, yielding the first example of carbaborane derivatives with a B–Hg bond: 3-*o*-carbaboranylmercury chloride[85,86]:

$$(\mathrm{I}) + \mathrm{HgCl_2} \xrightarrow{110^\circ} \mathrm{HC{-}CH}\ (\mathrm{B_{10}H_9HgCl}) \xrightarrow{\mathrm{Br_2}} \mathrm{HC{-}CH}\ (\mathrm{B_{10}H_9Br})\ .$$

When the latter is treated with bromine, demercuration takes place readily.

Further development of this branch of the chemistry of carbaborane derivatives with *B*-functional groups was associated with the discovery in 1976 of the reaction involving the mercuration of carbaboranes[88]. It was found that a powerful mercurating agent, such as mercury trifluoroacetate, reacts with *o*-, *m*-, and p-carbaboranes to form carbaboranylmercury trifluoroacetate, in which the trifluoroacetate anion is readily exchanged for chlorine or iodine[88–90]:

$$\mathrm{HCB_{10}H_{10}CH} \xrightarrow{(\mathrm{CF_3COO)_2Hg}} \mathrm{HCB_{10}H_9(HgOCOCF_3)CH} \xrightarrow{\mathrm{NaX}} \mathrm{HCB_{10}H_9(HgX)CH}\ ;\quad \mathrm{X = Cl\ or\ Br}\ .$$

The electrophilic monomercuration of *o*-carbaborane leads to the formation of 15–20% of the 8-substituted derivative and 80–85% of the 9-substituted derivative, while the mercuration of *m*-carbaborane takes place in the 9-position to the extent of 99%. The formation of *B*-polymercurated carbaboranes has also been observed[89,91]. In the reaction of *o*-carbaborane with mercury trifluoroacetate in CF_3COOH mono-, di-, tri-, tetra-, and penta-mercuri-derivatives are formed in succession[89,91]:

$$\mathrm{HC{-}CH}\ (\mathrm{B_{10}H_{10}}) + \mathrm{Hg(OCOCF_3)_2} \rightarrow \mathrm{HC{-}CH}\ (\mathrm{B_{10}H_{10-n}(HgOCOCF_3)_n})\ ;\quad n = 1-5\ .$$

In the case of *m*-carbaborane the reaction proceeds with greater difficulty and after 30 h mainly the trimercuri-derivative is formed[91]:

$$m\text{-}\mathrm{HCB_{10}H_{10}CH} + \mathrm{Hg(OCOCF_3)_2} \rightarrow m\text{-}\mathrm{HCB_{10}H_{10-n}(HgOCOCF_3)_nCH}\ ;\quad n = 1-3\ .$$

Carbaboranes are also mercurated on treatment with mercury acetate in CH_3COOH in the presence of catalytic amounts of $HClO_4$.[91]

Carbaboranes have been thallated under similar conditions with formation of derivatives having a B–Tl bond[92,93]:

$$\mathrm{HCB_{10}H_{10}CH} + \mathrm{Tl(OCOCF_3)_3} \rightarrow \mathrm{HCB_{10}H_9[Tl(OCOCF_3)_2]CH}\ .$$

Symmetrisation of salts of *B*-mercurated carbaboranes is achieved by treatment with a solution of the naphthalene radical-anion or (better) with cadmium amalgam[89,90]:

$$\mathrm{HCB_{10}H_9(HgOCOCF_3)CH} \xrightarrow[\text{or } \mathrm{Cd/Hg}]{\mathrm{C_{10}H_8^-\,Li^+}} \mathrm{(HCB_{10}H_9CH)_2Hg}\ .$$

Asymmetric carbaboranylmercury compounds have been obtained by the reaction of carbaboranylmercury trifluoroacetate with a Grignard reagent:

$$\mathrm{HCB_{10}H_9(HgOCOCF_3)CH} + \mathrm{C_2H_5MgBr} \rightarrow \mathrm{HCB_{10}H_9(HgC_2H_5)CH}\ .$$

Asymmetric *B*-mercuricarbaboranes are much less stable than their *C*-analogues—they disproportionate even at 100 °C with formation of symmetrical products:

$$HCB_{10}H_9(HgC_2H_5)CH \xrightarrow{100^\circ} (HCB_{10}H_9CH)_2Hg + (C_2H_5)_2Hg .$$

In contrast to *C*-mercuricarbaboranes, symmetrical *B*-substituted compounds readily react with $HgCl_2$, Br_2, and HCl:[89-91]

$$HCB_{10}H_9(HgCl)CH \xleftarrow{HgCl_2} (HCB_{10}H_9CH)_2Hg \begin{cases} \xrightarrow{Br_2} HCB_{10}H_9BrCH \\ \xrightarrow{HCl} HCB_{10}H_9(HgCl)CH \end{cases} .$$

The enhanced electron affinity of the B–Hg bond in *p*-carbaborane under the conditions of polarographic reduction, relative to the corresponding derivatives of *o*- and *m*-carbaboranes, has been noted[94,95].

Bis-carbaboranyl derivatives of mercury can be used in reactions with non-transition metal salts in order to synthesise other derivatives containing a σ-bond between boron and the non-transition element[92,93,96-98]:

$$\left(\begin{matrix}HC-CH\\ \diagdown\ \diagup\\ B_{10}H_9\end{matrix}\right)_2 Hg + EX_3 \xrightarrow{\Delta} \begin{matrix}HC-CH\\ \diagdown\ \diagup\\ B_{10}H_9EX_2\end{matrix} + \begin{matrix}HC-CH\\ \diagdown\ \diagup\\ B_{10}H_9HgX\end{matrix} ;$$

E = As, Sb, or Tl .

When biscarbaboranylmercury is treated with $SnCl_2$, a tin derivative containing a B–Sn bond is formed smoothly[98]:

$$(HCB_{10}H_9CH)_2Hg + SnCl_2 \rightarrow (HCB_{10}H_9CH)_2SnCl_2 .$$

Heating of bis-*m*-carbaboranylmercury with sulphur in a sealed tube at 350 °C leads to the formation of biscarbaboranyl disulphide:

$$(HCB_{10}H_9CH)_2Hg + S \rightarrow (HCB_{10}H_9CH)_2S_2 + Hg .$$

An interesting compound containing a B–S–Hg–B bond has been obtained on adding tetrabutylammonium iodide to a mixture of biscarbaboranylmercury and sulphur[98]:

$$(HCB_{10}H_9CH)_2Hg + S \xrightarrow[DMF]{I^-} \begin{matrix}HCB_{10}H_9CH\\ |\\ S\\ |\\ Hg\\ |\\ HCB_{10}H_9CH\end{matrix} .$$

The formation of derivatives with B–Ge and B–P bonds has been claimed[96].

Biscarbaboranyl derivatives of mercury can be used to synthesise carbaboranes with B–C bonds. For example, when bis-*o* or bis *m*-carbaboranylmercury is acted upon by CH_3COCl in the presence of $AlCl_3$, *B*-acetylcarbaborane is formed[99]:

$$(HCB_{10}H_9CH)_2Hg + CH_3COCl \xrightarrow{AlCl_3} HCB_{10}H_9(GOCH_3)CH + HCB_{10}H_9(HgCl)CH .$$

Mercury derivatives have also been used in the synthesis of carbaboranes with a B–Pt σ-bond by the oxidative addition of 9-chloromercuri-derivatives of *o*- and *m*-carbaboranes to $Pt(Ph_3P)_3$:[100]

$$HCB_{10}H_9(HgCl)CH + Pt(Ph_3P)_3 \xrightarrow[20^\circ]{C_6H_6} HCB_{10}H_9[PtCl(Ph_3P)_2]CH .$$

The intramolecular oxidative addition of the B–H bond in 1-dimethylphosphino-*o*-carbaborane to an iridium atom is of interest.[101,102] It proceeds via the intermediate formation of the complex L_3IrCl, which has not been isolated in a pure state:

$$[Ir(C_8H_{14})_2Cl]_2 + 6\,(CH_3)_2PC(H)-CH(B_{10}H_{10}) \xrightarrow{\Delta} [2\,L_3IrCl] \rightarrow \begin{matrix}(CH_3)_2PC(H)-CH(B_{10}H_{10})\\ |\\ L\\ \diagdown\\ L-Ir-B_{10}H_9\\ \diagup\\ Cl\ \ H\end{matrix} ;$$

$$L = (CH_3)_2PC(H)-CH(B_{10}H_{10}) .$$

The iridium atom is coordinated to the boron atom in the 4(5)-positions in the *o*-carbaborane nucleus.

Another version of the synthesis of complexes with B–Ir bonds involves the intermolecular oxidative addition of the B–H bonds in *o*-, *m*-, and *p*-carbaboranes to the corresponding iridium complexes[102,103]:

$$L_2IrCl + HCB_{10}H_{10}CH \rightarrow \underset{(IV)}{HCB_{10}H_9(IrL_2HCl)CH} ;$$

$$L = Ph_3P \text{ or } Ph_3As .$$

When CO is passed through a solution of compound (IV) in benzene or when compound (IV) is heated with triphenylphosphine in toluene, the σ-linked carbaboranyl ligand is readily split off[102]:

$$HCB_{10}H_{10}CH \xleftarrow{CO} (IV) \xrightarrow{Ph_3P} HCB_{10}H_{10}CH .$$

III. THE ELECTRONIC EFFECTS OF *B*-CARBABORANYL GROUPS

As a consequence of the non-uniformity of the distribution of electron density in carbaborane nuclei, the electronic effects of the carbaboranyl groups depend on the site in the nucleus to which the substituent is linked. This postulate was put forward in 1966 by Zakharkin, Kalinin, and Shepilov in connection with the determination of the electronic effects of the 3-*o*-carbaboranyl group[41]. As a result of the advances made in the synthesis of various boron-substituted carbaboranes, the electronic effects of the *B*-carbaboranyl groups have now been investigated in fair detail. The known σ-constants of the *B*-carbaboranyl groups are compiled in the Table.

The σ-constants of the carbaboranyl groups.

Carbaboranyl group	Hammett constants*		References	Inductive and resonance constants**		References
	σ_p	σ_m		σ_I	σ_R^0	
1-*o*-	0.46	0.47	104	0.375	0.003	104
1-*o*-	0.43	0.49	42	0.38	0	43
3-*o*-	0.19	0.19	42	0.11	0.07	43
3-*o*-	—	—	—	0.01	0.06	44
4-*o*-	−0.05	−0.03	48	−0.04	+0.02	47, 48
9-*o*-	—	—	—	−0.23	−0.02	47, 48
1-*m*-	0.33	0.25	42	0.194	−0.089	104
1-*m*-	—	—	—	0.21	−0.05	43
2-*m*-	0.15	0.14	45	0.12	0.05	45
4-*m*	0.02	−0.02	49, 50	−0.04	0.02	49, 50
1-*p*-	—	—	—	0.14	−0.02	105

* Determined from the reaction series for the ionisation of carbaboranylbenzoic acids in 75% ethanol.

** Determined from the ^{19}F chemical shifts in the NMR spectra of fluorophenylcarbaboranes in inert solvents by the Taft method using the equations $\delta_m^F = -7.10\sigma_I + 0.6$ and $\delta_p^F - \delta_m^F = -29.5\sigma_R^0$.

The electronic effects of the *B*-*o*-carbaboranyl groups, for which a change in the nature of the electronic influence from the electron-accepting 3-*o*-carbaboranyl group to the virtually electrically neutral 4-*o*-carbaboranyl group and then the highly electron-donating 9-*o*-carbaboranyl group has been observed, have been studied most fully.

The inductive constants have been calculated for the 3-*o*- and 2-*m*-carbaboranyl groups by Charton's method from the ionisation constants of carbaboranylacetic acids in 80% methylcellosolve. The values of σ_I obtained amount to 0.12 and 0.11 respectively[63].

Evidently the electronic effects of the carbaboranyl groups are to a large extent determined by the charges on the corresponding carbon and boron atoms. Despite the somewhat approximate nature of the quantum-chemical calculations on carbaboranes, which are complex multiatomic systems, the available data (see the relevant reviews[106,107]) for the partial charges on the boron and carbon atoms are consistent with the pK_a of hydroxy-, amino-, and carboxy-carbaboranes[11].

The introduction of substituents at the boron atoms in the carbaborane nuclei is reflected in the nature of the C–H bond. For example, the significant influence of the electronic effects of the substituents at the boron atoms on the integral intensity of the C–H stretching vibration band in the region of 3060 cm^{-1} [108] and on the equilibrium CH acidity of carbaboranes[109] has been demonstrated.

---o0o---

A series of studies of interest for the problem under consideration have been published recently. The decarboxylation of oxomercury salts of 9-*o*- and 9-*m*-carbaboranecarboxylic acids under the influence of peroxide initiators or ultraviolet radiation leads to salts of 9-*o*- and 9-*m*-carbaboranylmercury[110]. The first examples of peroxides containing the B–C–O–O bond system have been synthesised from the chloride of 9-*m*-carbaboranecarboxylic acid and t-butyl hydroperoxide or hydroxymethyl t-butyl peroxide[111]. 9-Amino-*m*- and 2-amino-*p*-carbaboranes have been obtained and their pK_a determined[112]. The pK_a of 9-carboxy-*o*-, 9-carboxy-*m*-, and 2-carboxy-*p*-carbaboranes have been revised in the same study. Detailed data on the synthesis of 9-acetyl-*o*- and 9-acetyl-*m*-carbaboranes via the corresponding biscarbaboranylmercury derivatives have been published[113]. $LiAlH_4$ has been proposed as a convenient symmetrising agent for 9-chloromercuricarbaboranes[113]. The unusual chemical and thermal stabilities of borothallated carbaboranes compared with their aryl analogues have been noted[114]. A new method for the introduction of substituents at the boron atoms of carbaboranes has been proposed[115].

REFERENCES

1. R.N.Grimes, "Carboranes" (Translated into Russian), Izd.Mir, Moscow, 1974.
2. V.N.Kalinin, Candidate's Thesis, Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow, 1967.
3. A.I.Klimova, Candidate's Thesis, Moscow State University, Moscow, 1970.
4. V.I.Stanko, Doctoral Thesis, Moscow State University, Moscow, 1975.
5. L.I.Zakharkin and V.N.Kalinin, Izv.Akad.Nauk SSSR, Ser.Khim., 473 (1967).
6. L.I.Zakharkin and V.N.Kalinin, Izv.Akad.Nauk SSSR, Ser.Khim., 2577 (1967).
7. L.I.Zakharkin and V.N.Kalinin, Izv.Akad.Nauk SSSR, Ser.Khim., 2310 (1971).
8. L.I.Zakharkin and V.N.Kalinin, Izv.Akad.Nauk SSSR, Ser.Khim., 2585 (1967).
9. L.I.Zakharkin, V.N.Kalinin, and V.V.Gedymin, J.Organometal.Chem., **16**, 371 (1969).
10. V.A.Brattsev and V.I.Stanko, Zhur.Obshch.Khim., **39**, 2144 (1969).
11. V.N.Kalinin, Doctoral Thesis, Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow, 1977.
12. L.I.Zakharkin, V.N.Kalinin, N.P.Skvortsova, and V.V.Gedymin, USSR P.507575 (1976); Byul. Izobret., No.11 (1976).
13. L.I.Zakharkin, V.N.Kalinin, and V.V.Gedymin, Izv.Akad.Nauk SSSR, Ser.Khim., 1669 (1976).
14. V.V.Korshak, N.I.Bekasova, L.G.Komarova, L.I.Zakharkin, V.N.Kalinin, and V.M.Dmitirev, USSR P.539907 (1976); Byul.Izobret., No.47 (1976).
15. V.V.Korshak, N.I.Bekasova, L.G.Komarova, L.I.Zakharkin, and V.N.Kalinin, USSR P.569584 (1977); Byul.Izobret., No.31 (1977).
16. L.I.Zakharkin, V.N.Kalinin, and L.S.Podvisotskaya, Izv.Akad.Nauk SSSR, Ser.Khim., 2310 (1967).
17. L.I.Zakharkin, V.N.Kalinin, V.V.Gedymin, and G.S.Dzarasova, J.Organometal.Chem., **23**, 303 (1970).
18. L.I.Zakharkin and V.N.Kalinin, Izv.Akad.Nauk SSSR, Ser.Khim., 685 (1968).
19. L.I.Zakharkin, V.N.Kalinin, and V.V.Gedymin, Zhur.Obshch.Khim., **40**, 2653 (1970).
20. L.I.Zakharkin, V.N.Kalinin, B.A.Kvasov, and E.I.Fedin, Izv.Akad.Nauk SSSR, Ser.Khim., 2415 (1968).
21. L.I.Zakharkin, V.N.Kalinin, and V.V.Gedymin, Zhur.Obshch.Khim., **44**, 708 (1974).
22. L.I.Zakharkin, V.N.Kalinin, and E.G.Rys, Synth. React.Inorg.Met.-Org.Chem., 5, 257 (1975).
23. T.V.Potapova and B.M.Mikhailov, Izv.Akad.Nauk SSSR, Ser.Khim., 2367 (1967).
24. J.S.Roscoe, S.Kongpricha, and S.Papetti, Inorg. Chem., **9**, 1561 (1970).
25. I.Ugi, Angew.Chem., **70**, 702 (1958).
26. L.I.Zakharkin, V.N.Kalinin, and V.V.Gedymin, Izv.Akad.Nauk SSSR, Ser.Khim., 1209 (1970).
27. L.I.Zakharkin, V.N.Kalinin, and V.V.Gedymin, Synth.Inorg.Met.-Org.Chem., 1,45 (1971).
28. L.I.Zakharkin, V.N.Kalinin, and V.V.Gedymin, Synth.Inorg.Met.-Org.Chem., **3**, 93 (1973).
29. L.I.Zakharkin, V.N.Kalinin, and V.V.Gedymin, Zhur.Obshch.Khim., **43**, 1974 (1973).
30. V.I.Stanko and Yu.V.Gol'tyapin, Zhur.Obshch. Khim., **46**, 1418 (1976).
31. V.I.Stanko, Yu.V.Gol'tyapin, T.P.Klimova, N.I.Kirillova, and Yu.T.Struchkov, Zhur.Obshch. Khim., **47**, 2248 (1977).
32. N.I.Kirillova, Yu.V.Gol'tyapin, Yu.T.Struchkov, and V.I.Stanko, Zhur.Strukt.Khim., **17**, 68 (1976).
33. S.L.Clark and D.I.Mangold, US P.3092664 (1963); Chem.Abs., **59**, 11555 (1963).
34. L.I.Zakharkin, I.V.Pisareva, and R.Kh.Bikkineev, Izv.Akad.Nauk SSSR, Ser.Khim., **641** (1977).
35. T.L.Heying, J.W.Ager, S.L.Clark, D.I.Mangold, H.L.Goldstein, M.Hillman, R.J.Polak, and J.W.Szymanski, Inorg.Chem., **2**, 1089 (1963).
36. M.F.Hawthorne and P.A.Wegner, J.Amer.Chem.Soc., **87**, 4392 (1965).
37. M.F.Hawthorne and P.A.Wegner, J.Amer.Chem.Soc., **90**, 896 (1968).
38. B.M.Mikhailov and T.V.Potapova, Izv.Akad.Nauk SSSR, Ser.Khim., 1629 (1967).
39. L.I.Zakharkin and V.N.Kalinin, Izv.Akad.Nauk SSSR, Ser.Khim., 1423 (1968).
40. L.I.Zakharkin, E.I.Kukulina, and L.S.Podvisotskaya, Izv.Akad.Nauk SSSR, Ser.Khim., 1866 (1966).

41. L.I.Zakharkin, V.N.Kalinin, and I.P.Shepilov, Izv.Akad.Nauk SSSR, Ser.Khim., 1286 (1966).
42. L.I.Zakharkin, V.N.Kalinin, and I.P.Shepilov, Dokl.Akad.Nauk SSSR, **174**, 606 (1967).
43. L.I.Zakharkin, V.N.Kalinin, A.P.Snyakin, and B.A.Kvasov, J.Organometal.Chem., **18**, 19 (1969).
44. R.G.Adler and M.F.Hawthorne, J.Amer.Chem.Soc., **92**, 6174 (1970).
45. L.I.Zakharkin and V.N.Kalinin, Zhur.Obshch.Khim., **43**, 853 (1973).
46. V.N.Kalinin, N.I.Kobel'kova, and L.I.Zakharkin, Zhur.Obshch.Khim., **47**, 963 (1977).
47. V.N.Kalinin, N.I.Kobel'kova, A.V.Astakhin, and L.I.Zakharkin, Izv.Akad.Nauk SSSR, Ser.Khim., 2376 (1977).
48. V.N.Kalinin, N.I.Kobelkova, A.V.Astahin, A.I.Gusev, and L.I.Zakharkin, J.Organometal. Chem., **149**, 9 (1978).
49. V.N.Kalinin, N.I.Kobel'kova, and L.I.Zakharkin, Zhur.Obshch.Khim., **48**, 938 (1978).
50. V.N.Kalinin, N.I.Kobelkova, and L.I.Zakharkin, J.Organometal.Chem., **172**, 391 (1979).
51. V.F.Mironov, V.I.Grigos, and S.Ya.Pechurina, USSR P.412198 (1973); Byul.Izobret., No.3 (1974).
52. V.F.Mironov, V.I.Grigos, S.Ya.Pechurina, and A.F.Zhigach, Zhur.Obshch.Khim., **42**, 2583 (1972).
53. V.F.Mironov, V.I.Grigos, and S.Ya.Pechurina, USSR P.425913 (1974); Byul.Izobret., No.16 (1974).
54. V.F.Mironov, V.I.Grigos, S.Ya.Pechurina, A.F.Zhigach, and V.N.Siryatskaya, Dokl.Akad.Nauk SSSR, **210**, 601 (1973).
55. S.Ya.Pechurina, Candidate's Thesis, GNIIKhTEOS MKhP SSSR, Moscow, 1975.
56. S.N.Gurkova, N.V.Alekseev, A.I.Gusev, S.Ya.Pechurina, and V.I.Grigos, Zhur.Strukt.Khim., **18**, 384 (1977).
57. V.S.Nikitin, V.I.Grigos, and S.Ya.Pechurina, Zhur.Obshch.Khim., **46**, 1508 (1976).
58. V.N.Bochkarev, A.I.Polivanov, S.Ya.Pechurina, and V.I.Grigos, Zhur.Obshch.Khim., **43**, 681 (1973).
59. V.N.Bochkarev, A.N.Polivanov, V.I.Grigos, and S.Ya.Pechurina, Zhur.Obshch.Khim., **43**, 2407 (1973).
60. L.I.Zakharkin, V.N.Kalinin, and N.I.Kobelkova, Synth.React.Inorg.Met.-Org.Chem., **6**, 91 (1976).
61. V.I.Grigos, S.Ya.Pechurina, A.T.Gladchenko, and V.F.Mironov, Zhur.Obshch.Khim., **45**, 2098 (1975).
62. V.F.Mironov, S.Ya.Pechurina, and V.I.Grigos, Dokl.Akad.Nauk SSSR, **230**, 865 (1976).
63. L.I.Zakharkin, V.N.Kalinin, and V.V.Gedymin, Tetrahedron, **23**, 1317 (1971).
64. A.I.L'vov, Candidate's Thesis, Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow, 1968.
65. V.V.Gedymin, Candidate's Thesis, Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow, 1973.
66. W.H.Knoth, J.C.Saver, I.H.Balthis, H.C.Miller, and E.L.Muetterlies, J.Amer.Chem.Soc., **89**, 4842 (1967).
67. W.H.Knoth, J.C.Saver, D.C.England, W.R.Hertler, and E.L.Muetterties, J.Amer.Chem.Soc., **86**, 3973 (1964).
68. V.F.Mironov, V.I.Grigos, S.Ya.Pechurina, A.F.Zhigach, and V.N.Siryatskaya, Symposium, "Khimiya Elementoorganicheskikh Soedinenii" (The Chemistry of Organoelemental Compounds), Izd.Khimiya, Leningrad, 1976, p.24.
69. L.I.Zakharkin, V.N.Kalinin, and L.S.Podvisotskaya, Izv.Akad.Nauk SSSR, Ser.Khim., 1713 (1965).
70. L.I.Zakharkin, V.N.Kalinin, and L.S.Podvisotskaya, Zhur.Obshch.Khim., **36**, 1786 (1966).
71. V.A.Brattsev and V.I.Stanko, Zhur.Obshch.Khim., **40**, 1664 (1970).
72. V.I.Stanko, V.A.Brattsev, N.N.Ovsyannikov, and T.P.Klimova, Zhur.Obshch.Khim., **44**, 2482 (1974).
73. V.A.Brattsev, S.P.Knyazev, G.N.Danilova, T.N.Vostrikova, and V.I.Stanko, Zhur.Obshch. Khim., **46**, 2752 (1976).
74. W.Gerrard, "The Organic Chemistry of Boron" Academic Press, London, 1961 (Translated into Russian), Izd.Khimiya, Leningrad, 1966.
75. V.N.Kalinin and L.I.Zakharkin, Izv.Akad.Nauk SSSR, Ser.Khim., 2353 (1971).
76. L.I.Zakharkin, V.N.Kalinin, and N.I.Kobelkova, Synth.React.Inorg.Met.-Org.Chem., **6**, 65 (1976).
77. A.V.Astakhin, V.N.Kalinin, V.V.Romanov, A.I.Gusev, N.I.Kobel'kova, and L.I.Zakharkin, Zhur.Strukt.Khim., **19**, 555 (1978).
78. J.Plešek and S.Heřmanek, Chem.Ind.(London), 360 (1977).
79. J.Plešek and S.Heřmanek, Coll.Czech.Chem.Comm., **43**, 1325 (1978).
80. J.Plešek, Z.Janousek, and S.Heřmanek, Coll. Czech.Chem.Comm., **43**, 1332 (1978).
81. L.I.Zakharkin, I.V.Pisareva, and T.Agakhanova, Izv.Akad.Nauk SSSR, Ser.Khim., 2831 (1978).
82. L.I.Zakharkin and L.V.Orlova, Izv.Akad.Nauk SSSR, Ser.Khim., 2417 (1970).
83. L.I.Zakharkin and L.V.Orlova, Izv.Akad.Nauk SSSR, Ser.Khim., 1847 (1971).
84. L.I.Zakharkin and L.V.Orlova, Izv.Akad.Nauk SSSR, Ser.Khim., 209 (1972).
85. L.I.Zakharkin, L.V.Orlova, B.V.Lokshin, and L.A.Fedorov, J.Organometal.Chem., **40**, 15 (1972).
86. L.V.Orlova, Candidate's Thesis, Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow, 1972.
87. L.I.Zakharkin, L.V.Orlova, and L.I.Denisovich, Zhur.Obshch.Khim., **42**, 2217 (1972).
88. V.I.Bregadze, V.Ts.Kampel, and N.N.Godovikov, J.Organometal.Chem., **112**, 249 (1976).
89. V.I.Bregadze, V.Ts.Kampel, and N.N.Godovikov, J.Organometal.Chem., **136**, 281 (1977).
90. V.I.Bregadze, V.Ts.Kampel', and N.N.Godovikov, Izv.Akad.Nauk SSSR, Ser.Khim., 1630 (1977).
91. L.I.Zakharkin and I.V.Pisareva, Izv.Akad.Nauk SSSR, Ser.Khim., 1885 (1977).
92. V.I.Bregadze, V.Ts.Kampel', A.Ya.Usyatinskii, and N.N.Godovikov, Izv.Akad.Nauk SSSR, Ser. Khim., 1467 (1978).
93. V.I.Bregadze, V.Ts.Kampel, A.Ya.Usiatinskii, and N.N.Godovikov, J.Organometal.Chem., **154**, C1 (1978).
94. V.Ts.Kampel', K.P.Butin, V.I.Bregadze, and N.N.Godovikov, Izv.Akad.Nauk SSSR, Ser.Khim., 1454 (1977).
95. V.Ts.Kampel', K.P.Butin, V.I.Bregadze, and N.N.Godovikov, Izv.Akad.Nauk SSSR, Ser.Khim., 1508 (1978).
96. L.I.Zakharkin and I.V.Pisareva, Izv.Akad.Nauk SSSR, Ser.Khim., 1226 (1978).
97. V.I.Bregadze, V.Ts.Kampel', and N.N.Godovikov, Izv.Akad.Nauk SSSR, Ser.Khim., 1951 (1978).
98. V.I.Bregadze, V.Ts.Kampel, and N.N.Godovikov, J.Organometal.Chem., **157**, C1 (1978).

99. L.I.Zakharkin and I.V.Pisareva, Izv.Akad.Nauk SSSR, Ser.Khim., 1950 (1978).
100. L.I.Zakharkin and I.V.Pisareva, Izv.Akad.Nauk SSSR, Ser.Khim., 252 (1978).
101. E.L.Hoel and M.F.Hawthorne, J.Amer.Chem.Soc., **95**, 2712 (1973).
102. E.L.Hoel and M.F.Hawthorne, J.Amer.Chem.Soc., **97**, 6388 (1975).
103. E.L.Hoel and M.F.Hawthorne, J.Amer.Chem.Soc., **96**, 6770 (1974).
104. M.F.Hawthorne, T.E.Berry, and P.A.Wegner, J.Amer.Chem.Soc., **87**, 4746 (1965).
105. L.I.Zakharkin, V.N.Kalinin, and E.G.Rys, Izv.Akad. Nauk SSSR, Ser.Khim., 2632 (1974).
106. K.Wade, Adv.Inorg.Radiochemistry, **18**, 1 (1976).
107. V.I.Stanko, V.V.Khrapov, and T.A.Babushkina, Uspekhi Khim., **43**, 1357 (1974) [Russ.Chem.Rev., No.8 (1974)].
108. L.E.Vinogradova, L.A.Leites, V.V.Gedymin, V.N.Kalinin, and L.I.Zakharkin, Izv.Akad.Nauk SSSR, Ser.Khim., 2817 (1973).
109. V.N.Kalinin, E.S.Petrov, N.I.Terekhova, N.I.Kobel'kova, L.I.Zakharkin, and A.I.Shatenshtein, Izv.Akad.Nauk SSSR, Ser.Khim., 2828 (1976).
110. Yu.A.Ol'dekop, N.A.Maier, A.A.Erdman, and V.P.Prokopovich, Dokl.Akad.Nauk SSSR, **243**, 933 (1978).
111. Yu.A.Ol'dekop and L.A.Churkina, Zhur.Obshch. Khim., **48**, 2628 (1978).
112. V.N.Kalinin, N.I.Kobel'kova, and L.I.Zakharkin, Zhur.Obshch.Khim., **50**, 919 (1980).
113. L.I.Zakharkin and I.V.Pisareva, Izv.Akad.Nauk SSSR, Ser.Khim., 1886 (1979).
114. V.I.Bregadze, A.Ya.Usyatinskii, and N.N.Godovikov, Izv.Akad.Nauk SSSR, Ser.Khim., 1876 (1979).
115. L.I.Zakharkin, A.I.Kovredov, V.A.Ol'shevskaya, and Zh.S.Shaugumbetova, Izv.Akad.Nauk SSSR, Ser.Khim., 1691 (1980).

Institute of Organoelemental Compounds,
USSR Academy of Sciences, Moscow

Translated from *Uspekhi Khimii*, **49**, 2213-2240 (1980) U.D.C. 541.128 + 541.64

The Mechanism of the Catalytic Polymerisation of Olefins Based on the Number of Active Centres and the Rate Constants for Individual Stages

V.A.Zakharov, G.D.Bukatov, and Yu.I.Ermakov

New data on the numbers of active centres and rate constants for individual stages in the catalytic polymerisation of olefins in the presence of two-component catalysts, obtained by the method of selective radioactive inhibitors, are considered. Certain general aspects of the mechanism of the catalytic polymerisation of olefins are examined on the basis of these data as well as the results of the study of one-component organometallic catalysts and quantum-chemical investigations of the propagation reaction.
The bibliography includes 102 references.

CONTENTS

I. Introduction 1097
II. Determination of the number of propagation centres using selective radioactive inhibitors 1097
III. The number of propagation centres and propagation rate constants for catalysts based on titanium chlorides 1100
IV. The mechanism of the propagation reaction 1102
V. Polymer chain transfer reactions 1107
VI. Conclusion 1108

I. INTRODUCTION

One of the main problems arising in the study of the kinetics and mechanism of catalytic polymerisation involves the determination of the number of active centres (AC). The active centre (propagation centre) is understood as a transition metal compound containing metal–carbon alkyl-type σ-bond whereby the monomer is inserted in this bond via repeated addition steps:

$$L_xM-CH_2\sim\sim + CH_2=CH_2 \rightarrow L_xM-CH_2-CH_2-CH_2\sim\sim, \qquad (I)$$

where M is the metal, L_x are ligands, and $CH_2\sim\sim$ is the polymer chain.

For solid catalysts, the active centre is an organometallic surface compound. Information about the influence of the composition and conditions of the preparation of the catalyst, the polymerisation conditions, and the nature of the monomer on the number and reactivity of the AC constitutes the basis of the study of processes involving the formation of AC, their composition, and the polymerisation mechanism.

The difficulty of determining the number of AC arises from the fact that this quantity constitutes as a rule a small fraction of the total number of transition metal atoms in the catalyst. Studies designed to determine the number of AC in the catalytic polymerisation of olefins were begun by Natta[1,2], Chien[3], and Feldman and Perry[4]. Subsequently numerous investigations were devoted to this problem and have been considered in a number of reviews[5–9]. The greatest difficulties in the determination of the number of AC arise for polymerisation in the presence of two-component Ziegler–Natta catalysts, since in this case the reaction medium contains, apart from the active titanium–polymer bonds, also inactive aluminium–polymer bonds, formed as a result of the transfer of the polymer chain with the organoaluminium compound. It has therefore been suggested that selective radioactive inhibitors, which interact, like the olefin, with the active transition metal–polymer bond but not with aluminium–polymer bonds, be used to determine the number of AC in two-component systems[10,11]. This approach to the determination of the number of AC has been used recently to investigate catalytic systems based on titanium chlorides. A series of new data were obtained concerning the influence of the composition of the catalyst and the polymerisation conditions on the number of AC and the rate constants for the individual stages; together with the results of the study of polymerisation mechanism in the presence of one-component organometallic catalysts and individual organometallic compounds as well as quantum-chemical investigations of the mechanism of the propagation reaction, these data make it possible to consider certain general aspects of the mechanism of the propagation reaction in catalytic polymerisation.

II. DETERMINATION OF THE NUMBER OF PROPAGATION CENTRES USING SELECTIVE RADIOACTIVE INHIBITORS

1. General Remarks Concerning the Method

The determination of the number of AC by the method of radioactive inhibitors is based on the introduction of a radioactive label into the growing polymer chain when the inhibitor interacts with the active metal–polymer bond:

$$L_xM-CH_2\sim\sim + RO^3H \rightarrow L_xM-OR + {}^3HCH_2\sim\sim. \qquad (IIa)$$

Calculations of the number of AC (c_p = mol per mol of transition metal) and the propagation rate constant (k_p) are performed using the following equations:

$$c_p = Ag/aQ, \qquad (1)$$

$$k_p = v/3{,}6c_p c_m M, \qquad (2)$$

where A is the radioactivity of the polymer (c g^{-1}), g the amount of the polymer (g), a the amount of the catalyst (mol of transition metal), Q the specific radioactivity of the inhibitor (c mol^{-1}), k_p the propagation rate constant (litre mol^{-1} s^{-1}), v the rate of polymerisation at the instant of the introduction of the inhibitor (g per mmol of transition metal per hour), c_m the concentration of the monomer (M), and M the molecular weight of the monomer.

The principal criteria for the quantitative determination of c_p are as follows: (1) agreement between the values of c_p and k_p obtained using different inhibitors, interacting with

the metal–polymer active bond via different mechanisms; (2) the independence of the k_p determined with the aid of the same inhibitor of the polymerisation termination conditions, for example, of the concentration and specific radioactivity of the inhibitor, its residence time in the reaction medium after the cessation of polymerisation, the rate of polymerisation at the instant of the introduction of the inhibitor, etc.

Table 1. The values of c_p and k_p for the polymerisation of ethylene in the presence of $TiCl_2$ at 75 °C with $c_m = 0.33$ M (residence time of ^{14}CO in the reaction medium 20 min).

Inhibitor	Q, μc mol^{-1}	c_i, mol/mol Ti	v, s/mmol Ti h	$10^5 c_p$, mol/mol Ti	$10^{-4}k_p$, litre mol^{-1} s^{-1}	Refs.
^{14}CO	1210	0.01	9.2	2.3	1.2	10
$^{14}CO_2$	2760	0.04	14.5	3.4	1.25	10,16
$^{14}C_3H_7I$	450	0.85	7.5	2.2	1.0	10,15
$^{35}SO_2$	2230	0.02	20	4.5	1.35	16
$CH_3O^{32}H$	2680	0.14	37	3.6	31	16

Note. Q is the specific activity of the inhibitor, c_i the concentration of the inhibitor, and γ the kinetic isotopte effect.

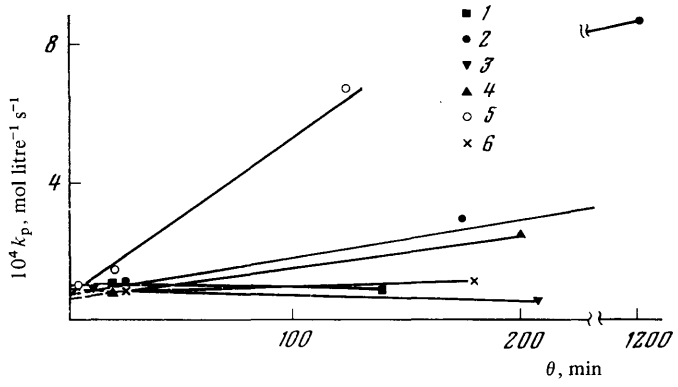


Figure 1. Dependence of the calculated quantity $1/k_p$ on the residence time of inhibitors of various types in the reaction medium after the cessation of polymerisation at 75 °C; $[C_2H_4] = 0.33$ M;[18] 1)–3) $TiCl_2$ catalyst; 4)–6) $TiCl_2$ + $AlEt_2Cl$ catalyst (Al/Ti = 1); 1) and 4) $^{14}CO_2$; 2) and 5) ^{14}CO; 3) and 6) $^{35}SO_2$. $1/k_p$ is proportional to the number of radioactive labels in the polymer.

^{14}CO and $^{14}CO_2$ have been suggested as selective inhibitors[10,11]. Labelled carbon dioxide can be used to determine the number of active bonds (for example Ti–C) in the presence of organoaluminiumhalogeno-compounds:

$$L_xTi{-}CH_2{\sim\!\sim} + {}^{14}CO_2 \rightarrow L_xTi{-}O{-}\overset{\overset{O}{\|}}{{}^{14}C}{-}CH_2{\sim\!\sim}. \qquad \text{(IIb)}$$

It is known that, in contrast to trialkyl derivatives of aluminium, CO_2 does not interact with the Al–C bond when even one alkyl group at the aluminium atom is substituted by a halogen[12]. The use of ^{14}CO as the selective inhibitor is based on the familiar reaction involving the insertion of carbon monoxide in the transition metal–carbon bond[13]:

$$L_xM{-}R + CO \rightleftarrows \underset{\downarrow}{\overset{CO}{L_xM}}{-}R \rightarrow L_xM{-}\overset{\overset{O}{\|}}{C}{-}R. \qquad \text{(IIc)}$$

This reaction proceeds via the preliminary coordination of CO to the transition metal ion, as has been suggested for the olefin in the polymer chain propagation reaction[14].

2. The Use of Radioactive Inhibitors for One-Component Catalysts

The possibility of using ^{14}CO and $^{14}CO_2$ for the quantitative determination of c_p has been tested[10,14,16] on the one-component $TiCl_2$ catalyst active in the absence of an organoaluminium cocatalyst. The propagation rate constants in the polymerisation of ethylene in the presence of $TiCl_2$, determined with the aid of various inhibitors, are similar (Table 1). A more convenient inhibitor for the above catalytic system is $^{14}CO_2$, since, unlike the system with ^{14}CO, in this case there is no accumulation of the labels in the polymer as a function of the residence time of the inhibitor in the reaction medium (Fig.1). Quantiative data for the interaction of $^{14}CO_2$ with the propagation centre in the polymerisation of ethylene in the presence of $TiCl_2$ have been obtained[16] in experiments where the polymerisation termination conditions were varied (the concentration of the inhibitor, its specific radioactivity, the rate of polymerisation at the instant of termination, the yield of polymer, etc).

3. The Use of Selective Inhibitors for Two-Component Catalysts

A preliminary study of the possibility of determining c_p with the aid of ^{14}CO and $^{14}CO_2$ in the presence of organoaluminium compounds was made in the presence of the $TiCl_2$ + $AlEt_2Cl$ catalytic system[9,10]. With increased residence time of these inhibitors in the reaction medium after the cessation of polymerisation, an increase in the number of labels in the polymer is observed, and hence a decrease of the calculated k_p (Fig.1). The increase of the number of labels in the $TiCl_2$ + $AlEt_2Cl$ + $^{14}CO_2$ system (Fig.1, curve *4*) can apparently be accounted for by the regeneration of the active centre by the organoaluminium compound:

$$L_xTi{-}O{-}\overset{\overset{O}{\|}}{{}^{14}C}{-}CH_2{\sim\!\sim} + AlEt_2Cl \rightarrow L_xTi{-}Et + EtAl(Cl){-}O{-}\overset{\overset{O}{\|}}{{}^{14}C}{-}CH_2{\sim\!\sim}. \qquad \text{(IId)}$$

The involvement of $AlEt_2Cl$ in this process is indicated by the finding that the number of labels in the polymer in the presence of the $TiCl_2$ + $^{14}CO_2$ system (in the absence of $AlEt_2Cl$) is almost independent of the residence time of $^{14}CO_2$ in the reaction medium (Fig.1, curve *1*).

In the $TiCl_2$ + $AlEt_2Cl$ + ^{14}CO system the increase of the number of labels in the polymer with the residence time of ^{14}CO (Fig.1) can be attributed to the slow copolymerisation of carbon monoxide with the olefin, apart from a reaction analogous to (IId). The possibility of this reaction was demonstrated in the polymerisation of ethylene in the presence of the $TiCl_2$ one-component catalyst, for which there is no reaction (IId). It was found that, for a sufficiently long residence time of ^{14}CO (more than 20 min), the number of labels in the polymer exceeds the number of propagation centres determined using other inhibitors[14].

The possibility of a quantitative determination of the number of propagation centres with the aid of ^{14}CO has been tested in detail on the $TiCl_2$ + $AlEt_2Cl$ [10] and $TiCl_3.0.3AlCl_3$ +

$AlEt_3$ [17] catalytic systems in the polymerisation of ethylene and on the $TiCl_3.0.3AlCl_3$ + $AlEt_2Cl$ system[11,17,18] in the polymerisation of propene and the following data were obtained.

(1) The nature of the variation of the number of labels in the polymer with the residence time of ^{14}CO after the cessation of polymerisation indicates a sharp alteration of the rate of accumulation of labels in the first minutes after the termination of polymerisation (Fig.2).[18] Apparently there is initially a fairly rapid insertion of the first ^{14}CO molecule in the Ti–C bond, after which a slow increase of the number of labels in the polymer is observed as a result of the copolymerisation of ^{14}CO with the olefin. It is noteworthy that the processes involving the accumulation of labels in the polymer as a function of the inhibitor residence time are fairly slow when either ^{14}CO or $^{14}CO_2$ are used. Extrapolation of the number of labels to the initial instant, when the influence of side processes leading to the accumulation of radioactivity has been reduced to a minimum, shows (Fig.1) that, regardless of the inhibitor employed, the constant k_p in the polymerisation of ethylene in the presence of $TiCl_2$ lies within a fairly narrow range of values [$(1.5 \pm 0.5) \times 10^4$ litre mol^{-1} s^{-1}].

(2) the insertion of ^{14}CO in the Ti–C bond is an irreversible process (there is no decarboxylation reaction), which is indicated by the conservation of the number of labels in the polymer after the removal of ^{14}CO from the reaction medium, despite the restoration of the activity of the catalytic system under these conditions[18].

(3) The copolymerisation process can be stopped by adding phosphine to the reaction medium. The constant k_p, determined from the number of labels in experiments with the addition of PH_3 for long reaidence times of the ^{14}CO + PH_3 mixture in the reaction medium, is close to the value of k_p found for short residence times of ^{14}CO.[11]

(4) The constant k_p calculated from the number of labels after a short residence time of ^{14}CO is independent of the polymerisation termination conditions—the inhibitor concentration, the yield of the polymer, the surface concentration of the propagation centres, etc.[17]

(5) As for the catalysts based on $TiCl_2$, the value of k_p found using ^{14}CO for the $TiCl_3$ + $AlEt_2Cl$ + C_3H_6 system is close to that found with the aid of another inhibitor—$^{14}CO_2$.[11]

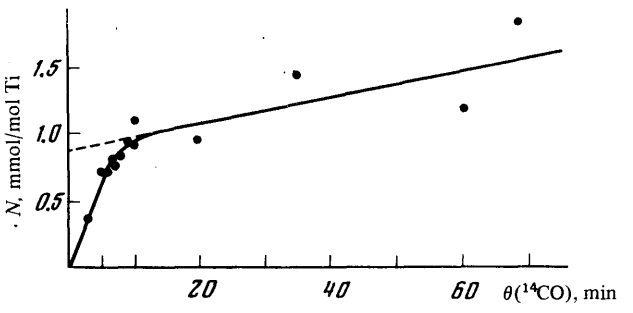


Figure 2. Dependence of the number of labels (N) in non-atactic polypropylene on the residence time of ^{14}CO in the reaction medium after the cessation of polymerisation[18]; catalyst—δ-$TiCl_3.0.3AlCl_3$ + $AlEt_2Cl$; 70 °C; [Ti] = (1–2) × 10^{-3} M; [$AlEt_2Cl$] = 3 × 10^{-3} M; [C_3H_6] = 1 M; molar ratio $^{14}CO/Ti$ = 0.5–1.0.

Thus a quantitative determination of c_p and k_p in the polymerisation of olefins in the presence of two-component catalysts is possible when the ^{14}CO and $^{14}CO_2$ selective catalysts are used. ^{14}CO is preferable, since $^{14}CO_2$ is a less effective inhibitor (at the same concentrations) than ^{14}CO and can be used only in two-component systems containing a halogen-substituted cocatalyst.

4. The Use of an Alcohol RO^3H as an Inhibitor

The use of an alcohol RO^3H as an inhibitor in two-component catalysts is possible, as stated previously[19], when the following factors are taken into account. Firstly, in the case of non-stationary polymerisation kinetics, where c_p varies with the reaction time, the number of propagation centres must be determined from the dependence of the total number of metal–polymer bonds on the yield of the polymer but not on the polymerisation time. Secondly, the use of an alcohol for the determination of c_p is possible when the number of inactive metal–polymer bonds differs comparatively little from c_p. This can be observed either for very low yields of the polymer or under conditions and for catalytic systems such that the rate of formation of inactive metal–polymer bonds is fairly low, for example, in the polymerisation of 4-methylpent-1-ene in the presence of VCl_3 + $Al(iso\text{-}Bu)_3$.[20] Thirdly, in the study of the influence of polymerisation conditions and catalyst composition on the number of propagation centres, account must be taken of the fact that, when these parameters are varied, there is a possibility also of a change in the rate of formation of metal–polymer bonds.

Table 2. The values of ν_{max}, c_p^{max}, and k_p for "massive" and deposited catalysts based on titanium chlorides.

Catalyst	Cocatalyst [(3–10) × 10^{-3} M]	ν_{max}, g/polymer/mmol Ti h atm	$10^4 c_p^{max}$, mol/mol Ti	$10^{-2}k_p$, litre mol^{-1} s^{-1}
Polymerisation of ethylene, 75 °C				
$TiCl_2$	—	8.0	1.1	120[10,16]
$TiCl_2$	$AlEt_2Cl$	5.5	0.75	120[10]
α-$TiCl_3$	$AlEt_3$	35.0	4.0	140[17]
δ-$TiCl_3$·0,3 $AlCl_3$	$AlEt_3$	72.0	9.7	120[17]
δ-$TiCl_3$·0,3 $AlCl_3$	$Al(iso\text{-}Bu)_3$	96.0	11.2	140[17]
$TiCl_3$ on SiO_2	$AlEt_3$	960	110	140[23]
α-$TiCl_3$·0,5 $AlCl_3$ on polyethylene	$AlEt_3$	720	89	130[23]
$TiCl_4$ on R_xMgCl_y	$AlEt_3$	29 000	3600	130[23]
Polymerisation of propene, 70 °C				
$TiCl_2$	—	0.005	0.013	0.76[10]
$TiCl_2$	$AlEt_2Cl$	0.004	0.0085	0.94[10]
α-$TiCl_3$	$AlEt_2Cl$	0.11	0.33	0.71[17]
δ-$TiCl_3$·0,3 $AlCl_3$	$AlEt_2Cl$	7.7	17	0.90[11,17]
δ-$TiCl_3$·0,3 $AlCl_3$	$AlEt_3$	28	58	1.00[17]
δ-$TiCl_3$·0,3$AlCl_3$	$Al(iso\text{-}Bu)_3$	36	80	0.90[17]
α-$TiCl_3$·0,5$AlCl_3$ on polyethylene	$AlEt_2Cl$	10	20	1.0

Note. In the case of the polymerisation of propene data are given for the polymer fractions insoluble in boiling ether (for $TiCl_3$) and n-heptane (for $TiCl_2$).

The correct application of a radioactive alcohol as an inhibitor enabled some workers to obtain values of k_p = 20–50 litre mol^{-1} s^{-1} in the polymerisation of propene in the presence of the $TiCl_3$ + organoaluminium cocatalyst system[21,22], differing comparatively little from the corresponding k_p obtained with the aid of ^{14}CO and $^{14}CO_2$ (Table 2).

III. THE NUMBER OF PROPAGATION CENTRES AND PROPAGATION RATE CONSTANTS FOR CATALYSTS BASED ON TITANIUM CHLORIDES

1. The Number and Composition of Propagation Centres

The number of AC depends significantly on the catalyst preparation and polymerisation conditions (for example, the purity of the reactants). When problems concerning the composition of the AC and the mechanism of their formation are considered, data concerning the maximum number of AC (c_p^{max}) for the system investigated are important. The quantity c_p^{max} can be calculated from the maximum observed rate of polymerisation and k_p for the given catalytic system.

Table 2 presents the values of c_p^{max} for different catalytic systems based on titanium chlorides[24]. Evidently the conditions in the preparation of titanium chlorides and the catalyst composition as well as the nature of the organoaluminium cocatalyst and the monomer influence significantly the number of AC. In the case of the $TiCl_2$ one-component catalyst (specific surface 25 $m^2\ g^{-1}$) the maximum number of propagation centres (approximately 10^{-4} mol per mol of titanium) does not exceed approximately 0.3% of the number of surface titanium atoms[16], which is apparently associated with the fact that the alkylation of titanium ions by ethylene takes place only on surface defects of the $TiCl_2$ crystals with a high degree of coordination unsaturation. Naturally, the fraction of such surface atoms cannot be large. For $TiCl_2$ and $TiCl_3$ 0.1–1 μm crystals (specimens which are not specially activated by grinding), the fraction of surface titanium atoms having one or two chlorine vacancies is 10^{-2}–10^{-3} and 10^{-4}–10^{-6} mol/mol Ti respectively. The latter value agrees with the number of propagation centres for $TiCl_2$ (Table 2).

In typical Ziegler–Natta catalysts based on $TiCl_3$, the number of propagation centres depends significantly on the preparation conditions and composition of titanium trichloride. The maximum number of propagation centres in catalysts based on $TiCl_3$ is 1×10^{-2} mol/mol Ti, i.e. 1% of the total content of titanium ions in the catalyst (Table 2). In estimating the surface concentration of propagation centres, account must be taken of the possibility of a change in the specific surface as a result of the comminution of the catalyst by the crystalline polymer in the polymerisation process; experimental evidence for this has been obtained in a number of studies[25,26]. Comminution of the catalyst in the polymerisation process apparently constitutes the physical basis of the correlation observed[27,28] between the size of the primary crystallites, determined by X-ray diffraction, and the activity in the polymerisation of propene. In this case the number of propagation centres must be referred to the surface area of the primary crystallites (calculated from their dimensions), which is formed in the polymerisation process as a result of the comminution of the catalyst and can be significantly greater than the surface area of the initial catalyst.

When titanium chloride is deposited on silica gel or powdered polyethylene, it is possible to increase the number of propagation centres in the polymerisation of ethylene approximately by an order of magnitude and to attain the same values as in the polymerisation of propene in the presence of massive $TiCl_3$ (Table 2). A finely dispersed $TiCl_3$ phase is formed as the active component on the surface of silica gel and polyethylene[29,30]. The use of these carriers hardly influences the number of propagation centres in the polymerisation of propene (Table 2).

Titanium–magnesium catalysts, obtained by depositing $TiCl_4$ on magnesium chloride or alkylmagnesium chloride, exhibit a maximum activity among all known catalytic systems[31]. In this case the number of AC can reach approximately 40% of the total number of titanium atoms in the catalyst (Table 2). The activity of the above catalysts probably reaches a limiting value for catalytic systems based on titanium chlorides. Strong binding of titanium tetrachloride to magnesium chloride is achieved by the insertion of titanium ions in defect sites of the disordered crystal structure of magnesium chloride[32]. This type of the interaction ("structural" binding) ensures a high degree of utilisation of titanium ions and their stability under the polymerisation conditions[33].

The difference between the activities of catalytic systems based on titanium chlorides, reaching four orders of magnitude (Table 2), is also caused by the change of the number of AC; the reactivity of a single propagation centre for a given olefin hardly changes. These data show that the AC in Ziegler catalysts are monometallic, i.e. their composition includes only one transition metal ion.

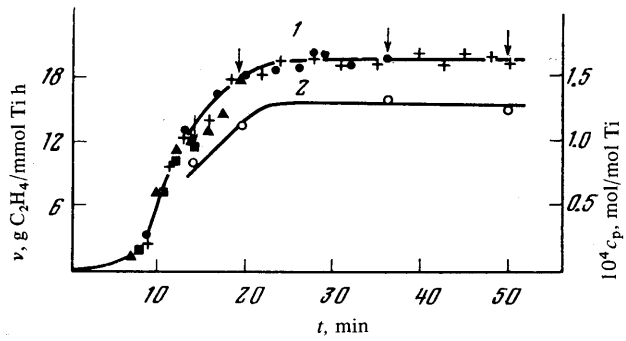


Figure 3. Dependence of the rate (v) of polymerisation of ethylene (curve *1*) and of the number of propagation centres (c_p) (curve *2*) on the polymerisation time *t*; $TiCl_2$ catalyst; 60 °C; $[C_2H_4] = 0.2$ M.[16] The arrows indicate the instants of the introduction of the $^{14}CO_2$ inhibitor in individual experiments where the number of propagation centres was determined.

2. Description of the Kinetics on the Basis of the Number of Propagation Centres

Data have been obtained[16,17,34,35] for the influence of polymerisation conditions (time, monomer concentration, and temperature) on the rate of polymerisation, the number of propagation centres, and the propagation rate constant in the polymerisation of ethylene and propene in the presence of the $TiCl_2$, δ-$TiCl_3.0.3AlCl_3$ + $AlEt_3$, and δ-$TiCl_3.0.3AlCl_3$ + $AlEt_2Cl$ catalysts. The variations of the rate of polymerisation of ethylene and of the number of propagation centres with the reaction time are compared in Fig. 3 for $TiCl_2$. Evidently the rate of polymerisation and the number of AC vary in parallel. Similar relations have been obtained also for other catalysts[17]. These results show that the propagation rate constant being determined is independent of the polymerisation time and of the yield of the polymer. Consequently the

hypotheses, occasionally encountered in the literature, concerning the influence on k_p of the length of the polymer chain or diffusion-dependent limitations in the polymer formed in the presence of such catalysts are not well founded. The constant k_p is independent of the monomer concentration[17,34]; the number of AC , which determines the steady-state reaction rate, is also independent of the monomer concentration.

On the basis of data for the variation of the steady-state rate of polymerisation, k_p, and c_p with the reaction temperature, it is possible to calculate the corresponding effective activation energies E_{eff}, the activation energies for the propagation step E_p, and the temperature coefficient of the change in the number of active centres ($E_{c_p} = E_{eff} - E_p$).

The energies obtained (kcal mol^{-1}) for the polymerisation of ethylene and propene in the presence of titanium trichloride[35] are listed below:

Catalyst	Monomer	E_{eff}	E_p	E_{c_p}
$TiCl_3$+$AlEt_3$	ethylene	6.0	3.0	3.0
$TiCl_3$+$AlEt_2Cl$	propene	11.0	5.5	5.5

Evidently appreciable differences between E_p and E_{eff} are observed for two-component catalysts. This is caused by the increase of the number of propagation centres with increase of polymerisation temperature, which is associated with the reversible adsorption of the organoaluminium cocatalyst on the propagation centres[10,35,36].

The values of E_p found for titanium chlorides are low compared to the activation energy in radical polymerisation (Table 3).

Table 3. The coefficients of the equation $k_p = 10^5 A_p \cdot \exp(-E/RT)$ for the catalytic polymerisation of olefins.

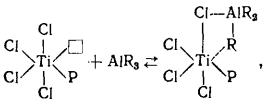
Catalyst	Monomer	A_p, litre mol^{-1} s^{-1}	E_p, cal mol^{-1}	Refs.
CrO_3/SiO_2	C_2H_4	4.5	4 500	37
$TiCl_3$+$AlEt_3$	C_2H_4	8.0	3 000	35
$TiCl_3$+$AlEt_2Cl$	C_2H_4	3.0	5 500	35
$AlEt_3$	C_3H_6	0.02	12 000	62
Radical initiator	C_2H_4	67	5 000	38

3. The Role of the Organometallic Cocatalyst

Comparative study of the one-component $TiCl_2$ catalyst and $TiCl_n$ + AlR_xCl_y two-component systems gives rise to new possibilities for the elucidation of the role of the organometallic cocatalyst in the regulation of the activity and stereospecificity of Ziegler–Natta catalytic systems.

The stereospecificity of the active centres. The data obtained for the polymerisation of propene in the presence of $TiCl_2$ concerning the stereoregular structure of the polymer (60% of X-ray-amorphous atactic polymer and 25% of the highly crystalline fraction)[10,36] show that at least two types of active centres exist on the surface of titanium chloride—non-stereospecific centres leading to the formation of the atactic polymer and isospecific centres giving rise to the stereoregular polymer. The difference between them apparently consists in the number and steric dispositions of the chloride ions surrounding the titanium ion (in conformity with the ideas of Cossee and Arlman[39,40]).

Adsorption of the organoaluminium catalyst on the active centre. It has been shown[9,10] that the rate of polymerisation of ethylene and propene decreases following the addition of $AlEt_2Cl$ to $TiCl_2$. Under these conditions, there is mainly a decrease in the number of non-stereospecific polymerisation centres. This explains the higher stereospecificity of the $TiCl_2$ + $AlEt_2Cl$ system compared with $TiCl_2$ alone. When the organoaluminium cocatalyst (OAC) is added to $TiCl_2$, it apparently undergoes equilibrium adsortion on the AC:



(III)

(P is the polymer chain and □ a free coordination site), as a result of which the propagation centre passes temporarily from the active to the inactive state.

Ideas concerning the possibility of the reversible adsorption of the OAC on the active centres of the VCl_3 + AlR_3 catalyst were also formulated by Tait and coworkers[41].

Analogous processes can occur during chain propagation also in the presence of $TiCl_3$. The adsorption of the OAC on the propagation centres formed on the $TiCl_3$ surface can explain the experimentally observed decrease of c_p with decrease of temperature, i.e. $E_{c_p} > 0$, and with increase of the OAC concentration[42]. The equilibrium constant for the adsorption of $AlEt_3$ on the AC (K_A) of the $TiCl_3.0.3AlCl_3$ + $AlEt_3$ catalytic system was calculated from the temperature variation of c_p. It amounts to $3.9 \times 10^{-10} e^{18\,500/RT}$ litre mol^{-1} [42] and the effective heat of adsorption of $AlEt_3$ on the active centre is approximately 10 kcal mol^{-1} after the subtraction of the heat of dissociation of the dimeric molecule $[AlEt_3]_2$.

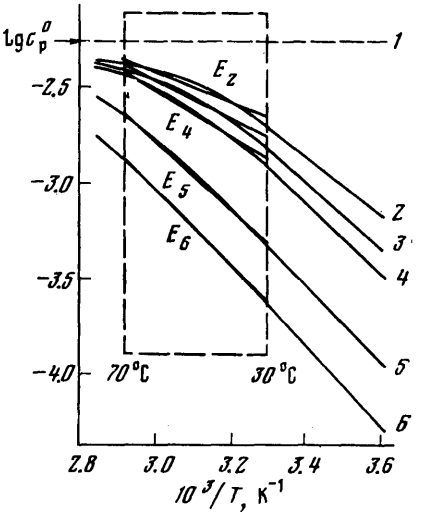


Figure 4. Calculated relations between the number of propagation centres (c_p) and the polymerisation temperature at different $AlEt_3$ concentrations[42]: 1) 0; 2) 6×10^{-3}; 3) 1.5×10^{-2}; 4) 3×10^{-2}; 5) 3×10^{-1}; 6) 1.5; corresponding activation energies (kcal mole^{-1}): $E_2 = 2.8$; $E_4 = 5.0$; $E_5 = 8.3$; $E_6 = 9.2$.

The number of AC (and correspondingly the rate of polymerisation) can be calculated from K_A at different temperatures and $AlEt_3$ concentrations (Fig.4). The temperature coefficient of the change in the number of propagation centres E_{c_p}, characterising the slope of the curves in Fig.4, varies both with polymerisation temperature at the same $AlEt_3$ concentration and as the OAC concentration is varied for the same temperature range. In the range 30–70 °C, which is most commonly investigated, the quantity E_{c_p} varies only slightly with temperature at the same $AlEt_3$ concentration (within the limits of experimental error). More appreciable changes in E_{c_p} in the above temperature range are observed as the $AlEt_3$ concentration is varied (Fig.4, cf. curves *2* and *6*). Thus, at a fairly high OAC concentration, amounting to 1.5 M, calculation leads to the expectation of an increase in the effective activation energy for the polymerisation of ethylene and propene up to 12 and 14.5 kcal mol^{-1} respectively, which is close to the experimental values of E_{eff} obtained under these conditions[42].

It follows from the data in Fig.4 that at low temperatures a change in the OAC concentration can influence c_p appreciably. Indeed at 30 °C in the $AlEt_3$ concentration during the experiment leads to a significant alteration of the rate of polymerisation, which is reversible and agrees satisfactorily with calculated data[42].

The influence of the nature of the organoaluminium cocatalyst on activity and stereospecificity. Since the OAC does not enter into the composition of the propagation centres, the influence of the type of OAC on the catalytic properties can be due to a change in the total number of propagation centres and the ratios of the numbers of centres of different types. In the polymer chain propagation stage this can occur as a result of the adsorption of the OAC on the AC. The influence of the nature of the OAC on the nature and heat of chemisorption can be determined by two factors: the Lewis acidity and the size of the OAC molecule.

Accordingly, in the case of the $TiCl_2$ + AlR_xCl_y catalyst one should expect a decrease of activity in the sequence $AlEt_3$ > $AlEt_2Cl$ > $AlEtCl_2$, which has been confirmed by experimental data[36]. The decrease of the degree of isotacticity of polypropylene in the same sequence can apparently be accounted for by the influence of the size of the OAC on adsorption on centres with different steric environments. Evidently, in adsorption on isospecific propagation centres, which are least accessible, the influence of the size of the OAC molecule is greater than in adsorption on non-stereospecific centres. With decreased size of the OAC molecule, one should expect a decrease in the fraction of isospecific propagation centres in the active state.

For $TiCl_3$, the heat of adsorption also depends on the type of OAC. Among the organoaluminium cocatalysts investigated by the present authors[35], $Al(iso\text{-}Bu)_3$ shows the least tendency towards complex formation and there is correspondingly an insignificant temperature variation of the number of propagation centres in its presence (E_{c_p} = 1.5 kcal mol^{-1}). When $AlEt_2Cl$, with the smallest size and highest Lewis acidity among the cocatalysts employed, is used as a cocatalyst, an appreciable decrease of the number of propagation centres with decrease of polymerisation temperature is observed (E_{c_p} = 5.5 kcal mol^{-1}). For $AlEt_3$, we have E_{c_p} = 3 kcal mol^{-1}.

For two-component catalytic systems based on $TiCl_3$, the influence of the OAC is manifested to a large extent in the stage involving the formation of propagation centres (alkylation of surface titanium ions). For all such catalysts, the nature of the OAC can therefore influence both the total number of AC and the ratios of the propagation centres of different stereospecificity already in the initiation stage and hence can determine the activity and stereospecificity of the catalytic system as a whole. The nature of the transition metal compound can play a significant role in this process. Hence, whereas for one transition metal compound it is possible to observe a particular series based on the changes in stereospecificity as a function of the type of organometallic cocatalyst, for another transition metal compound the series may be completely different[43]. However, despite this, the stereospecific propagation centres for catalysts of different compositions can have the same structure. The ^{13}C NMR data indicating the identical structures of the most stereoregular polymer fraction, insoluble in boiling n-heptane (or octane), for catalysts with different transition metal compounds ($TiCl_2$, δ-$TiCl_3$, β-$TiCl_3$, $CrCl_3$, and $ZrCl_4$) can serve as experimental confirmation of this[44,45].

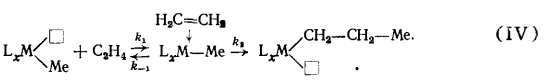
IV. THE MECHANISM OF THE PROPAGATION REACTION

1. One-Stage and Two-Stage Mechanisms

Two main mechanisms of the propagation reaction are considered in the literature.

(1) The one-stage mechanism, in which the propagation reaction takes place as a result of the interaction of a bulk-phase olefin molecule directly with the metal–carbon bond[5,7,46]; in this case the rate of the propagation reaction corresponds to the rate of the insertion reaction.

(2) The two-stage mechanism proposed by Natta[47] and analysed in greater detail by Cossee[48]. According to this mechanism, the propagation reaction includes a preliminary stage, in which the olefin is adsorbed on the transition metal ion with subsequent insertion of the adsorbed olefin in the metal–carbon bond:



(IV)

In this case the experimental constant k_p is defined by the following expression:

$$k_p = k_1k_2/(k_2 + k_{-1} + k_1c_m). \quad (3)$$

Depending on the ratios of the rate constants for the individual elementary stages, the following instances can be observed:

$$\text{(a)}\ k_2 \gg k_{-1} + k_1c_m,\ k_p = k_1; \quad (4)$$

$$\text{(b)}\ k_{-1} \gg k_2 + k_1c_m,\ k_p = k_2k_1/k_{-1}; \quad (5)$$

$$\text{(c)}\ k_1c_m \gg k_{-1} + k_2;\ k_p = k_2/c_m. \quad (6)$$

The observed first order kinetics of the propagation reaction with respect to the monomer can correspond to either the one-stage mechanism or to cases (a) and (b) of the two-stage mechanism.

Table 3 presents the experimental quantities E_p, k_p, and pre-exponential factors for the polymerisation of ethylene and propene in the presence of catalysts of different composition. The table includes for comparison the propagation rate constants in the radical polymerisation of ethylene and the rate contants for the addition of propene to the aluminium–carbon bond in triethylaluminium.

The experimental pre-exponential factors can be compared with the calculated values for the elementary stages, which may constitute the propagation reaction (Table 4). The experimental data for different types of catalysts (the chromium oxide catalyst, titanium trichloride) are consistent with

the two-stage mechanism, which can include as the limiting stage the adsorption of the olefin on the transition metal ion with formation of a π-complex. At the same time, low values of the pre-exponential factor can also be observed for the one-stage mechanism, which involves direct interaction of the olefin with the metal–carbon bond, leading to the formation of a four-centre transition state. Thus the pre-exponential factor cannot serve as a criterion which would permit a differentiation between one- and two-stage mechanisms. For this purpose, one must use other experimental data. We shall enumerate briefly the experimental evidence available hitherto, which confirms the two-stage mechanism of the propagation reaction.

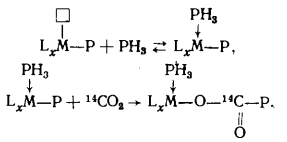
Table 4. The calculated pre-exponential factors of the rate constants for the possible elementary reactions constituting the propagation reaction in the catalytic polymerisation of olefins.

Elementary stage	Method of calculation	$10^{-5}A$, litre mol^{-1} s^{-1}
Adsorption of ethylene on a titanium ion	collision theory (Ref.34)	10^3 (7–70)
Adsorption of ethylene on a transition metal ion with formation of a π-complex	activated complex method (Ref.34)	0.3–3
Bimolecular impact interaction between bulk-phase ethylene and the metal–carbon bond	collision theory (Ref.7)	10^5
Interaction of bulk-phase propene with the metal–carbon bond to form a four-centre activated complex	activated complex method	0.1–1

1. In a study of the relative reactivities of different styrene derivatives in copolymerisation reactions, Natta[47] established that the rate of the propagation reaction is independent of the nature of the terminal unit of the polymer chain linked to the titanium ion. These data suggest that the reaction proceeds in two stages and that the adsorption of the monomer on the titanium ion is rate-limiting.

2. In the catalytic polymerisation of olefins the propagation reaction is usually first order with respect to the monomer. For certain types of Ziegler catalysts, a transition of the propagation reaction from first to zero order with respect to the monomer was observed[49–51]. This is possible in the two-stage mechanism of the propagation reaction, where virtually all the centres are "complexed" by the adsorbed monomer and the insertion of the coordinated olefin in the metal–carbon bond constitutes the rate-limiting stage.

3. An important condition, necessary for the operation of the two-stage mechanism of the propagation reaction, is coordination unsaturation of the metal ions on the active centre, which in the given instance is understood to be the ability of the transition metal ion to increase its coordination number in the adsorption of the olefin. Direct experimental evidence for coordination unsaturation was obtained in a study of the interaction of radioactive inhibitors of different types with the propagation centres. In particular, when compounds such as phosphine are introduced into the polymerisation medium, the polymerisation ceases, but metal–polymer bonds (M–P) are preserved [reaction (V)]. This can be demonstrated on the basis of the radioactivity of the polymer formed by the subsequent decomposition of the metal–polymer bonds by radioactive alcohol or carbon dioxide; the number of labels in the polymer in experiments with preliminary introduction of PH_3 corresponded to the number of propagation centres[14]:



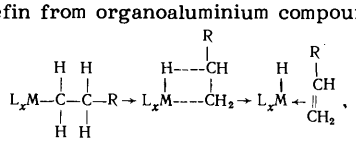
(V)

(VI)

Data showing a preliminary coordination of ethylene on the metal ion in the active centre were also obtained in EPR studies of a number of deposited organometallic catalysts[52,53]. In particular, it has been shown that at low temperatures the benzyl and hydride titanium(III) and zirconium(III) complexes, fixed on the carrier surface, adsorb ethylene, while, following an increase of temperature, ethylene is bound irreversibly, which corresponds to the insertion of the adsorbed ethylene in the metal–hydrogen and metal–benzyl bonds.

2. The Rate-Limiting Stage of the Propagation Reaction

The observed first order of the polymerisation reaction with respect to the monomer can correspond to cases (a) and (b) of the two-stage mechanism [Eqns.(4) and (5)]. It is possible to estimate the pre-exponential factor (A_p) for the propagation rate constant in case (b). For a single unimolecular desorption reaction, a normal value $A_{-1} = 10^{13}$–10^{14} s^{-1} is to be expected. At the same time, in the case of a unimolecular reaction involving the insertion of the adsorbed olefin, proceeding with a low activation energy via an involved four-centre activated complex, one may expect a pre-exponential factor significantly lower than the theoretical value. Pre-exponential factors of 10^8–10^{10} s^{-1} have been quoted in the literature[54,55] for reactions proceeding via the formation of a four-centre activated complex, for example, for the β-elimination of an olefin from organoaluminium compounds:



(VII)

Low-pre-exponential factors for the insertion rate constant (A_2) compared with A_{-1}, i.e. $A_2 \ll A_{-1}$, can also be expected for the insertion of a coordinated olefin, which proceeds via a similar transition state. Consequently in case (b) [Eqn.(5)] we have $A_p = A_1A_2/A_{-1} \ll A_1$. The closeness of the experimental values of A_p to the calculated pre-exponential factor associated with the rate constant for the adsorption of the olefin on the metal ion (Tables 3 and 4) suggests that the rate-limiting stage of the propagation reaction is the adsorption of the olefin on the active centre [case (a), Eqn.(4)].

Low activation energies for the propagation reaction (3–6 kcal mol^{-1}) (Table 3), which do not exceed E_p for radical polymerisation, are characteristic of the catalytic polymerisation of olefins in the presence of transition metal compounds. On passing from transition metal compounds to those of non-transition elements, the activation energy for the propagation reaction (the addition of the olefin to the metal–carbon bond) increases appreciably (see the next Section).

The energy diagram for the two-stage propagation reaction has been examined[56] on the assumption of a linear relation between the change in the activation energy ΔE and in the heat of reaction Δq, of the type

$$\Delta E = \alpha \Delta q \quad (0 < \alpha < 1). \qquad (7)$$

It follows from this diagram that an increase in the heat of adsorption of the olefin on the metal ion can lead to a

decrease of the activation energy for the propagation reaction in both case (a) [Eqn.(4)] and case (b) [Eqn.(5)].

We may note that, whereas the donor–acceptor interaction makes the main contribution to the metal–olefin bond, which is entirely likely for Group IV metals in the highest oxidation states and has been confirmed by quantum-chemical calculations (see subsection 4 of this Section), following a decrease of electron density on the metal ion, a decrease of the activation energy for the propagation reaction is to be expected.

3. The Mechanism of Reactions Involving the Addition of Olefins to Aluminium–Carbon and Aluminium–Hydrogen Bonds

The catalytic oligomerisation of ethylene in the presence of triethylaluminium, which includes reactions involving the addition of the olefin to aluminium–carbon and aluminium–hydrogen bonds, can be represented as follows[12]:

$$R_2Al{-}R + CH_2{=}CH_2 \rightarrow \underset{(A)}{R_2Al{-}CH_2{-}CH_2{-}R}, \qquad (VIII)$$

$$A \xrightarrow{(CH_2=CH_2)} \underset{(B)}{R_2Al\,(CH_2{-}CH_2)_{n+1}{-}R}, \qquad (IX)$$

$$B \rightarrow R_2AlH + CH_2{=}CH{-}(CH_2{-}CH_2)_n{-}R, \qquad (X)$$

$$R_2AlH + CH_2{=}CH_2 \rightarrow R_2Al{-}CH_2CH_3. \qquad (XI)$$

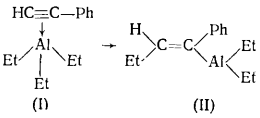
Depending on the process conditions (pressure and temperature), it is possible to obtain α-olefins ranging from C_4 to C_{20}. The interaction of aluminium trialkyls with higher α-olefins takes place as a rule under conditions where the addition of the first olefin molecule is followed by the β-elimination reaction [as in reactions (VII) and (X)]. In this case the process can be catalytic in relation to dialkylaluminium hydride, since the insertion of the α-olefin in the Al–H bond under these conditions is followed again by the β-elimination reaction with formation of a new α-olefin[12].

The catalytic olefin polymerisation processes in the presence of transition metal compounds and processes leading to the formation of higher α-olefins in the presence of organoaluminium compounds are based on reactions involving the addition of olefins to metal–carbon and metal–hydrogen bonds. The observed quantitative differences between the rates of the processes and between the degrees of polymerisation can be attributed to the differences between the rate constants for the chain propagation and termination reactions involving the above groups of catalysts, provided that all these reactions have a single mechanism. Thus reactions involving the addition of olefins to aluminium–hydrogen and aluminium–carbon bonds can be regarded as models for reactions of this type.

Numerous kinetic studies of the addition of olefins to the aluminium–carbon bond in trialkylaluminium[57–63] have shown convincingly that the active centre is the monomeric form of the trialkylaluminium molecule, which is as a rule present in solution in the associated form as Al_2R_6 dimers. The addition of the monomeric coordination-unsaturated form of the organoaluminium compound in the addition reaction ensures the possibility of a preliminary interaction of the olefin with the free *p* orbitals of the aluminium ion to form a π-complex before the step involving the insertion of the olefin in the aluminium–carbon bond[57,58].

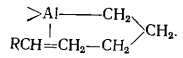
The first order with respect to the monomer[57–59,63–66] suggests that the concentration of π-complexes relative to the monomeric form of the OAC is low and they cannot therefore be detected by physical methods at elevated temperatures under the reaction conditions. With decrease of temperature, one may expect an increase in the concentration of these complexes, but under these conditions the dimerisation of the OAC molecules predominates, the dimer being incapable of coordinating with the olefin.

On the other hand, in many special cases data have been obtained concerning the possibility of the formation of π-complexes of olefins with the monomeric form of the OAC. For example, the formation of π-complexes in the reaction of phenylacetylene with triethylaluminium has been demonstrated[67] by ^{1}H NMR. The heat of this reaction is 0.7 ± 0.2 kcal mol^{-1}. When account is taken of the heat of dissociation of the Al_2Et_6 molecule, amounting to 17 kcal mol^{-1},[68] the strength of the π-bond between phenylacetylene and the aluminium ion is estimated as 9 kcal mol^{-1}. The insertion of phenylacetylene in the aluminium–ethyl bond is of first order with respect to π-complex (I), in conformity with the reaction equation



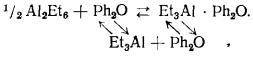
(I) (II) (XII)

The formation of intramolecular π-complexes in aluminium trialkenyls has been established[69–71] by infrared spectroscopy and ^{1}H NMR:



In contrast to their alkyl analogues, the alkenyl compounds of aluminium exist in the monomeric form. The energy of formation of the π-complex should be in this case more than 2–5 kcal mol^{-1} in order to stabilise them in the monomeric form[71].

The necessity for a free coordination site in the trialkylaluminium molecule for the addition of the olefin to take place has received significant confirmation by data concerning the influence of electron-donating compounds on the kinetics of this reaction. The kinetics of the addition of oct-1-ene to triethylaluminium in diphenyl ether, which reduces sharply the rate of this reaction, have been studied by ^{1}H NMR.[72] Under the given conditions, there is a system of equilibria



(XIII)

It has been established[72] that only the monomeric form of triethylaluminium is active in the olefin addition reaction, while the complex $Et_3Al.Ph_2O$ is inactive.

The rate constants for the addition of olefins to the Al–C and Al–H bonds. Table 5 presents the activation energies and the pre-exponential factors associated with the rate constants for the addition of olefins of different structures to triethylaluminium. Some uncertainty in the determination of the rate constants for this reaction is associated with the possibility of using in the calculations of the concentration of the monomeric form of triethylaluminium of different dissociation constants K_d of the dimeric molecule Al_2Et_6 obtained in different investigations[60,62,68,74]. The results presented in Table 5 have therefore been grouped in accordance with the values of K_d used in the calculations. In the series from propene to oct-1-ene the activation energies increase from 12.2–15.4 to 16.6–19.4 kcal mol^{-1}. The pre-exponential factors also tend to increase in this series by about an order of magnitude.

The addition of olefins to $Al(Me)_3$ is much slower than the addition of $AlEt_3$, which is associated, firstly, with the higher heat of dissociation of the $[AlMe_3]_2$ molecule[74,75] and with the higher activation energy for the addition reaction (Table 6).

The interaction of ethylene with triethylaluminium has been studied in the gas phase under the conditions of the preferential formation of α-butylene[66,76]. The kinetic characteristics obtained for this reaction are listed in Table 6. One must bear in mind that, in the calculation of the rate constants for the addition reaction, a number of addition assumptions were introduced in this instance concerning the concentrations of different forms of the OAC and the ratio of the rate constants for different reactions. Apparently not all the assumptions are valid and the activation energies for the addition of ethylene in Table 6 are too high. In this connection one should note that Ziegler[12,77] established the following series based on the variation of the reactivity in the addition of olefins to organoaluminium compounds: $CH_2{=}CH_2 > CH_2{=}CHR > CH_2{=}CR_2$.

Table 5. The activation energies E (kcal mol^{-1}) and the pre-exponential factors A of the rate constants for the addition of olefins to triethylaluminium.

Monomer	From data in Refs. 59, 60, 65, and 73		From data in Refs. 62 and 63			
	E*	lg A*	E**	lg A**	E***	lg A***
Propene	15.5	5.5	12.1	3.3	14.4	4.2
But-1-ene	16.4	5.8	13.2	3.6	15.4	4.5
Pent-1-ene	18.5	6.8	15.1	4.6	17.8	5.5
Hex-1-ene	17.2	6.2	15.0	4.8	17.3	5.6
Oct-1-ene	18.4	6.6	16.5	5.0	19.6	6.3
Cyclohexene	17.8	4.6				
Methylpent-1-ene	17.0	5.8				
3-Methylpent-1-ene	18.8	6.5				
3,3-Dimethylbut-1-ene	25.4	9.4				

*K_d from Hay et al.[60], ΔH_d = 10.2 kcal mol^{-1}, ΔS_d = 14.9 cal mol^{-1} K^{-1}.

**K_d from Smith[68,74], ΔH_d = 17 kcal mol^{-1}, ΔS_d = 3.2 cal mol^{-1} K^{-1}.

***K_d from Allen and Byers[62], ΔH_d = 12.2 kcal mol^{-1}, ΔS_d = 27.8 cal mol^{-1}K^{-1}.

Table 6. The activation energies E (kcal mol^{-1}) and the pre-exponential factors A of the rate constants for the addition of olefins to different OAC.

OAC	E	lg A	E	lg A
	Oct-1-ene (Ref.61)		Ethylene (Refs.66,76)	
$AlEt_3$	18.4	6.6	16.8	6.2
$AlMe_3$	20.5	6.7	22.7	7.2

On passing from metal–carbon to metal–hydrogen bonds, there is a sharp increase of reactivity for the addition of olefins due to the decreased activation energy (Table 7). The activation energy for the addition to the Al–H bond is virtually the same for different monomers and for a single monomer increases in the sequence $R_2AlH < R_2GaH < R_2BH$.

The data examined above are in best agreement with the hypothesis that the addition of olefins to the metal–carbon bond takes place via a single two-stage mechanism for compounds of both transition and non-transition metals. The reaction proceeds with participation of coordination-unsaturated metal alkyls via the intermediate formation of π-complexes. The pre-exponential factors associated with the rate constant for this reaction are close for active centres of different compositions and the higher reactivity of transition metal compounds compared with organoaluminium compounds is determined mainly by the low activation energy for this process. Many facts show that the polarity of the bonds does not determine the reactivity of the metal alkyls in the addition of olefins. Presumably the most significant factor is the ability of metal alkyls to form π-complexes with the possibility of interaction with the metal–carbon bond via a concerted mechanism.

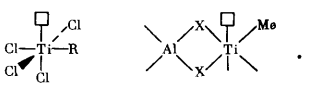
Table 7. The activation energies for the addition of olefins to the metal–hydrogen bond in the organometallic compound $(iso\text{-}C_7H_9)_2MH$.

Monomer	M	E, kcal mol^{-1}	Refs.
Ethylene	Al	5.0—6.0	78,79
But-1-ene	Al	5.0—6.0	78,79
2-Methylpropene	Al	5.0—6.0	78,79
2-Methylpropene	Ga	8.8	80
2-Methylpropene	B	12	81

4. Quantum-Chemical Analysis of the Mechanism of the Propagation Reaction†

The first studies on the quantum-chemical analysis of the propagation reaction in the polymerisation of olefins were carried out by Cossee[82,83]. The ideas developed in these investigations have been widely accepted. Later a further series of studies were carried out[84–89], including some using improved computational methods[85–89].

The AC models. The AC model proposed by Cossee[82,83], incorporating an octahedral titanium(III) complex which exists on the surface of the titanium trichloride crystal [complex (IV)], is fully consistent with the experimental data discussed above. The titanium ion in this complex contains an alkyl group and a chlorine vacancy. This AC model has been used in many computational studies[82–84,89]. AC models of more complex composition, for example the Ti_2Cl_{10} cluster[90], and simplified models containing either no metal–alkyl bond or a free vacancy[91–94] have also been analysed.



(IV) (V)

The AC model proposed for soluble catalytic systems has been analysed[85,86]. In this case the AC consists of a titanium(IV) complex linked to an organoaluminium compound [complex (V)].

The metal–alkyl bond and the influence of the coordination of the olefin on its strength. The Ti–C bond is predominantly covalent with $Ti^{\delta+}$–$C^{\delta-}$ polarisation[89]. The titanium–carbon bond length changes only slightly on passing from the methyl to the ethyl complex, i.e. the properties of this bond are presumably independent of the chain length. On

† This Section was written together with V.I.Avdeev and I.I.Zakharov.

formation of a π-complex with ethylene, an appreciable proportion of the electron density is transferred to the titanium ion (~0.25e).

The metal–olefin bond is formed as a result of the donor–acceptor and dative interactions[95,96]. Fig.5 illustrates the variation of the energy ΔE of transition from the σ_R orbital, involved in the formation of the metal–alkyl bond, to the half-filled or vacant d_π orbital of the metal on coordination of the olefin to the titanium ion. Presumably the lower the value of ΔE, the higher the probability of the $\sigma_R \rightarrow d_\pi$ transition and hence the more effective is the electron transfer from the metal–carbon bond to the metal. This process leads to an increased electron density on the metal and to a decrease in the M–C bond strength. If only the donor–acceptor interaction between the AC and the ligand is taken into account (Fig.5*a*), then the energy of the $\sigma_R \rightarrow d_\pi$ transition increases on complex formation ($\Delta E' > \Delta E$) and the M–C bond is strengthened. When account is taken of both the donor–acceptor and the dative interactions (Fig.5*b*), it is possible to obtain $\Delta E' > \Delta E$ or $\Delta E' < \Delta E$ depending on their relative contributions ($\Delta\varepsilon$ and $\Delta\varepsilon'$ respectively). In the first case the coordination of the olefin strengthens the M–C bond, while in the second it destabilises it.

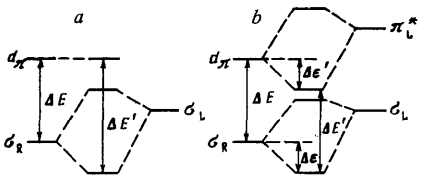
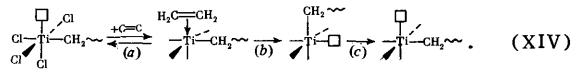


Figure 5. A simplified scheme of the changes in the one-electron levels of the AC (σ_R, d_π) in the interaction with the donor (σ_L) and acceptor (π^*_L) orbitals of the coordinating ligand[89]: *a*) allowance for the donor–acceptor interaction of the AC and the ligand; *b*) allowance for the donor–acceptor and dative interactions.

The nature of the metal–olefin bond. In the early studies[82–84] no estimates were made of the relative contributions of these interactions. The hypothesis[83] of the dominant role of the dative interaction does not appear convincing, since the metal ions in the highest oxidation states [for example the d^1 configuration for titanium(III)] can hardly transfer effectively the electron density from the d_π orbitals (which are actually unoccupied) to the antibonding π* orbitals of ethylene. It is therefore not surprising that Armstrong[85] arrived at the opposite conclusion for titanium(IV) complexes on the basis of calculations by the CNDO method, namely that the contribution of the donor–acceptor interaction predominates. This conclusion has been confirmed by calculations on the π-complexes $Ti^{3+}F_5.C_2H_4$ and $Ti^{3+}Cl_5.C_2H_4$ carried out by the Slater–Johnson method[91,92]. According to these calculations, the contribution of the dative interaction does not exceed 12% for the fluoride complexes and is significantly lower for the chloride complex. Thus the calculated data suggests that the metal–olefin bond in the AC incorporating titanium(III) ions is formed mainly as a result of the donor–acceptor interaction.

The monomer insertion stage. Cossee[82,83] was the first to analyse this reaction theoretically, assuming that it is the rate-limiting stage of the propagation reaction [stage (b) in reaction (XIV)]:

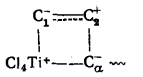


(XIV)

After the *cis*-insertion of the monomer, the geometry of the active centre is restored but with an interchange of the vacant site and the alkyl. Analysis of the orbital contributions to the molecular orbital localised at the Ti–C bond shows that the metal–alkyl bond persists along the entire reaction pathway. The vacant d_{xy} orbital of titanium plays an important role in this process. The energy losses on passing from the Ti–C_α bond to the Ti–C_1 bond do not exceed 20% of the bond strength and are fully compensated by the formation of a new C_2–C_α bond [reaction (XVII)].[89] Cossee[83] classified such reactions as concerted and characterised by a synchronous redistribution of electron density in the ruptured and reformed bonds, which is the reason for the low activation energies for these reactions.

On the basis of calculated data demonstrating a marked destabilisation of the σ_R and d_π orbitals and an increase of ΔE (Fig.5) in the monomer insertion process, Cossee[83] proposed a relation between the activation energy for the propagation reaction and ΔE. The same conclusion was reached by Begley and Penella[84] using the same computational methods, on the basis of estimates of ΔE for the series of complexes CH_3TiCl_3, $CH_3TiCl_4.\square$ (octahedron with a vacancy), and $CH_3TiCl_4.C_2H_4$. They postulated that $\Delta E'$ (Fig.5) represents the energy barrier which is overcome when the coordinated olefin is introduced into the metal–carbon σ-bond and $\Delta E'$ can therefore be compared with the activation energy for the chain propagation reaction. However, this conclusion was not confirmed in calculations by the more effective CNDO method[85,86,89]. It has been shown[89] that $\Delta E'$ depends greatly on the metal–alkyl and metal–ethylene bond lengths chosen, it is therefore important to determine the equilibrium lengths of these bonds by minimising the total energy. This factor was not taken into account by Cossee et al.[83] and Begley and Penella[84] and the attempt to relate the activation energy for the insertion reaction to $\Delta E'$ is therefore unjustified.

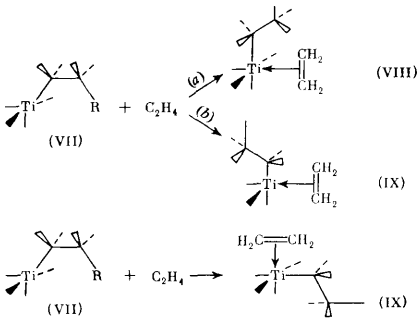
The insertion reaction for the AC [complex (V)] in a homogeneous catalyst has been analysed[85,86] by the CNDO method. It was observed that the behaviour of the one-electron levels following the insertion of ethylene is analogous to that found earlier by Cossee and the process is activated but the total energy of the system decreases along the reaction coordinate. Hence the authors[85,86] concluded that the insertion stage does not have an activation energy. In contrast to earlier workers[83–86], Avdeev et al.[89] attemped to determine the optimum reaction pathway in the insertion of ethylene taking into account the mutual influence of the metal–olefin and metal–alkyl bonds. We may note certain characteristic features of the insertion stage, which follow from the results of this study. In the initial stage of the process a four-centre complex (VI) of the type



is formed, its polarisation ensuring its energetic suitability compared with the initial complex. The transition to the final stage, where the *cis*-opening of the double bond is completed, requires that an insignificant energy barrier be overcome (approximately 1 kcal mol^{-1}), which is consistent with

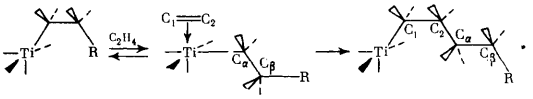
the results of Armstrong et al.[85] and Novaro et al.[86] However, Avdeev et al.[89] found that the stable state of the AC corresponds to structure (VII) [Eqns.(XV) and (XVI)], in which the Ti–C bond occupies a position intermediate between the octahedral sites and the propyl group has the *cis*-configuration.

Coordination of the olefin. Armstrong[85] was the first to note that the total energy of the AC decreases when the structure is deformed to a trigonal bipyramid. Formally there is no vacancy in such a deformed AC, so that it is necessary that in the adsorption of ethylene the octahedral geometry of the AC should be restored. Such a rearrangement requires energy, which can be identified as the activation energy for the adsorption stage. Avdeev et al.[89] analysed in detail, within the framework of the CNDO method, the stage involving the coordination of ethylene on the active centre, having structure (VII), which they showed to correspond to the free energy minimum. There are several ways in which ethylene can be incorporated in the coordination sphere of the metal ion:



A characteristic feature of the first case [reaction (XV)] is that the olefin and the alkyl change places in the coordination sphere of the metal ion during the chain propagation process. The second case [reaction (XVI)] corresponds to the adsorption of the monomer to the same coordination site in repeated propagation steps. Calculation of the potential surfaces for coordination of ethylene in relation to reaction (XV) shows that it involves the overcoming of an energy barrier [approximately 25 kcal mol^{-1} for reaction (XV*a*) and 65 kcal mol^{-1} for reaction (XV*b*)]. The coordination of etheylene via reaction (XVI) is also activated, but with a much smaller activation energy (approximately 4 kcal mol^{-1}). The low activation energy in the latter case is due to the fact that the energy evolved on coordination of the monomer compensates for the energy expended in the migration of the alkyl group and its transition to the *trans*-configuration. On the other hand, in reaction (XV) the rearrangement of the AC must take place before the energy compensation due to the adsorption of ethylene begins. The conclusions reached on the basis that the monomer is adsorbed at the same site in the coordination sphere of titanium provide a more natural explanation of the isospecificity of the addition of the monomer in the polymerisation of α-olefins in the presence of titanium chlorides. The need to introduce a special alkyl migration stage, proposed in some investigations[48,82] [reaction (XIV*c*)], is eliminated.

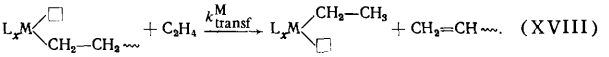
Comparison of the one-stage and two-stage mechanisms. The potential energy surface has been calculated[89] for the one-stage mechanism of the propagation reaction; the results obtained were compared with data for the adsorption reaction and the insertion of the coordinated olefin. It was found that the insertion of ethylene in the metal–polymer bond directly from the gas phase requires that a considerably larger energy barrier be overcome than in its insertion via preliminary coordination. Consequently the two-stage mechanism of the propagation reaction is preferable, and according to Avdeev et al.[89] it can be represented as follows:


(XVII)

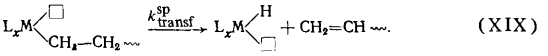
V. POLYMER CHAIN TRANSFER REACTIONS

In the catalytic polymerisation of olefins the following main reactions which limit the propagation of the polymer chain take place.

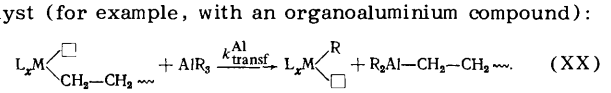
1. Transfer with the monomer:


(XVIII)

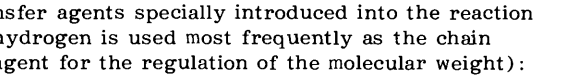
2. Spontaneous chain transfer reaction:


(XIX)

3. Reaction involving chain transfer with the organometallic cocatalyst (for example, with an organoaluminium compound):


(XX)

4. Reactions involving chain termination by impurities or chain transfer agents specially introduced into the reaction medium (hydrogen is used most frequently as the chain transfer agent for the regulation of the molecular weight):


(XXI)

All the reactions enumerated above are polymer chain transfer reactions, after which the kinetic chain is preserved and a new polymer molecule is formed on the AC. In the catalytic polymerisation of olefins a large number of polymer molecules (from tens to thousands) are therefore formed as a rule on a single AC.

The equation proposed by Natta is usually employed to calculate the chain transfer rate constants:

$$\frac{1}{\bar{P}_W} = \frac{k^{M}_{transf}}{k_p\omega} + \left(\frac{k^{sp}_{transf}}{k_p\omega} + \frac{k^{Al}_{transf}[Al]^n}{k_p\omega} + \frac{k^{X}_{transf}[X]^m}{k_p\omega} \right) \frac{1}{c_M}, \qquad (8)$$

where $\bar{P}_W$ is the weight-average degree of polymerisation, k^{M}_{transf}, k^{sp}_{transf}, k^{Al}_{transf}, and k^{X}_{transf} are the rate constants for the corresponding transfer reactions [see schemes (XVIII)–(XXI)], c_M, [Al], and [X] are the concentrations of the monomer, the organoaluminium cocatalyst, and the chain transfer agent X, for example, hydrogen, and ω is the coefficient of the polydispersity of the polymer. The ratios of the chain transfer rate constants to the chain propagation rate constant (k^{i}_{transf}/k_p) can be calculated by Eqn.(8) from the experimental relations between the molecular weight of the polymer and the concentrations of the chain transfer agents[97,98]. The values of k_p, determined independently by the method of radioactive inhibitors (see Sections II and III), were used[16,34,99,100] for the subsequent calculation of the absolute rate constants, listed in Table 8, for chain transfer with the monomer and hydrogen as well as spontaneously. The rate constants for chain transfer with the organoaluminium cocatalyst, listed in Table 8,[19,100] were calculated from

the experimental relations between the number of metal–polymer bonds (q) and the yield of the polymer (G) in accordance with the expression[2,6,19]:

$$[q]=c_p+\frac{k^{Al}_{transf}[Al]^n G}{k_p c_m}, \qquad (9)$$

where $[q]$ is the total number of aluminium–polymer and titanium–polymer bonds, determined by a method involving the termination of the polymerisation by a radioactive alcohol RO^3H. In the calculation of k^{Al}_{transf} the values of k_p determined independently by a method involving the termination of polymerisation by ^{14}CO were also used[17,23].

Chain transfer with the monomer and spontaneous chain transfer are the main chain transfer processes in the case of one-component catalysts. Chain transfer with the monomer predominates at temperatures below 90 °C,[16,101] whilst spontaneous transfer predominates above 120 °C.[101] For two-component catalysts based on $TiCl_3$ chain transfer with the monomer predominates at 70–80 °C.[99,100] Experimental data concerning the molecular structure of the polymers {vinyl unsaturation for polyethylene and vinylidene unsaturation for polypropylene arising via reactions (XVIII) and (XIX)} confirm the occurrence of these processes under the conditions investigated[99,100].

Table 8. The rate constants for chain transfer in the catalytic polymerisation of olefins[16,19,34,99,100].

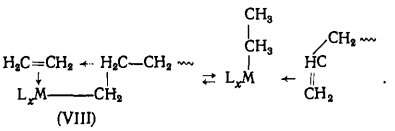
Catalyst	k^{M}_{transf}/ω, litre mol^{-1} s^{-1}	k^{Al}_{transf}, litre$^{0.5}$ mol$^{-0.5}$ s^{-1}	$k^{H_2}_{transf}/\omega$, litre$^{0.5}$ mol$^{-0.5}$ s^{-1}	$\bar{\tau}\cdot\omega$, s*
CrO_3/SiO_2**	$1.2\cdot10^8\exp(-11\,700/RT)$; 0.0064	—	—	60
$TiCl_3$	$0.8\cdot10^8\exp(-9000/RT)$; 0.2	—	—	12
$TiCl_3+AlEt_3$	0.084	2.3	2.3	25
$TiCl_3+AlEt_3$***	0.004	0.045	0.59	160
$TiCl_4/MgCl_2+AlEt_3$	0.22	1.7	—	10

*The average polymer chain propagation time $\bar{\tau}$ was calculated from the relation $\bar{\tau}=\bar{P}_W/\omega k_p c_m$ with $c_m = 0.5$ M at 80 °C for ethylene and at 70 °C for propene.

**k^{sp}_{transf}/ω, $c^{-1} = 2.2\times10^5\exp(-13\,500/RT)$.

***Monomer—C_3H_6; the rate constants for 70 °C are indicated; in the remaining cases the monomer is C_3H_6 and the rate constants for 80 °C are indicated.

The pre-exponential factors associated with the rate constant for chain transfer with the monomer (Table 8) are close to the calculated pre-exponential factor of the rate constant for the adsorption of monomer on the metal ion with formation of a π-complex (Table 4) or to the pre-exponential factor of the propagation rate constant (Table 3). Presumably chain transfer with the monomer, like the propagation reaction, proceeds via a stage in which the monomer is adsorbed on the metal ion in the AC [reactions (XV) and (XVI)]. Depending on the steric disposition of the adsorbed olefin and the alkyl group, either the insertion reaction takes place in this instance [after the formation of complex (IX) via reaction (XVI)] or reaction (XXII), involving the transfer of hydrogen from the β-carbon atom of the alkyl group to the adsorbed monomer [provided that complex (VIII) is formed via reaction (XVa)]:



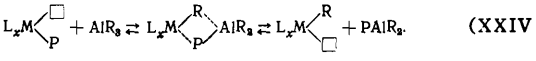
(VIII) (XXII)

As mentioned in the previous Section, the formation of a π-complex of type (VIII) via reaction (XVa) is energetically less favourable than the formation of complex (IX) via reaction (XVI), which is apparently due to the higher activation energy for chain transfer with the monomer compared with the propagation reaction.

The spontaneous chain transfer process (XIX) is a reaction involving the β-elimination of the olefin with formation of a metal hydride complex. This reaction is well known for organoaluminium compounds[12]. The low pre-exponential factors of the rate constants for the unimolecular spontaneous transfer process (Table 8) and the reactions involving the β-elimination of olefins from aluminium alkyls[54,55] are apparently caused by the fact that the process proceeds via an involved activated complex [reaction (VII)] the formation of which requires a specific steric disposition of the alkyl group, favourable for the migration of a hydrogen atom to the transition metal ion. When this reaction takes place in the coordination sphere of the metal, the C–H bond is dissociated with a relatively low activation energy [13.5 kcal mol^{-1} for the chromium oxide catalyst (Table 8) and 26–30 kcal mol^{-1} for organoaluminium compounds[54,55]].

Chain transfer with the organoaluminium cocatalyst plays a notable role in two-component catalysts. This reaction consists in essence of the exchange of the alkyl ligands between the OAC and the AC and apparently includes the following stages: dissociation of the dimeric OAC molecule and adsorption of the monomeric form of the OAC on the AC followed by desorption of the OAC molecule, in which the alkyl group is replaced by the polymer chain[19,102]:

$$[AlR_3]_2 \rightleftarrows 2\,AlR_3, \qquad (XXIII)$$



(XXIV)

Within the framework of this mechanism, it is possible to account for the experimental data[19,32] concerning the influence of the nature of the OAC [$AlEt_3$ and $Al(iso\text{-}Bu)_3$] and the monomer on k^{Al}_{transf}. For steric reasons, the adsorption of $Al(iso\text{-}Bu)_3$ on the AC via reaction (XXIV) should be hindered. This reduces the rate constant for chain transfer from $Al(iso\text{-}Bu)_3$ compared with $AlEt_3$. In the polymerisation of propene the presence of methyl substituents in the polymer chain, bound to the metal ion in the AC, gives rise to greater difficulties in the adsorption of the OAC compared with the polymerisation of ethylene. The rate constant for chain transfer from $AlEt_3$ in the polymerisation of propene is therefore significantly lower than in the polymerisation of ethylene (Table 8).

VI. CONCLUSION

The data obtained for the influence of the composition of catalysts and polymerisation conditions on the number of AC and the propagation rate constant constitute the experimental basis for the analysis of kinetic data and for the discussion of problems concerning the composition of the AC and the mechanism of the propagation reaction.

The basic cause of the comparatively low activity of the usual Ziegler–Natta catalysts is the small number of AC, not exceeding 0.01 mol per mol of the transition metal. In practice this quantity is considerably lower in most instances. A

sharp increase of the number of centres has been achieved using deposited catalysts. The employment of carriers such as polyethylene and silica gel, on the surfaces of which the active component exists as a finely dispersed titanium chloride phase, makes it possible to increase the number of AC in the polymerisation of ethylene approximately by an order of magnitude. The maximum number of propagation centres is attained as a result of the "structural" binding of titanium chloride by anhydrous highly dispersed magnesium chloride having a disordered structure.

The most important characteristic of the catalytic polymerisation, which to a large extent determines the process kinetics, is the influence of the polymerisation conditions and the composition of the reaction medium on the number of AC. Observations such as the influence of the polymerisation temperature and the nature and concentration of the OAC on the number of AC were explained in this connection by an adsorption mechanism for the reversible interaction of the OAC with the monometallic AC.

Numerous data, particularly those concerning the absence of an effect of the nature of the OAC on k_p, are consistent with the monometallic composition of the AC.

Increasing amounts of experimental data have been accumulated at the present time concerning the preliminary coordination of the monomer to the metal ion before the step involving the insertion of the olefin either into the transition metal–carbon bond in the far-reaching polymerisation of olefins or into the aluminium–carbon bond in the oligomerisation of the olefins. Kinetic as well as calculated data suggest that in many instances this stage can be rate-limiting in the propagation reaction.

The high reactivity of the AC containing a transition metal is determined by the low activation energy for the propagation reaction, which is comparable to the activation energy for radical polymerisation. The insertion of the olefin in the transition metal–carbon and aluminium–carbon bonds proceeds via the same two-stage mechanism, but in the case of a transition metal a significant decrease of the activation energy for the propagation reaction is achieved.

The method based on the inhibition of the polymerisation by a radioactive alcohol is useful for the direct determination of the rate constant for the transfer of the polymer chain from the OAC. This constant depends on the nature of the OAC and the structure of the polymer chain, which is due to the adsorption mechanism of this reaction. The rate constants for other chain transfer processes have been determined from the k_p.

Further development of ideas concerning the elementary stages in the propagation and polymer chain termination reactions can be achieved by using quantum-chemical and physical methods in the study of these reactions. In the formulation of investigations using physical methods it is as a rule necessary to employ catalysts in which the number of AC constitutes an appreciable fraction of the content of the transition metal in the catalyst; it is then necessary to estimate this value quantitatively. As a result of the selection of the optimum composition and preparation conditions for the catalyst (particularly in the deposition of a transition metal compound on a carrier), it is possible to increase sharply the number of AC and to obtain highly active one- and two-component catalysts. These catalysts are widely used nowadays and are at the same time convenient for the investigation of the composition of the AC and the polymerisation mechanism by physical methods. The results obtained by physical research methods together with the determinations of the rate constants for individual stages can serve as a basis for the establishment of relations between the composition of the AC, the state of the transition metal in the AC, and their reactivity in chain propagation and transfer reactions.

REFERENCES

1. G.Natta and I.Pasquon, Chim.e Ind.(Milano), **40**, 556 (1958).
2. G.Natta and I.Pasquon, Adv.Catal., **11**, 1 (1959).
3. J.W.C.Chien, J.Amer.Chem.Soc., **81**, 86 (1958).
4. G.F.Feldman, and E.Perry, J.Polymer Sci., **46**, 217 (1960).
5. J.Boor, Makromol.Rev., **2**, 115 (1967).
6. H.Schnecko and W.Kern, Chem.Ztg.Chem.Appar., **94**, 229 (1970).
7. N.M.Chirkov, "Proceedings of the IUPAC International Symposium on Macromolecular Chemistry, Budapest", Akad.Kiado, 1971, p.365.
8. Yu.I.Ermakov and V.A.Zakharov, Uspekhi Khim., **41**, 377 (1972) [Russ.Chem.Rev., No.3 (1972)].
9. Yu.I.Yermakov and V.A.Zakharov, "Coordination Polymerization" (Edited by J.C.W.Chien), Acad.Press, New York–London, 1975, p.91.
10. Yu.I.Yermakov, V.A.Zakharov, and G.D.Bukatov, "Proccedings of the Vth International Congress on Catalysis", Amsterdam–New York, 1973, Vol.1, p.399.
11. V.A.Zakharov, G.D.Bukatov, N.B.Chumaevskii, and Yu.I.Yermakov, React.Kinet.Catal.Letters, 1, 247 (1974).
12. K.Ziegler, Symposium, "Khimiya Metalloorganicheskikh Soedinenii" (The Chemistry of Organometallic Compounds) (Translated into Russian), Izd.Mir, Moscow, 1964, p.231.
13. J.P.Candlin, K.A.Taylor, and D.T.Thompson, "Reactions of Transition-Metal Complexes" (Translated into Russian), Izd.Mir, Moscow, 1970.
14. V.A.Zakharov, G.D.Bukatov, Yu.I.Ermakov, and E.A.Demin, Dokl.Akad.Nauk SSSR, **207**, 857 (1972).
15. V.A.Zakharov, G.D.Bukatov, and Yu.I.Ermakov, Kinetika i Kataliz, **12**, 263 (1971).
16. V.A.Zakharov, G.D.Bukatov, V.K.Dudchenko, and Yu.I.Ermakov, Kinetika i Kataliz, **16**, 417 (1975).
17. N.B.Chumaevskii, V.A.Zakharov, G.D.Bukatov, G.I.Kuznetsova, and Yu.I.Yermakov, Makromol. Chem., 177, 747 (1976).
18. G.D.Bukatov, V.A.Zakharov, and Yu.I.Yermakov, Makromol.Chem., 179, 2097 (1978).
19. G.D.Bukatov, N.B.Chumaevskii, V.A.Zakharov, G.I.Kuznetsova, and Yu.I.Yermakov, Makromol. Chem., 178, 953 (1977).
20. D.R.Burfield, P.J.T.Tait, and J.McKenzie, Polymer, **13**, 321 (1972).
21. H.W.Coover, Jr., J.E.Guillet, R.L.Combs, and F.B.Joyner, J.Polymer Sci., **58**, 2583 (1966).
22. K.A.Jung and H.Schnecko, Makromol.Chem., **154**, 227 (1972).
23. V.A.Zakharov, N.B.Chumaevskii, S.I.Makhtarulin, G.D.Bukatov, and Yu.I.Yermakov, React.Kinet.Catal. Letters, **2**, 329 (1975).
24. V.A.Zakharov, G.D.Bukatov, N.B.Chumaevskii, and Yu.I.Ermakov, Kinetika i Kataliz, **18**, 848 (1977).
25. V.M.Buls and T.L.Higgins, J.Polymer Sci., A1, 8, 1025 (1970).
26. W.R.Carradine and H.F.Rase, J.Appl.Polymer Sci., **15**, 889 (1971).
27. Z.W.Wilshinsky, R.W.Looney, and G.M.Tornqvist, J.Catal., 28, 351 (1973).

28. V.A.Zakharov, P.A.Zhdan, E.E.Vermel', and S.G.Artamonova, Kinetika i Kataliz, **16**, 1184 (1975).
29. V.A.Zakharov, V.N.Druzhkov, E.G.Kushnareva, and Yu.I.Ermakov, Kinetika i Kataliz, 15, 446 (1974).
30. M.G.Maksimov, E.G.Kushnareva, V.A.Zakharov, V.F.Anufrienko, P.A.Zhdan, and Yu.I.Ermakov, Kinetika i Kataliz, **15**, 738 (1974).
31. V.A.Zakharov and Yu.I.Ermakov, Symposium, "Katalizatory i Kataliticheskie Protsessy" (Catalysts and Catalytic Processes), Inst.Kataliza, Novosibirsk, 1977, p.135.
32. S.I.Makhtarulin, E.M.Moroz, E.E.Vermel, and V.A.Zakharov, React.Kinet.Catal.Letters, **9**, 269 (1978).
33. S.I.Mahtarulin, V.A.Zakharov, and Yu.I.Yermakov, React.Kinet.Catal.Letters, **9**, 137 (1978).
34. G.D.Bukatov, V.A.Zakharov, and Yu.I.Ermakov, Kinetika i Kataliz, **16**, 645 (1975).
35. V.A.Zakharov, N.B.Chumaevskii, G.D.Bukatov, and Yu.I.Yermakov, Makromol.Chem., **177**, 763 (1976).
36. V.A.Zakharov, G.D.Bukatov, and Yu.I.Yermakov, Makromol.Chem., **176**, 1959 (1975).
37. V.A.Zakharov and Yu.I.Yermakov, J.Polymer Sci., **A1**, 9, 3124 (1971).
38. Kh.S.Bagdasar'yan, "Teoriya Radikal'noi Polimerizatsii" (Theory of Radical Polymerisation), Izd.Nauka, Moscow, 1966.
39. E.J.Arlman and P.Cossee, J.Catal., **3**, 99 (1964).
40. E.J.Arlman, J.Catal., **5**, 178 (1966).
41. P.J.T.Tait, "Coordination Polymerization" (Edited by J.W.C.Chien), Acad.Press, New York–San Francisco–London, 1975, p.155.
42. V.A.Zakharov, G.D.Bukatov, N.B.Chumaevskii, and Yu.I.Yermakov, Makromol.Chem., **178**, 967 (1977).
43. G.Natta, A.Zambelli, I.Pasquon, and G.M.Giongo, Chim.e Ind.(Milano), **43**, 1307 (1966).
44. C.Wolfsgruber, G.Zannoni, E.Rigamonti, and A.Zambelli, Makromol.Chem., **176**, 2765 (1975).
45. G.D.Bukatov, V.A.Zakharov, Yu.I.Yermakov, and A.Zambelli, Makromol.Chem., **179**, 2093 (1978).
46. T.Keii, Kinetics of Ziegler–Natta Polymerization, Kodansha, Tokyo, 1972.
47. G.Natta, F.Danusso, and D.Sianesi, Makromol.Chem., **30**, 238 (1959).
48. P.Cossee, in "Stereochemistry of Makromolecules", Vol.1, (Edited by A.Ketley), M.Dekker, New York, 1967.
49. A.Zambelli, I.Pasquon, R.Signorini, and G.Natta, Makrmol.Chem., **112**, 160 (1968).
50. N.D.Zavorokhin, V.V.Belyaev, T.A.Vlasova, M.V.Favorskaya, and D.V.Sokol'skii, Dokl.Akad.Nauk SSSR, **215**, 593 (1974).
51. N.V.Bokareva, V.I.Tsvetkova, and F.S.D'yachkovskii, Vysokomol.Soed., **A20**, 2707 (1978).
52. N.G.Maksimov, V.K.Dudchenko, V.A.Zakharov, V.F.Anufrienko, and Yu.I.Ermakov, Teor.Eksper. Khim., **14**, 53 (1978).
53. N.G.Maksimov, G.A.Nesterov, V.A.Zakharov, V.P.Schastnev, V.F.Anufrienko, and Yu.I.Yermakov, J.Mol.Catal., **4**, 167 (1978).
54. W.L.Smith and T.Wartik, J.Inorg.Nuclear Chem., **29**, 629 (1967).
55. A.T.Clocks and K.W.Egger, J.Chem.Soc., Faraday Trans.I, **68**, 423 (1972).
56. Yu.I.Yermakov and V.A.Zakharov, Adv.Catal., **24**, 173 (1975).
57. K.Ziegler, W.R.Kroll, W.Larbig, and O.W.Stendel, Ann., **629**, 53 (1960).
58. K.Ziegler and H.Hoberg, Chem.Ber., **93**, 2944 (1960).
59. N.D.Zavorokhin, V.V.Belyaev, T.A.Vlasova, M.V.Favorskaya, and D.V.Sokol'skii, [No Journal given in Russian (Ed.of Translation)].
60. J.N.Hay, P.C.Hooper and J.C.Robb, Trans.Faraday Soc., **65**, 1365 (1969).
61. J.N.Hay, P.G.Hooper, and J.C.Robb, Trans.Faraday Soc., **66**, 2800 (1970).
62. P.E.M.Allen and A.E.Byers, Trans.Faraday Soc., **67**, 1718 (1971).
63. P.E.M.Allen, J.N.Hay, G.R.Jones, and J.C.Robb, Trans.Faraday Soc., **63**, 1636 (1967).
64. P.E.M.Allen, J.P.Allison, S.R.Majer, and J.C.Robb, Trans.Faraday Soc., **59**, 2080 (1963).
65. J.N.Hay, P.G.Hooper, and J.C.Robb, Trans.Faraday Soc., **66**, 2045 (1970).
66. K.W.Egger, Trans.Faraday Soc., **67**, 2638 (1971).
67. P.E.M.Allen and R.M.Lough, J.Chem.Soc., Faraday Trans.I, **69**, 849 (1973).
68. M.B.Smith, J.Phys.Chem., **71**, 364 (1967).
69. G.Hata, Chem.Comm., 7 (1968).
70. J.St.Dawies, J.P.Oliver, and J.B.Smart, J.Organomet. Chem., **44**, C 32 (1972).
71. T.W.Dobzine and J.R.Oliver, J.Amer.Chem.Soc., **96**, 1737 (1974).
72. P.E.M.Allen, A.E.Byers, and R.M.Lough, J.Chem.Soc., Dalton Trans., 479 (1972).
73. J.N.Hay, P.G.Hooper, and J.C.Robb, J.Organomet. Chem., **28**, 193 (1971).
74. M.B.Smith, J.Organomet.Chem., **46**, 211 (1972).
75. C.H.Henrickson and D.P.Eyman, Inorg.Chem., **6**, 1461 (1967).
76. K.W.Egger and A.T.Cocks, J.Amer.Chem.Soc., **94**, 1810 (1972).
77. K.Ziegler, W.R.Kroll, W.Larbig, and O.W.Steudel, Ann., **629**, 53 (1960).
78. K.W.Egger, J.Amer.Chem.Soc., **91**, 2867 (1969).
79. K.W.Egger, J.Chem.Soc., Faraday Trans.I, **68**, 423 (1972).
80. K.W.Egger, J.Chem.Soc.A, 3603 (1971).
81. A.T.Cocks and K.W.Egger, J.Chem.Soc.A, 3606 (1971).
82. P.Cossee, J.Catal., **3**, 80 (1964).
83. P.Cossee, P.Ros, and J.H.Schachtschneider, "Proceedings of the IVth International Congress on Catalysis (Moscow, 1968)", Acad.Kiado, Budapest, 1971, p.237.
84. J.W.Begley and F.Penella, J.Catal., 8, 203 (1967).
85. D.R.Armstrong, P.G.Perkins, and J.J.P.Stewart, J.Chem.Soc., Dalton Trans., 1972 (1972).
86. O.Novaro, S.Chow, and P.Magnonat, J.Catal., **41**, 91 (1976).
87. O.Novaro, S.Chow, and P.Magnonat, J.Catal., **42**, 131 (1976).
88. D.R.Armstrong, F.Fortune, and P.G.Perkins, J.Catal., **42**, 435 (1976).
89. V.I.Avdeev, I.I.Zakharov, V.A.Zakharov, G.D.Bukatov, and Yu.I.Ermakov, Zhur.Strukt.Khim., **18**, 525 (1977).
90. D.R.Armstrong, P.G.Perkins, and J.J.P.Stewar, Rev. Roumaine Chim., **19**, 1695 (1974).
91. P.Ros, "Proceedings of the International Symposium on Chemical and Biochemical Reactivity, Jerusalem, 1974", p.207.
92. N.Rösch and K.H.Jonson, J.Mol.Catal., 1, 395 (1976).
93. D.R.Armstrong, P.G.Perkins, and J.J.Stewart, Rev. Roumaine Chim., **20**, 177 (1975).

94. V.E.L'vovskii and G.B.Erusalimskii, Koord.Khim., **2**, 1221 (1976).
95. M.J.S.Dewar, Bull.Soc.chim.France, **18**, C79 (1971).
96. J.Chatt and L.A.Duncanson, J.Chem.Soc., 2939 (1953).
97. G.Natta, I.Pasquon, J.Svab, and A.Zambelli, Chim.e Ind.(Milano), **44**, 621 (1962).
98. V.I.Tsvetkova, A.P.Firsov, and N.M.Chirkov, Dokl. Akad.Nauk SSSR, **142**, 149 (1962).
99. V.A.Zakharov, N.B.Chumaevskii, Z.K.Bukatova, G.D.Bukatov, and Yu.I.Yermakov, React.Kinet. Catal.Letters, **5**, 429 (1976).
100. V.A.Zakharov, Z.K.Bukatova, S.I.Makhtarulin, N.B.Chumaevskii, and Yu.I.Ermakov, Vysokomol.Soed., **21A**, 496 (1979).
101. Yu.I.Ermakov, L.P.Ivanov, and A.G.Gel'dshtein, Kinetika i Kataliz, **10**, 183 (1969).
102. P.Cossee, Trans.Faraday Soc., **58**, 1926 (1962).

Institute of Catalysis,
Siberian Division of the
USSR Academy of Sciences,
Novosibirsk

Translated from *Uspekhi Khimii*, 49, 2241-2254 (1980) U.D.C. 666.1.056:620.197

The Attaching of Biologically Active Compounds to the Surfaces of Optical Materials

A.Baigozhin

The methods of forming chemisorbed molecular films with fungicidal, hydrophobic, and other useful properties on the surfaces of optical materials as well as the prospects for the employment of such films are surveyed.
The bibliography includes 105 references.

CONTENTS

I. Introduction 1112
II. Methods for the formation of biologically active films on the surfaces of optical components 1112
III. The grafting of biologically active compounds to the surfaces of optical materials 1113
IV. The mechanism of the fungicidal action of organoelementosiloxane films bound chemically to the surfaces of optical glasses 1116

I. INTRODUCTION

Under the conditions of a moist tropical climate, materials are infected with microorganisms, which leads to their premature ageing. Microscopic fungi cause considerable damage to materials such as leather, textiles, rubber, optical glass, and others[1-18]. It is known that under moist tropical conditions the surfaces of optical components (lenses, prisms, etc.) in instruments are coated by growing microscopic fungi and are damaged by them[2-12,17,18]. Even small amounts of fungi on the surface of optical components, invisible to naked eye on other materials, lower the quality of the optical systems of instruments. Many valuable optical instruments and optical equipment have been put out of order as a consequence of infection by microorganisms[3-6].

In order to protect from biological damage materials and articles designed for use under tropical conditions, it is suggested that substances with fungicidal or fungistatic properties be used; with the aid of fungicides, it is possible to increase the reliability and the useful lifetime of articles under the conditions of a moist tropical climate[16-18].

Volatile fungicides have been proposed[4,5,14,17,19-21] (impregnation of packing material, fungicide placed in cartridges and in porous materials, introduction of fungicide into greases, putty, and varnishes, used in the inner spaces within apparatus). However, these attempts did not yield the desirable results, because certain fungicidal substances, while protecting the instrument from biological growth, caused the corrosion of metallic components or, by condensing, formed deposits on the surfaces of optical components which impaired their light transmittance. In order to impart biological stability to different materials, they have been frequently impregnated with fungicidal solutions or emulsions[16-23]. In this case the fungicides protect the materials only for a short time, since they are washed away. Much attention has therefore been devoted to the creation of materials in which biologically active compounds would be attached to the surface by chemical bonds[18,22-24,49-54].

During recent years extensive experimental data have accumulated on the formation of chemisorbed molecular biologically active films on the surfaces of optical components, which do not change the optical properties of glasses but effectively protect them from biological growth and damage. This review is a brief survey of research devoted to the attaching of compounds with biological activity and other useful properties to the surfaces of optical materials. Its aim is to survey the accumulated data in this field, which is of significant theoretical importance and has a wide variety of practical applications.

II. METHODS FOR THE FORMATION OF BIOLOGICALLY ACTIVE FILMS ON THE SURFACES OF OPTICAL COMPONENTS

The classical study by Academician Grebenshchikov on the chemistry of glass has shown that the surface properties of glass are determined mainly not by its composition but by new formations arising in the course of its interaction with water[25]. Grebenshchikov used the term "prosvetlemie optiki" [deposition of non-reflective layers on optical glass] for the formation on glass of thin films leading to a decrease of the amount of light reflected from its surface. Studies on the coating of optical glass and the formation of thin transparent films on its surface have been surveyed in monographs[26,27]. Further investigation of the mechanism of the production of new formations and of their properties made it possible to modify specifically the properties of the surfaces of optical glasses over a wide range[28-30,51]. One of such methods involves the attaching of organoelemental compounds, with biological activity and other useful properties, to the surfaces of optical materials.

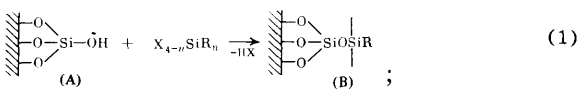
The attachment of biologically active compounds directly to the surfaces of optical materials presents considerable difficulties. The unmodified surface of the glass cannot retain appreciable amounts of the substance preventing the development of microscopic fungi. The modification of the surfaces of silicate materials by organosilicon compounds in order to impart to them hydrophobic properties[27,31,32], to form optical coatings[27,33,34], to reduce[35,36] or increase[36,37] the adhesion of polymeric resins, or as a finish to reinforced plastics has been the subject of a large number of studies surveyed in a series of reviews and monographs[27 31,37,43,47,48]. However, in these investigations the problems of attaching biologically active compounds to the surfaces of optical materials were not considered.

A series of investigations have been devoted to the development of fundamentally new methods, based on chemical reactions, for the specific modification of the surface properties of optical materials[18,49-54]. It was of interest to synthesise biologically active films by the chemical modification of glass. Such films must satisfy the following requirements:

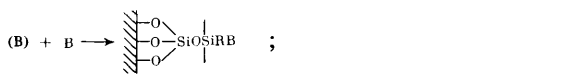
(a) they must adhere effectively to the glass and must be mechanically strong; (b) they must be stable during use under specified climatic conditions; (c) they must not impair the optical properties of glasses; (d) they must not act on the materials forming part of the construction of the instrument or apparatus.

For the chemical modification of the surface of glass, it proved promising to investigate organosilicon compounds of the type R_nSiX_{4-n}. The interest in this group of substances is due to the fact that they contain two types of reactive groups among which groups X (chlorine or lower alkoxy-groups) react with the OH groups on the surface of glass and groups R (organic substituent containing functional groups) interact with the binders. As a result of this, it is possible to carry out a wide variety of reactions on the basis of compounds of this type as a function of the type and nature of the functional groups and the reacting (binding) substances. Carbofunctional organosilicon compounds have found extensive applications for increasing the adhesion of polymeric resins to various materials[38–48] and particularly for increasing the resistance of transparent plastics to water[43,48].

The possibility of attaching biologically active substances to the surfaces of optical materials with the aid of organosilicon compounds containing functional groups has been demonstrated in a number of studies[18,49–54]. Biologically active films are synthesised via mechanisms (1) and (2):



(1)



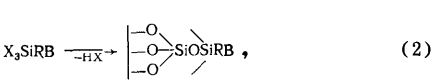
;

R=CH=CH₂, CH₂—CH=CH₂,
—(CH₂)₃—O—CH₂—CH—CH₂, —(CH₂)₃NH₂, X = Cl, OCH₃, or OC₂H₅ .

Here (A) is the surface of the glass, (B) the modified surface of the glass, and B the biologically active compound inhibiting the development of microorganisms.

Films are synthesised in two stages via mechanism (1)—initially a carbofunctional organosilicon compound and then the biologically active substance are deposited on the surface of the glass. This yields organoelementosiloxane films which protect the surfaces of optical components from microbiological growth and damage[49–52,54].

The synthesis of surface-active compounds via mechanism (2), where biologically active groups are already contained in the initial organosilicon compound, i.e. in the organic group R, is more promising and technologically more useful[53]. Thus it is possible to graft biologically active compounds to the surfaces of glass or other materials in a single stage:



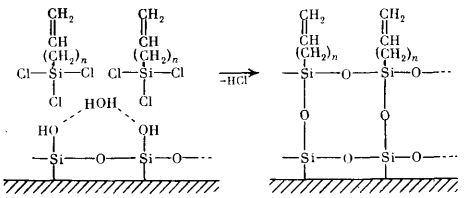
(2)

where R is an organic substitutent or a substituent containing a functional group, B is a biologically active group (for example, HgR′, AsR'_2, and SnR'_3, where R′ is an organic substituent or an acid residue), and X = OCH_3 or OC_2H_5.

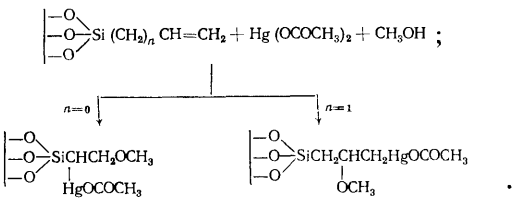
Mechanism (2) has been studied very little, since the methods of synthesis of organosilicon compounds containing biologically active fragments have been developed only recently [55–58]. The modification of the surfaces of materials by organoelemental siloxanes via mechanism (2) in order to alter specifically their surface properties is undoubtedly of great interest. Examples of the attaching of biologically active compounds to the surfaces of optical materials via the mechanisms described above will be considered below.

III. THE GRAFTING OF BIOLOGICALLY ACTIVE COMPOUNDS TO THE SURFACES OF OPTICAL MATERIALS

It is known that organomercury compounds are the most universal fungicides, effective against a wide range of microorganisms and active at very low concentrations[59–62]. For example, alkyl(aryl)mercury acetates prevent the growth of a wide variety of microorganisms at a dilution of $1 : 8 \times 10^6$ and some of them at a dilution of $1 : 2 \times 10^7$. A two-stage method for the synthesis of organomercurisiloxane films on the surfaces of optical glasses has been developed[49,50,54]. Optical components made of different brands of silicate glasses are treated initially with a solution of trichlorovinyl(or allyl)-silane in a non-polar solvent or with solution of triethoxy-vinyl(allyl)silane in water or alcohol. In the hydrolysis of alkenyltrichloro(ethoxy)silanes the aqueous film and the hydroxy-groups present on the surface of the glass are involved in the reaction. The reaction of alkenylsilanes with the surface of the glass is represented schematically as follows[38,44,50]:



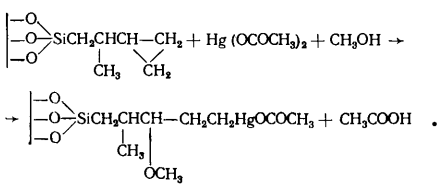
Hydrophobic alkenylsiloxane films are then formed on the surface of the component. These components are then treated further with a methanol solution of mercury acetate. Mercury acetate in methanol or aqueous solutions is known to add quantitatively to the ethylene linkage[62–66]. The reaction of the alkenylsiloxane film with mercury acetate can be represented by the following scheme:



As a result of the exposure to a methanol solution of mercury acetate of glass treated with trichloro(ethoxy)vinyl(or allyl)silane, molecular films of α-acetoxy-β-methoxymercuriethylsiloxane and 3-acetoxy-2-methoxymercuripropylsiloxane are formed respectively. The addition of mercury acetate in methanol to vinylsiloxane takes place contrary to the Markovnikov rule, the mercury atom with the acid residue forming a bond with the carbon atom containing fewer hydrogen atoms, which is caused by the electropositive properties of the silicon atom; the addition to allylsiloxane proceeds in conformity with the Markovnikov rule. The validity of these reaction mechanisms has been confirmed by the model synthesis with trimethylvinylsilane[67].

A method has been proposed for attaching an organomercury compound on the surface of glass using trichloro-2-(cyclopropyl)propylsilane instead of alkenylchlorosilanes[18]. Cyclopropane derivatives are capable of undergoing a reaction, involving the opening of the ring, with mercury acetate in methanol[68], and the products exhibit an extremely high

biological activity[69]. The formation of an organomercury compound on the surface of the glass can be represented by the following scheme:



The addition of mercury acetate to alkenylsiloxane groups proceeds in the course of 1–2 h (complete saturation with mercury), while the addition to 2-(cyclopropyl)propylsiloxane groups is somewhat slower: complete saturation takes place only after six days, but the resulting molecular film of 5-acetoxy-3-methoxy-2-methylmercuripentylsiloxane is stable over a period of time[18].

The addition of mercury acetate has been monitored on the basis of the variation of the wetting angle for the wetting of organosiloxane films with water, by determining the amount of mercury on the surface of the glass, and on the basis of the results of microbiological tests[18,50,51].

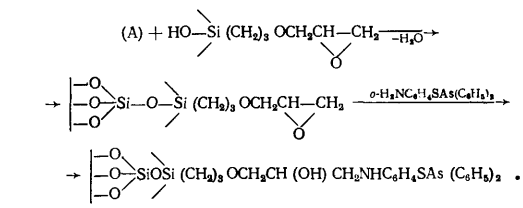
It has been shown[18] that the calculated area per hydroxy-group of the SiO_2 surface hydrated to the maximum extent varies from 10.4 to 16.8 Å^2. It has been established[70] that the actual surface of polished quartz is 2.4 times greater than the geometrical surface. On the basis of these data, it is easy to show in relation to a monomolecular layer that there should be approximately 0.9×10^{-6} g of mercury per cm^2 of the treated surface of the glas [it has been found[18,50] that the amount of mercury per cm^2 is $(1.0–1.2) \times 10^{-6}$ g].

Microbiological tests have demonstrated[50,51,71,72] that optical glasses coated by organomercurisiloxane films are not damaged by moulds when they are deliberately infected by aggressive fungal cultures under conditions imitating a moist tropical climate in the course of one and a half years, while control glasses are damaged by such fungi after 10–15 days. These results were confirmed by a special investigation under natural subtropical and moist tropical conditions[18,50,51]. One should note that the surface of the glass treated solely with organosilanes or solely with a methanol solution of mercury acetate without a preliminary deposition of an alkenyl- or cyclopropyl-siloxane film does not prevent the development of the spores of moulds or exhibits only a very weak activity which disappears after the first month of tests.

One should note that fungicidal organomercurisiloxane films with a thickness of 10–15 Å do not influence the optical properties of glasses[50–51]. These films can be formed on all optical silicate materials. They are also applicable to non-silicate materials when non-reflective layers are deposited on their surfaces. Optical materials are as a rule coated using refractory metal oxides (Ti, Zr, Hf, Se, etc. oxides). Non-reflective layers made of these oxides are obtained by a chemical method or by vacuum sputtering[27] and in multilayer coating the last layer is usually silica.

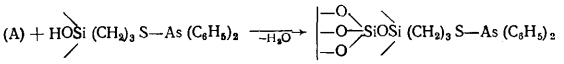
2. Organosiloxane Films Containing Arsenic

In order to obtain fungicidal films, certain organoarsino-siloxanes have been investigated. They are of interest, because they combine the known properties of polysiloxane with the ability to prevent the development of various micro-organisms. These properties permit their use both as agents imparting hydrophobic properties and as fungicides. According to mechanism (1), the glasses are initially treated for this purpose with an ethanol solution of 2,3-epoxypropoxypropyl-triethoxysilane and then with a toluene solution of *o*-amino-phenylthiodiphenylarsine[18]:



Optical glasses treated in accordance with this scheme are not affected by moulds under conditions imitating those in a moist tropical climate.

In recent years methods have been developed for the formation of trialkoxysilylalkyl esters of arsenic(III) thioacids[73,74]. The most active compound—triethoxy-γ-(diphenylarsinothio)-propylsilane—forming thin transparent fungicidal films on the surface of glass, was selected from these esters[53]:



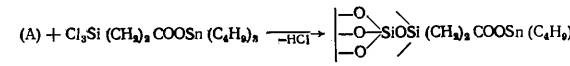
The γ-(diphenylarsinothio)propylsiloxane film is mechanically strong and is not washed away by organic solvents. Optical glasses protected in this way are resistant to microbiological growth[85].

3. Films Based on Organotin(Silicon) Compounds

It has been established[75,76] that organotin compounds of the type R_3SnX, where R = alkyl and X is an organic or inorganic acid residue, exhibit an extremely high fungicidal activity, comparable to that of mercury compounds. In contrast to R, the nature of the acid residue does not have a significant influence on the activity of the compound. It has been shown[76] that, among asymmetric acyltrialkylstannanes, maximum toxicity to fungi is shown when the total number of carbon atoms is 9–12, regardless of the nature of the individual groups.

Organotin compounds of the type indicated above have found extensive applications for the protection of a wide variety of materials against microbiological growth[77–83]. Among compounds of this class, triethylmethacryloxystannane (TEMS) proved to be of greatest interest. Its alcoholic solutions form on the surface of glass transparent but mechanically weak films. This disadvantage was eliminated by combining TEMS with tetraethoxysilane and polydimethylphosphorosiloxane (GSF-3).[84,85] Films obtained from a mixture of solutions of the above compounds are mechanically strong and effectively protect optical components made of chemically unstable glasses (of the type STK, TBF, TFK, and others) against biological damage[85]. Furthermore, TEMS mixed with a PTFE varnish forms a film on the surfaces of optical components made of LiF crystals, which does not alter the optical properties of the crystals and protects them against moisture and biological growth[86].

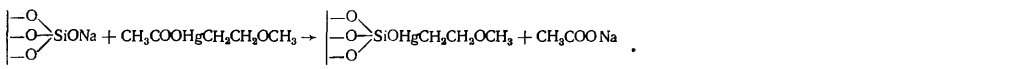
These films can be used to protect silicate and non-silicate materials. At the same time methods have been proposed for the grafting of organotin(silicon) compounds by treating the glass with solutions of trialkyltin trichlorosilylalkanoates, for example, tributyltin β-trichlorosilylpropionate[87]:



The β-(tributylstannylcarboxy)ethylsiloxane film is hydrolytically unstable and therefore protects the glass against biological growth only for a short time. A film with an increased hydrolytic stability has been obtained on the basis of β-(triethylstannylthio)ethyltriethoxysilane[105].

4. Films Containing the Si–O–M Group

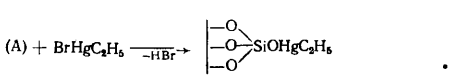
It has been suggested that glasses be treated with an ethanol solution of methoxyethylmercury acetate in order to protect optical components from damage by moulds[88,89]. It is suggested that such treatment results in the formation of a fungicidal coating—methoxyethylmercury silicate—via the mechanism[89]



When sodium ethyl- or methyl-siliconate is deposited on textile fabrics, the surfaces of the latter become hydrophobic. There is evidence[90,91] that, when fabrics treated in this way are immersed in an aqueous solution of a copper salt, sodium ions are replaced by copper ions and the fabric then requires resistance to moulds. On this basis and bearing in mind the use of the oligodynamic properties of noble metals, it was of interest to obtain such compounds on the surface of glass. For this purpose, glasses were initially coated with sodium ethyl- or methyl-siliconate and then with solutions of copper, silver, and platinum salts; as a result of such treatment, the glasses were not affected by fungi for two months[18,50].

It has been suggested that optical components be protected by depositing coatings from a mixture of an alcoholic solution of tetraethoxysilane, lead acetate, and boric acid[92]. Heat treatment (at ~400 °C) of this coating results in the formation of silicon, boron, and lead oxides on the surface of the glass; the oxides retard the development of moulds, but rapidly become turbid on the surface of the glass under the influence of atmospheric moisture. The composition of this coating resembles that of lead borate glasses (BSZ, TS8, etc.), which are chemically unstable and require protection from atmospheric moisture.

The authors of a patent[93] deposited a fungicidal coating from hydrolysable solutions of silicate and titanate esters in the presence of soluble copper or mercury compounds. However, the deposition of fungicidal coatings on the surface of glass from hydrolysable solutions of tetraethoxysilane with introduction of copper, silver, mercury, and lead salts as well as certain organic fungicides—chlorophenols, nitro-(fluoro)benzenes, and other compounds—proved to be insufficiently effective against damage by moulds[18,50,94]. A method has been proposed[95] for protecting optical components in accordance with the scheme

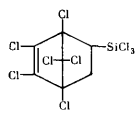
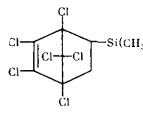
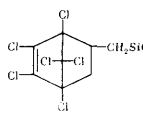
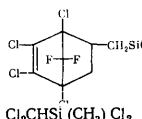


The fungicidal coating thus obtained inhibit the development of microorganisms only for a short time (for 2–3 months). This is because compounds containing the group $\geq$Si–O–M (where M = Hg, Ag, Cu, Pb, or B) are readily hydrolysed under the influence of atmospheric moisture, losing their fungicidal properties.

5. Halogeno-organosiloxane Films

The comparative study of the properties of chloro- and fluoro-derivatives of organosiloxanes on the surfaces of optical glasses appeared of interest because in many instances the introduction of a fluorine atom instead of chlorine or their joint presence in the composition of organic molecules greatly increases the fungicidal action of the compound. On this basis, films of compounds of the type R_nSiX_{4-n} [R = organochloro(fluoro)-group], the formulae of which are given in the Table, have been obtained on the surface of glass[18,50]. These compounds contain active chlorosilyl groups, which interact chemically with the surface of the glass on which there are covalently bound hydroxy-groups and adsorbed water molecules, and give rise to thin halogeno-organosiloxane films,

The fungicidal activities of organofluoro(chloro)siloxane films on the surface of glass[18,50].

No.	Formula of film-forming compound (Ref.96)	Resistance of glass* with a film to fungi
1		—
2		—
3		—
4		—
5	$Cl_2CHSi(CH_3)Cl_2$	—
6	$Cl_2CHSi(CH_3)(OC_2H_5)_2$	—
7	Cl_3CSiCl_3	—
8	$Cl_3CSi(CH_3)Cl_2$	—
9	$F_3CHCH_2Si(CH_3)Cl_2$	—
10	$F_3CHCF_2Si(CH_3)Cl_2$	—
11	$CF_2{=}CFSi(C_2H_5)Cl_2$	—
12	$F_3CHCF_2O(CH_2)_3SiCl_3$	—
13	$[F_2CHCF_2O(CH_2)_3]SiCl_2$	—
14	$4\text{-}FC_6H_4Si(CH_2CH_2CF_3)Cl_2$	—
15	$CF_3CH_2CH_2SiCl_3$	+
16	$(CF_3CH_2CH_2)_2SiCl_2$	+
17	$F_2CH(CF_2)_3Si(CH_3)Cl_2$	+

Note: "–"—not resistant to fungi; "+"—resistant to fungi.

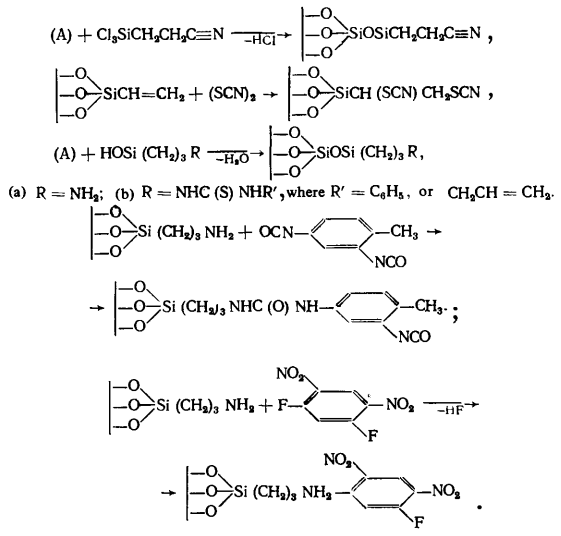
Chloro-organosiloxane films on the surface of glass do not prevent the development of moulds. Fluoro-organosiloxane films, obtained from compounds Nos.15–17 (see Table), suppressed the development of the spores of moulds in the course of 3–4 months, but subsequently the growth of fungi intensifies. The remaining fluoro-derivatives of silanes listed in the Table do not protect glass from the growth of moulds[18,50].

Iodine and its compounds are classical antiseptics. It is known that iodine adds quantitatively to unsaturated organic compounds and it has been shown that glasses with an

attached vinylsiloxane film, treated in iodine vapour or a solution of iodine in chloroform[18,52] are not overgrown by moulds in the course of 5 months under conditions imitating those in the tropics. However, iodo-organosiloxane films on the surface of glass have absorption bands in the visible region of the spectrum and in addition are unstable under the influence of light.

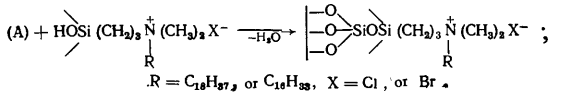
6. Nitrogen-Containing Organosiloxane Films

Since nitrogen-containing organosilicon compounds exhibit a high biological activity[55,56,97,99], it appeared of interest to attempt to use them for the formation of protective films on the surface of glass. For this purpose, the following reactions were carried out in succession on the surface of glass (A):[18,50,98,99]



Organosiloxane films containing cyano-, thiocyanato-, amino-, and phenyl(allyl)-thiourea groups and formed on the surface of the glass do not prevent the development of moulds. Fluoro(nitro)phenylaminopropylsiloxane films arrest the growth of fungi for a short time[18,50].

It has been shown[100] that the surfaces of materials, including glasses, are reistant to the action of a wide range of micro-organisms when they are treated with a solution of *N,N*-dimethyl-*N*-octadecyl-*N*-(3-trimethoxysilylpropyl)-ammonium chloride. As a consequence of a further development of these studies, the glasses were then treated with the products of the hydrolysis of organosilicon quaternary ammonium salts via the mechanism



Films obtained from the above compounds and tested by the method developed by Rodionova and coworkers[71,72] protected glasses from the growth of moulds for a short time.

It is noteworthy that the organosilicon quaternary ammonium compounds indicated above, deposited on the surface of glass, orient nematic liquid crytals homogeneously or homeotropically, depending on the functional groups in the organic substituent attached to the silicon atom and are used in the manufacture of liquid crystal devices[101].

IV. THE MECHANISM OF THE FUNGICIDAL ACTION OF ORGANOELEMENT SILOXANE FILMS BOUND CHEMICALLY TO THE SURFACES OF OPTICAL GLASSES

One of the current problems is the elucidation of the chemical mechanism of the action of fungicides, which is linked directly to their structure and reactivity. Numerous studies, surveyed in a number of reviews and monographs[61,102–104], have been devoted to the mechanism of the action of fungicides.

The majority of the known fungicides have been discovered empirically. Although complex biochemical and physicochemical mechanisms of the action of fungicides at a molecular level have been investigated inadequately, a definite idea about them has already been formulated. Three main types of action of fungicides have been distinguished[102–104]:

(1) inhibition of bioenergetic processes (cell respiration, oxidative phosphorylation, etc.);

(2) inhibition of the biosynthesis of low-molecular-weight (aminoacids, vitamins, etc.) and high-molecular-weight (proteins, DNA, RNA) compounds;

(3) the breakdown of the permeability of cell membranes (physicochemical breakdown of cell structures).

In general, the mechanisms of the action of fungicides bound chemically to the surface of glass agree with the mechanisms of the action of the usual fungicides indicated above, but they can have their characteristic features requiring amplification and refinement. It is known that enzymes (as biocatalysts) are involved in all biochemical processes in the cell and thus promote its growth and development. In this connection, we believe that the main function of organosiloxane films, containing biocidal groups in the organic substituent and bound chemically to the surface of glass, is to act against enzymes, i.e. the films should inhibit or disrupt the activity of vitally important "transport" enzymes with sulphydryl groups SH. This task can be fulfilled by organosiloxane films containing in the organic substituent heavy metal atoms, particularly Hg and Sn atoms. The methods for the synthesis of such organomercuri- and organostannyl-siloxane films on the surface of glass and their properties were examined above. These molecular films, with a thickness of ~10–15 Å, protect the glass from the growth of mould without altering its optical properties.

Next one must consider another possible mechanism of the action of organoelementosiloxane films on microorganisms. The majority of the cells in a living organism approach to some extent the crystalline state. A wide variety of types of molecules, occupying a more or less fixed position and oriented in a specific manner, exist in a "crystal-like state" in the cell. It is therefore possible that certain organoelementosiloxane films disrupt a specific orientation of the molecules within the cell and hence alter the normal cell metabolism, which suppresses its vital activity, i.e. the films act as fungistatic agents. For example, γ-trifluoropropyl- and bis-(γ-trifluoropropyl)-siloxane films prevent the development of fungi for 3–4 months under conditions where they are deliberately infected with the spores of moulds[18,50]. At the same time, it is known that organosiloxane films containing functional groups in the organic substituent give rise to a time-invariant orientation of the molecules of nematic liquid crystals towards the surface of the glass either homogeneously or homeotropically, depending on the type of substituents and their functional groups[101].

On the basis of experimental data, it is possible to arrive at quite definite conclusions concerning the principles governing the search for and selection of highly effective biologically active compounds and their use for the formation of molecular films on the surfaces of optical components,

which do not alter the optical properties of the glasses but protect them from microbiological growth and damage.

Evidently, according to the proposed working mechanisms (1) and (2), it is possible to set up organoelementosiloxane films with fungicidal and other useful properties. It has been shown that organomercuri(stannyl)siloxane films exhibit for a long time a fungistatic activity at very low concentrations, which is important for the protection of specific properties of materials. New highly effective fungicides have been found—film-forming tin compounds of the type R_3SnX, where R = ethyl or butyl and X is a residue of an unsaturated carboxylic acid (as, for example, in triethylmethacryloxystannane).

Tests on various organoelementosiloxane films on the surfaces of optical materials led to the following findings:

1. If the biologically active atom or group of atoms is bound to the organosiloxane fragment by a strong covalent bond, then the films do not prevent the development of moulds.

2. If the biologically active atom or group of atoms is bound to the organosiloxane fragment by an ionic, coordinate, or polar covalent bond, the films protect the optical components from the grown of moulds. The duration of action of the film depends on the nature of the chemical bond formed by the atom or group of atoms; it increases in the sequence ionic < coordinate < polar covalent bond.

In conclusion we may note that the data described above indicate fairly convincingly the extensive possibilities for the occurrence of a wide variety of reactions leading to the formation on the surfaces of optical materials of molecular films with useful properties. Similar reactions can be used to form films on other solid materials with covalently bound hydroxy- or other reactive groups on the surface. The present author believes that organoelementosiloxane films on the surfaces of materials can be used to set up models of enzymes or antienzyme systems, protein substances, highly effective medicinal preparations with a wide spectrum of therapeutic action, selective catalysts, corrosion inhibitors, orienting coatings for liquid crystals, and other systems.

REFERENCES

1. M.I.Khozyainov and M.M.Ioganson, Optiko-Mekhan. Prom., No.3, 3 (1935).
2. J.S.Turner, E.McLennan, J.Rogers, and E.Mathaei, Nature, **158**, 469 (1946).
3. G.Greathouse and C.Wessel, "Deterioration of Materials", New York, 1954.
4. L.Teitel and S.Berk, Ind.Eng.Chem., **44**, 1088 (1952).
5. S.Berk and L.Teitel, Ind.Eng.Chem., **46**, 778 (1954).
6. M.Rauschert, Z.Verein.Deutsch.Jng., **96**, 778 (1954).
7. A.G.Samartsev, Optiko-Mekhan.Prom., No.1, 3 (1957).
8. V.I.Mordasov, Optiko-Mekhan.Prom., No.1, 50 (1957).
9. A.Kaller, Feingeratetechnik, **8**, 359 (1959).
10. A.Kaller, Feingeratetechnik, **9**, 20, (1960).
11. A.Kaller, Feingeratetechnik, **11**, 45 (1962).
12. S.Minăr, Jemna mech.a optika, No.7, 235 (1959).
13. G.Polman and F.Oberlis, Glasstechn.Berichte, **35**, 60 (1962).
14. B.B.Saxena, S.S.Nigam, and S.R.Sengupta, Indian J. Technology, **1**, 283 (1963).
15. M.Richter and B.Bartakova, "Modification of Electrical Equipment for Tropical Conditions" (Translated into Russian from Czech), Gosenergoizdat, Moscow, 1962.
16. R.Blahnik and V.Zanova, "Mikrobialni Koroze" (Microbiological Corrosion) (Translated into Russian from Czech), Izd.Khimiya, Leningrad, 1965.
17. S.Nagamuttu, Intern.Biodeterior.Bull., **3**, 25 (1967).
18. A.Baigozhin, Candidate's Thesis, GOI, Leningrad, 1969.
19. P.W.Baker, Intern.Biodeterior.Bull., **3**, 59 (1967).
20. P.W.Baker, Intern.Biodeterior.Bull., **4**, 59 (1968).
21. A.Baigozhin, M.S.Rodionova, E.I.Panfilenok, L.V.Bereznikovskaya, L.V.Sergev, T.N.Naryshkina, and V.B.Geflikh, USSR P.210 561 (1966); Byul. Izobret., No.6 (1968).
22. Z.A.Rogovin, "Khimicheskie Prevrashcheniya i Modifikatsiya Tsellyulozy" (Chemical Transformations and Modification of Cellulose), Izd.Khimiya, Moscow, 1967, p.135.
23. A.D.Virnik, E.M.Akovbyan, L.S.Gal'braikh, and Z.A.Rogovin, Izv.Vys.Ucheb.Zaved., Tekhnol.Tekst. Prom., No.4, 103 (1968).
24. A.D.Virnik, Uspekhi Khim., **42**, 547 (1973) [Russ. Chem.Rev., No.3 (1973)].
25. I.V.Grebenshchikov and T.A.Favorskaya, Trudy GOI, 7, No.72 (1931).
26. I.V.Grebenshchikov, A.G.Vlasov, B.F.Neporent, and N.V.Suikovskaya, "Prosvetlenie Optiki" (Non-Reflective Coatings on Optical Materials), Gostekhizdat, 1946.
27. N.V.Suikovskaya, "Khimicheskie Metody Polucheniya Tonkikh Prozrachnykh Plenok" (Chemical Methods for the Preparation of Thin Transparent Films), Izd. Khimiya, Leningrad, 1971, pp.154, 172.
28. K.S.Evstrop'ev and V.S.Molchanov, Trudy GOI, **31**, 7 (1963).
29. A.Ya.Kuznetsov, Trudy GOI, **31**, 87 (1963).
30. N.V.Suikovskaya, Trudy GOI, **31**, 40 (1963).
31. V.Bažant, V.Chvalovsky, and J.Rathousky, "Organosilicon Compounds" (Translated into Russian from Czech), Moscow, 1960, p.285.
32. A.A.Pashchenko and M.G.Voronkov, "Kremniiorganicheskie Pokrytiya" (Organosilicon Coatings), Izd. Tekhnika, Kiev, 1969.
33. Z.V.Shirokshina, Optiko-Mekhan.Prom., No.9, 39 (1974).
34. A.P.Kuleshov, N.V.Suikovskaya, Z.V.Shirokshina, and K.V.Sarakhova, USSR P.550 356 (1977); Ref. Zhur.Khim., 24M169 (1977).
35. A.Ya.Korolev, Symposium, "Klei i Tekhnologiya Skleivaniya" (Adhesives and Technology of the Formation of Adhesive Bonds), Oborongiz, 1960, p.35.
36. P.V.Kozlov (Editor), Symposium, "Adgeziya Polimerov" (Adhesion of Polymers), Izd.Akad.Nauk SSSR, 1963, pp.3, 75, 99, 137.
37. W.A.Korel, K.Hoefelmann, and E.Plueddemann, Kunststoffe, **65**, 760 (1975).
38. J.Bjorksten, L.L.Yaeger, and J.E.Henning, Ind.Eng. Chem., **46**, 1632 (1954).
39. L.F.Biefeld and T.E.Phillips, Ind.Eng.Chem., **45**, 1281 (1953).
40. M.Jellinek, Mod.Plastics, **30**, 150 (1952).
41. N.M.Trivisonno, L.Lee, and S.Skinner, Ind.Eng. Chem., **50**, 912 (1958).
42. H.Clark and E.Plueddemann, Ind.Eng.Chem., **40**, 133 (1963).
43. B.A.Kiselev, Uspekhi Khim., **27**, 1101 (1958).
44. A.Baigozhin and L.V.Sergeev, Vysokomol.Soed., **4**, 972 (1962).
45. L.V.Sergeev, A.Baigozhin, and S.G.Fattakhov, Vysokomol.Soed., **4**, 977 (1962).
46. A.Baigozhin, L.V.Sergeev, A.K.Dabagova, and S.G.Fattakhov, Symposium, "Adgeziya Polimerov" (Adhesion of Polymers), Izd.Akad.Nauk SSSR, 1963, p.75.
47. S.Reichel, Plaste und Kautschuk, **15**, 501 (1968).
48. A.I.Mikhal'skii, Uspekhi Khim., **39**, 2050 (1970) [Russ. Chem.Rev., No.11 (1970)].

49. A.Baigozhin and A.T.Troshchenko, USSR P.116 493 (1958); Byul.Izobret., No.12 (1958).
50. A.Baigozhin, M.S.Rodionova, L.V.Bereznikovskaya, and L.V.Sergeev, Optiko Mekhan.Prom., No.7, 40 (1963).
51. A.Baigozhin, M.S.Rodionova, and L.V.Sergeev, Trudy GOI, **31**, 103 (1963).
52. A.Baigozhin, E.I.Panfilenok, M.S.Rodionova, L.V.Bereznikovskaya, and N.V.Suikovskaya, USSR P. 233 190 (1967); Byul.Izobret., No.2 (1969).
53. A.Baigozhin, E.I.Panfilenok, M.S.Rodionova, L.V.Bereznikovskaya, and N.A.Chadaeva, USSR P. 341 771 (1970); Byul.Izobret., No.19 (1972).
54. A.Baigozhin, A.I.Sviridova, M.S.Rodionova, E.I.Panfilenok, and L.V.Bereznikovskaya, USSR P. 544 626 (1977); Byul.Izobret., No.4 (1977).
55. M.G.Voronkov and E.Lukevics, Uspekhi Khim., **38**, 2173 (1969) [Russ.Chem. Rev., No.12 (1969)].
56. M.G.Voronkov, G.Zelcans, and E.Lukevics, "Kremnii i Zhizn'" (Silicon and Life), Izd.Zinatne, Riga, 1978.
57. N.F.Chernov and M.G.Voronkov, Zhur.Obshch.Khim., **47**, 794 (1977).
58. N.F.Chernov, Candidate's Thesis, Irkutsk Institute of General Chemistry, Siberian Division of the USSR Academy of Sciences, Irkutsk, 1977.
59. W.A.Sexton, "Chemische Konstitution und biologische Wirkung", Stuttgart, 1958.
60. N.N.Mel'nikov, I.L.Vladimirova, and S.N.Ivanova, "Khimicheskie Sredstva Predokhraneniya Nemetallicheskikh Materiallov ot Razrusheniya Mikroorganizmami. Trudy NIUIF" (Chemical Means of Protecting Non-Metallic Materials Against Decomposition by Microorganisms. Transactions of the NIUIF), Moscow, 1959, No.165.
61. J.G.Horsfall, "Principles of Fungicidal Action" (Translated into Russian), Inostr.Lit., Moscow, 1948.
62. F.C.Whitmore, "Organic Compounds of Mercury" (Translated into Russian), ONTI, Leningrad, 1938.
63. L.G.Makarova and A.N.Nesmayanov, "Sinteticheskie Metody v Oblasti Metallorganicheskikh Soedinenii Rtuti" (Synthetic Methods in the Field of Organometallic Compounds of Mercury), Izd.Akad.Nauk SSSR, Moscow, 1945, p.59.
64. J.Chatt, Chem.Rev., 7 (1951).
65. M.Das, Anal.Chem., **26**, 1086 (1954).
66. O.A.Reutov, "Teoreticheskie Osnovy Organicheskoi Khimii" (Theoretical Foundations of Organic Chemistry), Izd.Moskov.Gos.Univ., 1964, p.266.
67. D.Seyferth and N.Kohlen, Z.Naturforsch., **14**, 137 (1959).
68. R.Ya.Levina and V.N.Kostin, Zhur.Obshch.Khim., **23**, 1054 (1953).
69. N.N.Lebedev, S.A.Efremova, V.N.Kostin, and R.Ya.Levina, Vestnik Moskov.Gos.Univ., No.3, 149 (1957).
70. A.K.Pogodaev and D.P.Dobychin, Zhur.Fiz.Khim., **32**, 2637 (1958).
71. M.S.Rodionova, Optiko-Mekhan.Prom., No.7, 40 (1962).
72. A.Baigozhin, M.S.Rodionova, L.V.Bereznikovskaya, and L.V.Sergeev,Optiko-Mekhan.Prom.,No.6,46 (1963).
73. N.A.Chadaeva, K.A.Mamakov, and G.Kh.Kamai, USSR P.364 620 (1971); Ref.Zhur.Khim., 2N531 (1974).
74. N.A.Chadaeva, K.A.Mamakov, and G.Kh.Kamai, USSR P.368 276 (1971); Ref.Zhur.Khim., 20N514 (1973).
75. G.J.M.Van der Kerk and J.G.Luijten, J.Appl.Chem., **6**, 56 (1956).
76. G.J.M.Van der Kerk and J.G.Luijten, J.Appl.Chem., **4**, 314 (1954).
77. M.N.Arnold and H.J.Clarke, J.Oil and Colour Chem. Assoc., **39**, 900 (1956).
78. A.A.Goldberg and H.S.Jefferies, Paint Manuf., **27**, 436 (1957).
79. H.J.Hueck and J.G.Luijten, J.Soc.Dyers Colourists, **74**, 476 (1958).
80. D.A.Kochkin, P.I.Zubov, B.K.Flerov, S.M.Rzaev, I.V.Kazamanova, I.S.Novoderezhkina, N.A.Voronkov, K.P.Zabotin, V.V.Chebotarskii, M.M.Notkin, S.L.Semenov, L.A.Sukhareva, and P.A.Davidenko, USSR P.210 296 (1966); Byul.Izobret., No.30 (1973).
81. D.A.Kochkin and I.N.Azerbaev, "Olovo- i Svinetsorganicheskie Monomery" (Organotin and Organolead Monomers), Izd.Nauka, Alma-Ata, 1968, p.175.
82. W.N.Neumann, "Der organische Chemie des Zinns" Stuttgart, 1967.
83. R.G.Koroleva, E.I.Frost, and Yu.B.Rozhkov, Lakokrasochn.Materialy i Ikh Primenenie, No.4, 17 (1975).
84. A.Baigozhin, E.I.Panfilenok, I.V.Belova, M.S.Rodionova, L.V.Bereznikovskaya, and N.V.Suikovskaya, USSR P.562 525 (1975); Byul.Izobret., No.23 (1977).
85. A.Baigozhin, M.S.Rodionova, E.I.Panfilenok, L.V.Bereznikovskaya, and I.V.Belova, Optiko-Mekhan.Prom., No.7, 37 (1977).
86. M.S.Rodionova, A.Baigozhin, L.V.Bereznikovskaya, and I.V.Belova, Optiko-Mekhan.Prom., No.4, 34 (1977).
87. A.T.Troshchenko and G.I.Pustoshkin, USSR P.134 408 (1960); Ref.Zhur.Khim., 20K268 (1961).
88. A.T.Troshchenko and A.I.Sviridova, USSR P.106 455 (1956); Byul.Izobret., No.5 (1957).
89. A.T.Troshchenko, "Khimicheskie Sredstva Predokhraneniya Nemetallicheskikh Materiallov ot Razrusheniya Mikroorganizmami. Trudy NIUIF" (Chemical Means of Protecting Non-Metallic Materials Against Decomposition by Microorganisms. Transaction of the NIUIF), Moscow, 1959, No.165, p.75.
90. H.F.Payne, "Organic Coating Technology" (Translated into Russian), Goskhimizdat, Moscow, 1959, p.667.
91. G.D.Nassonova, E.K.Pogosyants, G.B.Markova, and K.P.Grinevich, Plast.Massy, No.1, 20 (1962).
92. G.A.Aleksandrov, USSR P.253 320 (1969); Byul. Izobret., No.13 (1970).
93. BRD P.1 032 899 (1958); Chem.Abs., **54**, 15 882 (1960).
94. A.I.Sviridova and N.V.Suikovskaya, Optiko-Mekhan. Prom., No.4, 61 (1957).
95. A.Kaller, DDR P.45 885 (1966); Chem.Abs., **65**, 9661 (1966).
96. V.A.Ponomarenko, Doctoral Thesis, Institute of General Chemistry, USSR Academy of Sciences, Moscow, 1962.
97. E.Lukevics and M.G.Voronkov, Dokl.Akad.Nauk SSSR, **216**, 103 (1974).
98. A.Baigozhin, Zhur.Obshch.Khim., **43**, 1408 (1973).
99. A.Baigozhin, I.V.Belova, and L.N.Arkad'eva, Zhur. Obshch.Khim., **45**, 2350 (1975).
100. A.J.Isquith, E.A.Abbott, and P.A.Walters, J.Appl. Microbiology, **24**, 859 (1972).
101. F.Kahn, Appl.Physics Letters, **22**, 386 (1973).
102. R.J.Lunkens, "Chemistry of Fungicidal Action", New York, 1971.
103. G.J.M.Van der Kerk, Bull.OEPP, No.10, 5 (1973).
104. Sistemfungizide, Internat.Symp.Reinhardsbrunn, Berlin, 1974; Ref.Zhur.Khim., 12O332 (1976).
105. A.Baigozhin, I.V.Belova, M.S.Rodionova, L.V.Bereznikovskaya, L.N.Kuznetsova, M.G.Voronkov, R.G.Mirskov, and O.S.Stankevich, USSR P.638 558 (1978); Byul.Izobret., No.47, 62 (1978).

RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

December 1980

Translated from *Uspekhi Khimii*, 49, 2257-2285 (1980)

U.D.C. 542.943 : 547.29 + 39 + 46 + 47

Oxidative Decarboxylation of Carboxylic Acids

Yu.A.Serguchev and I.P.Beletskaya

The present state of studies on the decarboxylation of carboxylic acids by various oxidation systems is described and the dependence of the yield and composition of the reaction products on the structure of the carboxylic acid, the type of oxidant and its ligand environment, the nature of the solvent, and the reaction mechanism is considered. The intermediate involvement of radicals and ions, produced by successive one-electron transfer processes, in the formation of a wide variety of decarboxylation products is discussed.
The bibliography includes 156 references.

CONTENTS

I.	Introduction	1119
II.	Thermal oxidative decarboxylation under the influence of transition metal salts and persulphates	1120
III.	Photochemical decarboxylation	1128
IV.	Initiated decarboxylation	1130
V.	The effect of ligands in the oxidative decarboxylation of carboxylic acids	1130

I. INTRODUCTION

The decarboxylation of carboxylic acids by the fusion of their alkali metal salts with caustic alkali and by the anodic oxidation of the acids and their salts (the Kolbe reaction) are familiar methods for the synthesis of alkanes. Together with alkanes, alkenes, alcohols, esters, and ethers are also formed in the Kolbe reaction and under certain conditions their yields can exceed that of alkanes[1-4].

The oxidative decarboxylation of carboxylic acids by transition metal salts and persulphates has been investigated vigorously in recent years. The practical value of the oxidative decarboxylation consists in the fact that, with the aid of this process, it is possible to obtain a series of important chemical products (alkanes, alkenes, ethers, esters, alcohols, alkyl halides, etc.). Decarboxylation takes place in the living organisms with participation of enzymes; some of these reactions are reversible and play an important role in the biological assimilation of carbon dioxide.

In the study of the mechanism of the oxidation process it is important to know whether the reaction takes place as a result of consecutive one-electron stages or as a two-electron process in a single stage. The yield and composition of the products depend in many respects on the kind of intermediate species formed—radicals and carbonium ions. Thus oxidative decarboxylation of carboxylic acids is a process in which the specific formation of the required synthetic products is closely related to the theoretical aspects of the oxidation reactions.

The decarboxylation of carboxylic acids by lead tetra-acetate has been used by a number of workers as a synthetic method[5-13]. The study of the mechanism of the decarboxylation of carboxylic acids was begun in the 1960s by Waters in aqueous media[14] and by Kochi in non-aqueous media[15]. The general mechanism of the decarboxylation reaction under the influence of oxidants[16] as well as anodic decarboxylation[4] is

represented as follows:

$$\mathrm{RCOOH} \begin{cases} \xrightarrow{-e,-H^+} \mathrm{RCOO^\cdot} \rightarrow \mathrm{R^\cdot} + \mathrm{CO_2} \\ \qquad\qquad\quad \downarrow -e \\ \xrightarrow{-2e,-H^+} \mathrm{R^+} + \mathrm{CO_2} \end{cases} \quad (1)$$

The radicals R· can react with hydrogen donors (for example, with the molecules of the solvent SH), giving rise to alkanes [Eqn.(2*c*)] and also dimerising with formation of R–R products [Eqn.(2*a*)] and disproportionating into alkanes RH and alkenes R(-H) [Eqn.(2*b*)]:

$$\mathrm{R^\cdot} \begin{cases} \xrightarrow[a]{\mathrm{R^\cdot}} \mathrm{R{-}R} \\ \xrightarrow[b]{\mathrm{R^\cdot}} \mathrm{RH} + \mathrm{R(-H)} \\ \xrightarrow[c]{\mathrm{SH}} \mathrm{RH} + \mathrm{S^\cdot} \end{cases} \quad (2)$$

Further oxidation of the radicals by metal salts leads to the formation of elimination products (alkenes) and substitution products (ethers, alcohols, and alkyl halides) via two-electron transfer mechanisms, which are known in inorganic chemistry as outer-sphere and inner-sphere mechanisms[16,17]:

$$\begin{array}{c} \mathrm{R^\cdot} + \mathrm{ML}_n \xrightarrow{a} [\mathrm{R^\cdot ML}_n] \xrightarrow{c} \mathrm{R^+} + \mathrm{ML}_{n-1} + \mathrm{L^{-1}} \\ \qquad\quad {\scriptstyle b}\swarrow \qquad\qquad {\scriptstyle d}\downarrow \mathrm{An^-(L)} \\ \mathrm{R(-H)} + \mathrm{RL} + \mathrm{ML}_{n-1} \qquad \mathrm{RA}\ (\mathrm{RL}),\ \mathrm{R(-H)}. \end{array} \quad (3)$$

In conformity with the inner-sphere mechanism or the ligand-transfer mechanism, substitution takes place in the complex without the intermediate formation of carbonium ions [Eqns.(3*a*) and (3*b*)]. The mechanism can therefore also yield alkenes. In the outer-sphere, solvolytic, or classical carbonium ion mechanism, carbonium ions are formed as intermediates and their subsequent transformation leads to alkenes as a result of the loss of a proton or to substitution products as a result of the interaction of the carbonium ion with an anion [Eqns.(3*a*), (3*c*), and (3*d*)]. The yield and composition of the oxidative decarboxylation products depend significantly on the oxidant, the structure of the carboxylic acid, and the nature of the anions and the ligands associated with the metal cations.

The aim of the present review is to examine and, as far as possible, to survey the results of studies on the decarboxylation of carboxylic acids under the influence of various oxidation systems. The literature quoted in the review covers mainly the period of the last thirty years. The review does not include the decarboxylation reactions of silver salts of carboxylic acids, which take place under the influence of halogens in aprotic solvents and lead to alkyl halides (the Borodin–Hunsdiecker reaction) and to esters (the Simonini reaction). A review[18] has been devoted to the Borodin–Hunsdiecker reaction, after which there were few publications in the literature concerning this process. Furthermore, both these reactions are of a complex type and their mechanisms are not altogether clear. Their study is frequently complicated by heterogeneous reaction conditions.

Decarboxylation under the influence of electrophiles (bromine, H^+) in protic media, decarboxylation in basic solvents, and enzymatic decarboxylation, which has its specific features, have also been excluded from consideration. A monograph has been devoted to decarboxylation reactions leading to organometallic compounds[19] and we shall therefore confine ourselves to considering only the general characteristics of reactions of this type. This also applies to decarboxylation reactions coupled with oxidation[20], i.e. to the reaction involving the oxidation of the hydrocarbon group of the acid, which is accompanied by decarboxylation.

II. THERMAL OXIDATIVE DECARBOXYLATION UNDER THE INFLUENCE OF TRANSITION METAL SALTS AND PERSULPHATES

The reactions of carboxylic acids with transition metal salts have been studied as a rule in water, acetonitrile, benzene, and the carboxylic acids themselves. The formation of the metal carboxylates constitutes a rapid pre-equilibrium stage of the decarboxylation reaction in carboxylic acids and in benzene in the presence of metal salts:

$$\mathrm{M(OAc)}_n + n\,\mathrm{RCO_2H} \rightleftarrows \mathrm{M(O_2CR)}_n + n\,\mathrm{HOAc}\ .$$

Metal carboxylates have been studied in detail by various physicochemical methods. Investigation of infrared and ultraviolet (220–270 nm) absorption spectra of lead carboxylates made it possible to classify them as charge-transfer complexes[21]. Solutions of cerium(IV) acetate in carboxylic acids have a yellow orange colour[22] and are stable for several days when kept in the dark in the absence of water and air. The cerium complex of acetic acid in aqueous solutions has an absorption band with a maximum at 286 nm.[23] Monomeric, dimeric, and trimeric cerium complexes of acetic acid have been detected spectrophotometrically[24]. Thallium(III) valerate in cyclohexane has a broad absorption band in the near ultraviolet below 360 nm.[25] Studies of the mass spectra of thallium(III) carboxylates led to the detection of the ions $(CH_3CO_2)_3Tl^+$ and $(C_6H_5CO_2)_nTl^+$, where $n = 1$ or 2.[26] In cobalt(III) acetate, which exists in a dimeric form in acetic acid, the acetoxy-groups are easily substituted by the anions of butyric, isobutyric, and pivalic acids[27]. Apparently one cannot always expect the complete substitution of the acetoxy-groups in metal acetates by the carboxylate groups of higher acids—incomplete substitution has been observed in the reaction of manganese(III) acetate with pivalic acid[28]:

$$\mathrm{Mn(OAc)_3} + \mathrm{RCO_2H} \rightleftarrows \mathrm{Mn(OAc)}_{3-n}\mathrm{(O_2CR)}_n + n\,\mathrm{HOAc}\ .$$

In an aqueous medium the Ce^{4+} [23] and Co^{3+} [14] cations interact with the undissociated forms of the acids:

$$\mathrm{Ce(H_2O)_8^{4+}} + \mathrm{RCO_2H} \rightleftarrows [\mathrm{Ce(H_2O)_7\,RCO_2}]^{3+} + \mathrm{H^+} + \mathrm{H_2O}\ ;$$

$$\mathrm{Co(H_2O)_6^{3+}} + \mathrm{RCO_2H} \rightleftarrows [\mathrm{Co(H_2O)_5\,RCO_2}]^{2+} + \mathrm{H^+} + \mathrm{H_2O}\ .$$

The decomposition of metal carboxylates, accompanied by decarboxylation, can occur on heating; we have called this process thermal oxidative decarboxylation. The yield and composition of the products of this reaction depend on the structure of the acid. Literature data are therefore considered below for different types of carboxylic acids.

1. Alkane- and Arylalkane- Carboxylic Acids

Thermal oxidative decarboxylation of alkane- and arylalkane-carboxylic acids yields alkanes, alkenes, esters, and other products, the yield of which depends significantly on the structure of the carboxylic acid RCOOH. For the same oxidant, the yield of alkenes and esters decreases in the following sequence of groups R: tertiary > secondary > primary. This sequence is correlated with the increase of the ionisation potentials of the radicals and with the decrease of the stability of the carbonium ions[16].

The yield and composition of the decarboxylation products also depend significantly on the kind of oxidant and on the reaction mechanism, so that further consideration of the thermal oxidative decarboxylation in this Section can be usefully related to the characteristics of the reaction mechanism for the following groups of oxidants: one-electron (Ce^{4+}, Ag^{2+},

Co^{3+}, and Mn^{3+}), two-electron (Pb^{4+} and Tl^{3+}), binary systems containing Cu^{2+} (Pb^{4+}–Cu^{2+}, Mn^{3+}–Cu^{2+}, and Co^{3+}–Cu^{2+}), and persulphates.

(a) *One-electron oxidants.* The equations of the decarboxylation reactions under the influence of Co^{2+},[27] Mn^{3+},[28] Ce^{4+},[29] and Ag^{2+},[30] in which mainly the products of one-electron and two-electron oxidation are formed, are as follows:

$$M^n(O_2CCH_2CH_2CH_3)_n \rightarrow M^{n-1}(O_2CCH_2CH_2CH_3)_{n-1} + CH_3CH_2CH_3 + CO_2 ,$$

$$2M^n[O_2CC(CH_3)_3]_n \rightarrow 2M^{n-1}[O_2CC(CH_3)_3]_{n+1} + (CH_3)_2C{=}CH_2 + CO_2 + (CH_3)_3CCOOH .$$

It is interesting to consider how the composition of the thermal oxidative decarboxylation varies with the type of metal ion. A clear-cut dependence of the yield of the decarboxylation products on the normal reduction potentials of the metal ions was not observed[16]. Thus the reduction potential of Cu^{2+} (0.153 eV) is much lower than that of Co^{3+} (1.84 eV), Ag^{2+} (2.0 eV), Ce^{4+} (1.70 eV), and Mn^{3+} (1.51 eV), but the yield of the total oxidation products (alkenes and esters) is greater when the reaction is carried out in the presence of Cu^{2+}.[15,16,31]

It follows from a series of data[27–30] that the dependence of the ratio of the yield of total oxidation products to the yield of one-electron oxidation products (alkanes) on the type of oxidant is different for acids of different structure. For butyric acid, the ratio varies in the sequence $Ag^{2+} > Ce^{4+} > Mn^{3+} > Co^{3+}$, for isobutyric acid the sequence is $Ce^{4+} > Ag^{2+} > Mn^{3+} > Co^{3+}$, and for pivalic acid the sequence is $Ag^{2+} \cong Co^{3+} > Mn^{3+} > Ce^{4+}$. However, the data presented above were taken from several investigations in which the reaction conditions were not identical, so that it is extremely difficult to reach reliable conclusions concerning the dependence of the yield of the reaction products on the type of oxidant. The yield and composition of the reaction products apparently depends to a much greater extent on the decarboxylation mechanism than on the reduction potential of the metal ion.

Kinetic studies have shown[23] that the rate-limiting stage in the decarboxylation of acetic acid on treatment with Ce^{4+} in an aqueous medium is the decomposition of the complex:

$$[Ce(H_2O)_7OAc]^{3+} \rightarrow [Ce(H_2O)_6]^{3+} + H_2O + OAc^{\cdot}$$

Further decomposition of the acetoxy-radical to the methyl radical leads to the formation of methane as the main product. The reaction is faster in the water–acetonitrile mixture than in pure water.

The kinetics of the oxidative decarboxylation by Ce^{4+} of alkane- and arylalkane-carboxylic acids have been studied in an aqueous medium[32–37] and Ag^{2+}.[38] The rate of reaction is described by a second-order kinetic equation (first order with respect to the oxidant and first order with respect to carboxylic acid). The reaction is catalysed by added Ag^+ and H^+ ions. According to the authors, the adduct of an acid molecule and Ag^+ is initially formed reversibly and then decomposes under the influence of Ce^{4+} with formation of the acyloxy-radicals $RCOO^{\cdot}$. The rate of reaction is limited by the stage involving the decomposition of the complex; this has received additional confirmation by the fact that the equilibrium constants of the process involving the formation of the Ce^{4+}–alcohol complex are insensitive to electronic effects[39], while the rate of decarboxylation depends significantly on the type of substituent. This is seen from the following data[23] {50°, $I = 1,2$, $[H^+] = 1M$}:

Carboxylic acid	Isobutyric	Propionic	Acetic	Chloroacetic
$10^4 k_2$, litre mol^{-1} s^{-1}	17.5	3.25	1.25	0.71

The logarithms of the relative rate constants for the decarboxylation of substituted phenylacetic acids in aqueous acetonitrile are correlated with the σ^+ constants of the substituents[40]. The quantity $\rho = -2.93 \pm 0.48$ obtained indicates a polar structure of the transition state:

$$ArCH_2COOH + Ce^{4+} \rightarrow ArCH_2\overset{O}{\underset{O}{\diagdown\!\diagup}}{:}Ce^{4+} \rightarrow ArCH_2^{\cdot} + CO_2 + Ce^{3+} + H^+ .$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad H$$

The formation of benzyl radicals in this reaction is indicated by the increased yield of benzaldehyde in the presence of oxygen.

It has been suggested[23] that the mechanism of the oxidation of carboxylic acids on treatment with Ce^{4+} is of the inner-sphere type. An analogous mechanism has been attributed to the reaction of carboxylic acids with Co^{3+} salts, in which the formation of benzyl radicals has been confirmed by the detection of bibenzyl in the reaction products (1%).[14] The formation of intermediate radicals in the oxidation of ω-phenylalkanecarboxylic acids by cobalt salts in aqueous acetone solutions was demonstrated using bromoform as a trapping agent and identifying the alkyl bromides obtained[41]. The rate of decarboxylation of aliphatic acids under the influence of Co^{3+} varies in the following sequence[14]:

$$CH_3COOH < CH_3CH_2COOH < (CH_3)_2CHCOOH < (CH_3)_3CCOOH .$$

In this sequence the activation energy decreases by 4 kcal mol^{-1} on replacement of the α-hydrogen atom by the methyl group. Since the inductive influence of the CH_3 group on the homolysis of the O–Co bond via the R–COO system should be weak, there is a possibility of a two-stage decomposition of the complex with the preliminary formation of an acyloxy-radical. However, since the stability of the radicals increases in the sequence $CH_3 < C_2H_5 <$ iso-$C_3H_7 <$ t-C_4H_9, the authors[14] believe that a synchronous mechanism for the decomposition of cobalt carboxylates is more likely[14].

The appreciable dependence of the rate of reaction on the nature of the alkyl groups in the carboxylic acid in accordance with the sequence pivalic acid > isobutyric acid > butyric acid under the influence of Co^{3+},[14,27] Mn^{3+},[28] or Ag^{2+}[38] leads to the conclusion that the formation of alkyl radicals $R^{\cdot}$ involves a synchronous mechanism. On the other hand, the small difference between the rates of decarboxylation of acids of different structure under the influence of Ce^{4+} [23,29] indicates the formation of acyloxy-radicals $RCOO^{\cdot}$.

The study of the kinetics of the decarboxylation of carboxylic acids by Co^{3+} [27] and Mn^{3+} [28] in solutions in the carboxylic acids themselves showed that the power exponent of the concentration of the corresponding metal carboxylate in the kinetic equation for the reaction is unity. The activation energy for the oxidation of pivalic acid by cobalt salts at 61–100 °C is 30 kcal mol^{-1}, while under the influence of manganese salts in the presence of 3.5M acetic acid the activation energy is 34.6 kcal mol^{-1}. These values are close to the energies of the decomposition of the carboxylates, which are less than 40 kcal mol^{-1}. The rate constant for the oxidation of pivalic acid by Mn^{3+} ($\sim 4.5 \times 10^{-4}$ s^{-1}, 70 °C) is higher than the rate constant for the analogous reaction with Co^{3+} ($\sim 0.8 \times 10^{-4}$ s^{-1}, 71 °C). For these two oxidants, different yields of products are also observed. On passing from Mn^{3+} to Co^{3+}, the ratio of the yield of the total oxidation products (alkenes, esters) to the yield of the one-electron oxidation products (alkanes) changes from 0.3 to 0.2 in the decarboxylation of butyric acids and from 0.5 to 0.3 in the decarboxylation of isobutyric acid. The increase of the yield of alkenes and esters is probably associated with the fact that the rate of oxidation of the radicals to carbonium ions by Mn^{3+} is greater than the rate of oxidation by Co^{3+}.

The concentration of protons in solution has a significant influence on the rate of decarboxylation and the yield of reaction products. The rate of decarboxylation of acetic acid by Ce^{4+} in an aqueous medium increases with increase in proton concentration, apparently as a consequence of the increase of the redox potential of the Ce^{4+}–Ce^{3+} system, which indicates a greater activity of the non-hydrolysed complexes[23]:

$$[Ce(H_2O)_7OH]^{3+} + H^+ \rightleftharpoons [Ce(H_2O)_8]^{4+} \quad .$$

In the reaction of carboxylic acids with Co^{3+} in water the hydrolysed complex having the composition $[Co(H_2O)_5(OH)]^{2+}$ interacts with acids more readily than the unhydrolysed complex, so that, with increase of the $HClO_4$ concentration, the rate of decarboxylation diminishes[14]. However, when carboxylic acids themselves are used as solvents, the carboxylation under the influence of all metals (Mn^{3+},[28] Co^{3+},[27] and Ce^{4+} [29]) is catalysed by added strong acids ($HClO_4$ and ClCCOOH). Under these conditions, the yield of alkenes and esters as a rule increases. It has been suggested that this is associated with the formation of a positively charged complex:

$$Ce(O_2CR)_4 + H^+ \rightleftharpoons [Ce(O_2CR)_3]^+ + RCOOH \quad .$$

which, being coordination unsaturated, undergoes oxidation-reduction decomposition with greater ease than the corresponding neutral complex[29]:

$$[Ce^{IV}(O_2CR)_3]^+ \rightarrow [Ce^{III}(O_2CR)_2]^+ + RCOO^{\cdot} \text{ etc.}$$

It is of interest to note that the hydrocarbon chain oxidation reactions compete with the decarboxylation of phenylacetic acids[14,42]:

$$PhCH_2COOH \begin{cases} \longrightarrow PhCH_2^{\cdot} + CO_2 \\ \longrightarrow PhC^{\cdot}HCOOH \end{cases} .$$

The H–C bond is oxidised fairly readily in the interaction of formic acid with Ag^{2+},[43] Mn^{3+},[44] Tl^{3+},[45] and Hg^{2+}.[46]

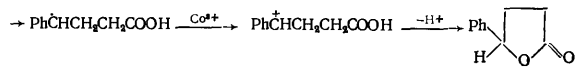
On the basis of the high value of ρ, atypical for a free-radical process, and the observation of EPR signals due to radical-cations, Dessau and Heiba[42] suggested that the oxidative decarboxylation of arylacetic acids by cobalt acetate in an aqueous medium includes a stage involving the one-electron oxidation of the benzene ring. A similar value of ρ, equal to −2.91, was obtained in the oxidative decarboxylation of substituted phenylacetic acids by cerium ammonium nitrate in 30% aqueous acetonitrile[40]. The intermediate formation of a radical-cation was observed also in the electrochemical oxidation of salts of methoxyphenylacetic acid[47–49].

One should note that, whereas the formation of free radicals in the first decarboxylation stage in aqueous solutions has been demonstrated fairly convincingly, their subsequent oxidation to carbonium ions has been studied to a much smaller extent. This is apparently due to the difficulty of the quantitative isolation and identification of the products in an aqueous medium and also to the possibility of secondary processes involving the oxidation of the products obtained from the radicals. The most convincing evidence for the intermediate formation of carbonium ions in the oxidation of arylacetic acids by cobalt salts in acetic acid is high (50 to 100%) yields of phenylacetates[42]:

$$PhCH_2COOH \xrightarrow[-Co^{3+}]{Co^{3+}} (PhCH_2COOH)^{+} \xrightarrow[-H^+]{-CO_2} PhCH_2^{\cdot} \xrightarrow[-Co^{2+}]{Co^{3+}} PhCH_2^{+} \xrightarrow{OAc^-} PhOAc \; .$$

The radical-cation mechanism of the decarboxylation of arenecarboxylic acids by cobalt salts is also supported by the formation of γ-phenylbutyrolactone (yield >25%) when γ-phenylbutyric acid interacts with cobalt acetate:

$$PhCH_2CH_2CH_2COOH \xrightarrow{Co^{3+}} (PhCH_2CH_2CH_2COOH)^{+} \xrightarrow{-H^+} \rightarrow PhCHCH_2CH_2COOH \xrightarrow{Co^{3+}} PhCHCH_2CH_2COOH \xrightarrow{-H^+}$$



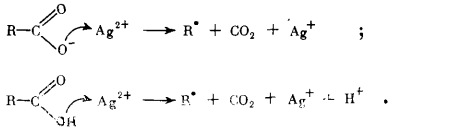
.

It has been suggested[29] that the oxidation of the radicals in the oxidative decarboxylation of carboxylic acids by Ce^{4+} takes place via an inner-sphere mechanism involving the formation of an alkylcerium intermediate. The latter is converted into Ce^{3+} and a carbonium ion, from which alkenes and esters are formed:

$$R^{\cdot} + Ce^{4+} \rightleftharpoons [RCe]^{4+} \rightarrow Ce^{3+} + R^+ \quad .$$

The mechanism of the oxidation of alkyl radicals by other one-electron oxidants, such as Cu^{2+}, Co^{3+}, and Mn^{3+}, is similar to the mechanism of the oxidation by Ce^{4+}.[16]

The problem of whether or not metal ions interact with undissociated acid molecules or with carboxylate ions is more complex. The rate of reaction of Ce^{4+} with formic acid is proportional to the $HClO_4$ concentration, which is attributed to the presence of the complexes $Ce^{4+}.HCOOH$ and $Ce^{4+}.HCOO^-$. It is assumed that the reaction proceeds almost exclusively with participation of the complex $Ce^{4+}.HCOO$.[50] It is believed that[38] the interaction of Ag^{2+} with carboxylic acids in an aqueous acid medium takes place with participation of both species—RCOOH and $RCOO^-$:



(b) *The two-electron oxidants Pb^{4+} and Tl^{3+}.* Two reviews have been devoted to the oxidative decarboxylation of carboxylic acids by lead tetra-acetate[16,51]. The reactions of alkane- and arylalkane-carboxylic acids with $Pb(OAc)_4$ yield mainly alkanes, alkenes, and esters, the yield of which depends on the structure of the acid. The relative rates of decarboxylation of the acids RCOOH by lead tetra-acetate decrease as a function of R in the following sequence: tertiary > secondary > primary. The yield of alkenes and esters decreases and the amount of alkanes increases in the same sequence. The stoichiometric equations for the decarboxylation of pivalic[52] and formic[53] acids by lead tetra-acetate show that the oxidant is of the two-electron type:

$$Pb(O_2CR)_4 \begin{cases} \longrightarrow Pb(O_2CR)_2 + RCO_2R + CO_2 \\ \longrightarrow Pb(O_2CR)_2 + R(-H) + RCO_2H + CO_2 \end{cases} ;$$

$$Pb(O_2CH)_4 \rightarrow Pb(O_2CH)_2 + HCOOH + CO_2 \quad ; \quad R = C(CH_3)_3 \quad .$$

It was assumed initially[53,54] that the reaction mechanism includes the heterolytic splitting of lead tetracarboxylates with formation of lead dicarboxylate and acyloxonium or carbonium ions as intermediates:

$$(RCO_2)_4Pb \rightarrow RCOO^+ + Pb(OCOR)_2 + RCOO^- \quad ,$$
$$(RCO_2)_4Pb \rightarrow R^+ + CO_2 + Pb(OCOR)_2 + RCOO^- \quad .$$

However, subsequently Kochi's work showed[15,52] that the decarboxylation of carboxylic acids by $Pb(OAc)_4$ is inhibited by oxygen and accelerated by radical reaction initiators, proceeding as a chain process via the following mechanism:

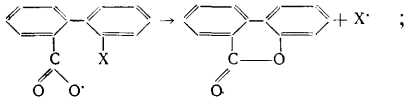
$Pb(OCOR)_4 \rightarrow Pb(OCOR)_3 + CO_2 + R^{\cdot}$ (initiation stage);
$Pb(OCOR)_3 \rightarrow Pb(OCOR)_2 + CO_2 + R^{\cdot}$ (chain propagation);
$Pb(OCOR)_4 + R^{\cdot} \rightarrow Pb(OCOR)_3 +$ alkene, ester;
$Pb(OCOR)_3 + R^{\cdot} \rightarrow Pb(OCOR)_2 +$ alkene, ester (chain termination);
$R^{\cdot} + SH$ (solvent) $\rightarrow RH + S^{\cdot}$
$R^{\cdot} + R^{\cdot} \rightarrow$ dimers, disproportionation products.

The decarboxylation of carboxylic acids by $Pb(OAc)_4$ begins, as in the case of other oxidants, with the pre-equilibrium formation of lead carboxylates[15,21]:

$$Pb(OAc)_4 + n\,RCO_2H \rightleftharpoons Pb(OAc)_{4-n}(O_2CR)_n + n\,HOAc \quad .$$

In the presence of pyridine, which accelerates decarboxylation, the pre-equilibrium complex has the form $Pb^{IV}(O_2Cr)_n.Py_m$. The reactions are promoted also by the addition of other nitrogen bases (triethylamine) as well as salts (acetates).

Lead carboxylates decompose with formation of Pb^{3+} and RCOO· or R·. The intermediate formation of carboxy-radicals was detected in certain cases from the yield of the corresponding products. When 2'-substituted biphenyl-2-carboxylic acids interact with lead tetra-acetate in boiling benzene under a nitrogen atmosphere, 3,4-benzocoumarin is formed in a high yield[55]:



X=H, CO_2H, Cl, NO_2, OCH_3, or CO_2CH_3 .

The formation of alkyl radicals was confirmed by EPR in the photolysis of lead carboxylates at low temperatures[21,56]. No evidence was obtained for the formation of Pb^{3+} by EPR,[57] but its formation is indicated by the results of kinetic studies of the oxidation of Co^{2+} and Ce^{3+} by lead tetra-acetate. The rates of these reactions are described by a common second-order kinetic equation (first-order with respect to each reactant), which suggests the intermediate formation of Pb^{3+} as a result of one-electron transfer in the rate-limiting stage of the reaction[58].

The involvement of alkyl radicals in a number of reactions has been demonstrated with the aid of spin-trapping agents, for which nitroso-compounds are used[59]:

$$R'NO + R\cdot \rightarrow R'\underset{\displaystyle O\cdot}{\underset{|}{N}}-R \quad .$$

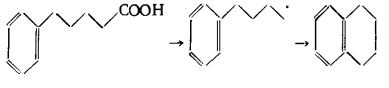
At −40 °C free radicals R' were trapped in methylene chloride as asymmetric nitroxy-radicals. At 25 °C secondary radicals, obtained as a result of the abstraction of α-hydrogen from the acid molecule, were trapped:

$$R\cdot + R''CH_2COOH \rightarrow R''\dot{C}HCOOH \xrightarrow{R'NO} R'-\underset{\displaystyle O\cdot}{\underset{|}{N}}-\underset{\displaystyle COOH}{\underset{|}{CH}}-R'' \quad .$$

In the presence of oxygen alkyl radicals can give rise to side products[15]:

$$CH_3CH_2\dot{C}HCH_3 + O_2 \rightarrow \underset{\displaystyle O_2\cdot}{\underset{|}{CH_3CH_2CHCH_3}} \rightarrow CH_3CH_2COCH_3 + CH_3CH_2CHOHCH_3 \quad .$$

In certain cases the intermediate radicals are converted into cyclic reaction products. The cyclisation of alkyl radicals in the decarboxylation of ethyl 2-carboxy-5-phenylvalerate by lead tetra-acetate leads to the formation of tetralincarboxylate derivatives[60]. The oxidative decarboxylation by lead tetra-acetate of 5-phenylvaleric acid in benzene solution in a nitrogen atmosphere yields tetralin as the main product[61]:



A similar reaction takes place with *p*-nitro- and *p*-methoxy-derivatives of phenylvaleric acid and also with 5-(*p*-methoxyphenyl)-5-phenylvaleric and 5-(β-naphthyl)valeric acids[62]. The oxidation of *o*-benzoylbenzoic acid by lead tetra-acetate in benzene leads to benzophenone, *o*-phenylbenzophenone, and fluorenone[63].

Thus the process is undoubtedly of a radical type. The question arises of the pathways whereby alkenes and esters are obtained in the reaction. These pathways can include further oxidation of the radicals to carbonium ions as a result of electron transfer [reaction (4)] or oxidative heterolysis [reaction (5)] of the organolead compound $RPb(OCOR)_3$, which is formed either via a reaction of the S_N2 type or by the interaction of the radical with $Pb(OCOR)_3$:

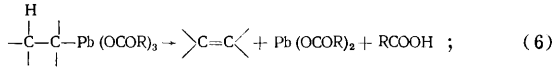
$$R\cdot + Pb(OCOR)_4 \rightarrow R^+ + Pb(OCOR)_3^- + RCO_2^- \quad ; \qquad (4)$$

$$R\cdot + Pb(OCOR)_4 \rightarrow RPb(OCOR)_3 + R\cdot + CO_2 \quad ;$$

$$R\cdot + Pb(OCOR)_3 \rightarrow RPb(OCOR)_3 \quad ;$$

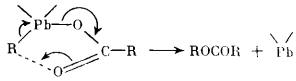
$$RPb(OCOR)_3 \rightarrow R^+ + Pb(OCOR)_2 + RCO_2^- \quad . \qquad (5)$$

The organolead compound can be converted into alkenes and esters without the intermediate formation of carbonium ions, as a result of the elimination [reaction (6)] or reactions (7) of the S_N2 type:



$$RCO_2^- + RPb(OCOR)_3 \rightarrow RCOOR + Pb(OCOR)_2 + RCO_2^- \quad . \qquad (7)$$

The possibility of the formation of esters directly in the decomposition of lead carboxylates via an intramolecular S_Ni mechanism (not only cations but also radicals should then be formed as intermediates) has also been suggested[66]. However, this mechanism (ligand transfer) is more likely for the decomposition of the organolead compound[65]:



Tertiary alkyl radicals are readily oxidised by lead tetra-acetate; on the other hand, primary radicals are oxidised with difficulty, as a result of which the decarboxylation under the influence of $Pb(OCOCH_3)_4$ leads mainly to the formation of alkanes. A thermodynamic assessment of the reactions[64] agrees with these results. The electrode potential of the Pb^{2+}/Pb^{4+} system ($E^0 = 1.69$ V) is not sufficiently high for the oxidation of primary radicals ($E^0 = 2.07$ V for the $C_2H_5/C_2H_5^+$ system) but is sufficient for the oxidation of secondary and tertiary radicals ($E^0 = 1.59$ V for iso-$Pr^{\cdot}$/iso-Pr^+ and $E^0 = 1.27$ V for t-Bu·/t-Bu) as well as allyl ($E^0 = 1.7$ V) and benzyl ($E^0 \cong 1.5$ V) radicals.

The electrode potential for the two-electron process $C_2H_5.COO^- \rightarrow R^+ + CO_2 + 2e^-$, equal to 1.68 V, is close to the potential for the Pb^{2+}/Pb^{4+} system, which accounts for the formation of esters from primary carboxylic acids.

It is of interest that, on decarboxylation of crystalline α-isobutyric acid by lead tetra-acetate at low temperatures, even tertiary radicals are not oxidised to carbonium ions and are converted quantitatively into alkanes[21].

The oxidation of primary alkyl radicals can proceed effectively via the ligand transfer mechanism. The decarboxylation of carboxylic acids under the influence of lead tetra-acetate in the presence of LiCl or LiBr results in almost quantitative formation of alkyl halides[67]. The reaction is important for the synthesis of alkyl chlorides, but it also proceeds with bromides and iodides. The optimum conditions require one equivalent of LiCl per equivalent of $Pb(OCOCH_3)_4$. The yield of alkyl halides obtained by this method decreases in the sequence of acids RCOOH as a function of the nature of R: tertiary > secondary > primary.

The 1.37–1.43 : 1 ratio of *erythro*- and *threo*-2-chloro-3-phenylbutanes in the halogenodecarboxylation of *erythro*- and *threo*-2-methyl-3-phenylbutyric acids indicates a radical mechanism of this process, since, on treatment of these acids with lead tetra-acetate, the *erythro*- and *threo*-acetates are formed via an ionic mechanism in equal amounts[68]. Furthermore, the halogenodecarboxylation is strongly inhibited by oxygen. On this basis, the following radical mechanism has been proposed for the halogenodecarboxylation reaction:

Pre-equilibrium stage:

$$Pb^{IV}(O_2CR)_4 + X^- \rightleftharpoons [(RCO_2)_4 Pb^{IV}X]^- \ .$$

Initiation stage:

$$[(RCO_2)_4 Pb^{IV}X]^- \rightarrow R^{\cdot} + CO_2 + [(RCO_2)_3 Pb^{III}X]^- \ ;$$
$$[(RCO_2)_4 Pb^{IV}X]^- \rightarrow X^{\cdot} + [(RCO_2)_4 Pb^{III}]^- \ .$$

Chain propagation:

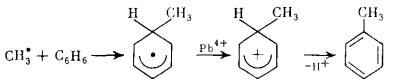
$$R^{\cdot} + [(RCO_2)_4 Pb^{IV}X]^- \rightarrow RX + [(RCO_2)_4 Pb^{III}]^- \text{ (ligand transfer)};$$
$$X^{\cdot} + [(RCO_2)_4 Pb^{IV}X]^- \rightarrow X_2 + [(RCO_2)_4 Pb^{III}]^- \ ;$$
$$[(RCO_2)_4 Pb^{III}]^- \rightarrow R^{\cdot} + CO_2 + [(RCO_2)_3 Pb^{II}]^- \ ;$$
$$R^{\cdot} + X_2 \rightarrow RX + X^{\cdot}, \text{ etc.}$$

Chain termination:

$$R^{\cdot} + [(RCO_2)_3 Pb^{III}X]^- \rightarrow RX + [(RCO_2)_3 Pb^{II}]^- \ .$$

The halide formation reaction proceeds via the ligand transfer mechanism. This is indicated particularly by the finding that the halogenodecarboxylation of cyclobutanecarboxylic and β,β-dimethylbutyric acids proceeds without a rearrangement and is accompanied by the formation of cyclobutyl chloride and neopentyl chloride[67]. It has been shown[69] that the ligand transfer reaction in the decarboxylation of phenylacetic acid and its substituted derivatives (R = *p*-NO_2 or *p*-Cl) is little influenced by the polarity of the substituent, while in the absence of LiCl both the products and the rate of reaction depend greatly on the substituents.

The oxidative decarboxylation of tertiary acids by lead tetra-acetate has been studied in relation to t-butylperoxy-2-methylpropanoic acid in benzene[70]. The mechanism of the formation of toluene proposed in the above study, according to which the active methyl radical obtained in the decomposition of the t-butoxy-radical adds to benzene and the subsequent oxidation of this product and the elimination of a proton lead to toluene, is of interest:



The decarboxylation of 2,3,3-trimethylbutyric acid by lead tetra-acetate in benzene and acetic acid yields mainly 3,3-dimethyl-2-butyl acetate and, when Cu^{2+} is involved in the reaction, the main product is 3,3-dimethylbut-1-ene.[65] The low yield of rearranged products in both cases suggests that ionic intermediates are not formed in the reaction. Organocopper and organolead compounds are apparently formed as intermediates in the reaction and decompose as a result of β-elimination with formation of alkenes [Eqn.(6)] or intramolecular substitution (ligand transfer mechanism or S_Ni mechanism) with formation of acetates.

The decarboxylation of carboxylic acids[25] in benzene by Tl^{3+} is much slower than under the influence of Pb^{4+}. All types of acids give rise to a large amount of radical products and a small amount of esters, which is due to the low reduction potential of the Tl^{3+}/Tl^{+} pair ($E^0 = 1.25$ V) and $Tl^{3+} + Cl^-/TlCl$ ($E^0 = 1.36$ V). The yield of esters decreases in the following sequence for acids RCOOH with different R: $C_6H_5CH_2$ (~20%) > tertiary (10–20%) > secondary > primary. This process is not greatly promoted by the addition of acetate salts and pyridine. However, the reaction is appreciably accelerated when it is carried out using carboxylic acids as solvents. The addition of strong acids ($HClO_4$, BF_3, CF_3.COOH) increases the rate of reaction still further. Under these conditions, the decarboxylation of isobutyric and butyric acid yields mainly esters and small amounts of alkanes and alkenes. The stoichiometric reaction equation obtained in this case indicates a two-electron mechanism of this process:

$$(RCO_2)_3 Tl^{III} \rightarrow \begin{cases} \rightarrow R{-}R + 2CO_2 + Tl^{I}O_2CR \\ \rightarrow R(-H) + CO_2 + RCO_2H + Tl^{I}OCOR \\ \rightarrow RCO_2R + CO_2 + Tl^{I}OCOR \end{cases} .$$

(c) *Binary systems containing* Cu^{2+}. The oxidative decarboxylation of carboxylic acids by the binary systems Mn^{3+}–Cu^{2+},[28] Co^{3+}–Cu^{2+},[27] Ag^{2+}–Cu^{2+},[30] and Pb^{4+}–Cu^{2+} [31] leads to an appreciable increase of the yield of alkenes. In the presence of catalytic amounts of copper salts the rate of decarboxylation increases appreciably and the reaction becomes of preparative importance for the synthesis of alkenes[31,52]. This type of effect has been explained by the marked ability of copper ions to trap and oxidise intermediate alkyl radicals. The rate constants for the oxidation of primary and secondary alkyl radicals by copper salts are 10^6–10^9 litre mol^{-1} s^{-1},[69,71,72] which indicates the following mechanism of the formation of alkenes:

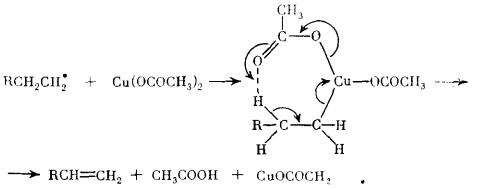
$$R^{\cdot} + Cu^{2+} \rightarrow R(-H) + Cu^{+} \ .$$

Under these conditions, the copper(I) ion is oxidised by lead tetra-acetate, propagating the chain:

$$Pb^{IV}(OCOR)_4 + Cu^{I}OCOR \rightarrow Pb^{III}(OCOR)_3 + Cu^{II}(OCOR)_2 \text{ etc.}$$

Torssell[64] believes that the low oxidation-potential of the Cu^{+}/Cu^{2+} (0.17 V) and $CuCl/Cu^{2+} + Cl^-$ (0.57 V) systems is inconsistent with this mechanism. However, since a large amount of alkenes and a small amount of esters, coupling products, and alkanes are formed in the oxidation of carboxylic acids in the presence of copper ions, the β-elimination mechanism has been proposed. The process $C_2H_5COO^- \rightarrow C_2H_4 + CO_2 + H^+ + 2e$ is characterised by the quantity $E^0 = 0.31$ V. $E^0 = 0.64$ V has been calculated for the $C_2H_5^{\cdot} \rightarrow C_2H_4 + H^+ + e$ system. These data suggested that the specific oxidising effect of copper ions involves simultaneous action on the β-hydrogen and the unpaired electron. Radicals without β-hydrogen should not then be actively oxidised by copper ions. Indeed the products and rate of decarboxylation of phenylacetic acid by lead tetra-acetate with and without added Cu^{2+} differ little. The weak influence of added copper salts on the decarboxylation of RCOOH with a tertiary substituent R on treatment with lead tetra-acetate is probably associated with this factor[57].

It has been suggested[73] that, when the copper ion interacts with a radical, an organocopper compound is formed, its β-elimination via a cyclic transiton state leading to a multiple bond:

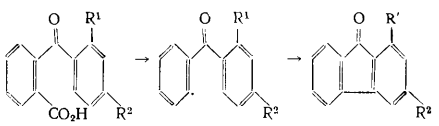


(d) *Persulphates.* The decarboxylation of aliphatic acids and their salts by sodium persulphate was studied initially by Fichter and coworkers in a series of investigations[74-77]. The reaction products are alcohols and olefins with an admixture of aldehydes and saturated hydrocarbons.

Decarboxylation in alkaline and acid media leads to products having different compositions. When acetic acid was oxidised with sodium persulphate in acid media, methane and succinic acid, which can be obtained from the intermediate free radicals, were detected in addition to CO_2 and CO. In alkaline media further-oxidation products (methanol and ethylene) were found in addition to methane and succinic acid. The oxidation of sodium acetate in the presence of sodium carbonate yielded methanol. Under the same conditions, sodium propionate yields ethanol and ethylene, the oxidation of sodium butyrate leads to the formation of propene, while isobutene and isobutyl isovalerate are obtained from the salt of isovaleric acid[75]. Such variation of the composition of the products with increase of chain length and with branching of the alkyl residue is apparently associated with the facilitation of the oxidation of the intermediate radicals R· and with the increase of the stability of the intermediate carbonium ions formed under these conditions.

The formation of radicals in the oxidation of phenylacetic acid and a number of related acids in an aqueous medium on treatment with the $Na_2S_2O_8$–Tl^{3+} system has been demonstrated by EPR.[78] The formation of aryl radicals in the decarboxylation of benzoic, phenylacetic, and diphenylacetic acids with $Na_2S_2O_8$ has been confirmed by the isolation of the products by the dimerisation of the corresponding radicals—biphenyl, 1,2-diphenylethane, and 1,1,2,2-tetraphenylethane[79]. In the presence of pyridine the oxidation of benzoic acid results in the formation of approximately 5% of phenylpyridines.

The cyclisation of the intermediate radicals on decarboxylation of substituted *o*-benzoylbenzoic acids yielded substituted fluorenones[79]:



R^1=H, R^2=H, Cl, Br, CH_3, or OCH_3; R^1=R^2=OCH_3, or CH_3 .

Active oxidising agents arise in the homolytic decomposition of persulphate ions on heating. The energy of this reaction is approximately 30 kcal mol^{-1} [80]:

$$S_2O_8^{2-} \xrightarrow{k_1} 2SO_4^{\cdot-} \quad .$$

Further reactions of the radical-anion in an aqueous medium in the presence of a carboxylic acid are described by the following equations[79,81]:

$$SO_4^{\cdot-} + H_2O \xrightleftharpoons{k_2} HSO_4^- + OH^{\cdot} \quad ;$$

$$SO_4^{\cdot-} \text{ (or } {}^{\cdot}OH) + RCO_2^- \xrightleftharpoons{k_3} SO_4^{2-} \text{ (or } {}^{-}OH) + RCOO^{\cdot} \longrightarrow \underset{\text{products}}{\searrow} R^{\cdot} + CO_2 \quad .$$

This reaction mechanism has been confirmed by the composition of the products and by the form of the kinetic equation[81]:

$$\frac{d[CO_2]}{dt} = \frac{d[RCO_2^-]}{dt} = k_3[SO_4^{\cdot-}][RCO_2^-] \quad .$$

Measurement of the relative rate constants for substituted phenylacetic acids demonstrated a correlation between the logarithms of the rate constants and σ^+ with a low value of ρ, characteristic of radical reactions:

$$\lg(k/k_0) = -0.436\,\sigma^+ + 0.06 \quad (r = 0.983,\ s = 0.035) \quad .$$

The rate of decarboxylation of acids by sodium persulphate increases in the presence of Ag^+ and the reaction is of first order with respect to the silver ion and peroxydisulphate and of zero order with respect to the acid[82,83]:

$$\frac{d[CO_2]}{dt} = \frac{d[S_2O_8^{2-}]}{dt} = k_2[Ag^+][S_2O_8^{2-}][RCOOH]^0 \quad .$$

The mechanism of the reaction involving silver ions includes the formation of the unstable Ag^{2+} ion in the rate-limiting stage, which rapidly reacts with the carboxylic acid:

$$Ag^+ + S_2O_8^{2-} \rightarrow Ag^{2+} + SO_4^{2-} + SO_4^{\cdot-} \quad ;$$
$$Ag^+ + SO_4^{\cdot-} \rightarrow Ag^{2+} + SO_4^{2-} \quad ;$$
$$Ag^{2+} + RCOOH \rightarrow Ag^+ + RCOO^{\cdot} + H^+ \quad ;$$
$$RCOO^{\cdot} \rightarrow R^{\cdot} + CO_2 \quad ;$$
$$R^{\cdot} + Ag^{2+} \rightarrow R^+ + Ag^+ \text{ etc.}$$

The intermediate radicals give rise to alkanes by reacting with the carboxylic acid or another hydrogen donor *HS*. The mechanism has been confirmed by the increased yield of alkanes on increasing the concentration of carboxylic acid. In this case the stoichiometry of the reaction corresponds to the following equation:

$$2RCOOH + S_2O_8^{2-} + 2HS \xrightarrow{Ag^+} 2RH + 2CO_2 + H^+ + 2SO_4^{2-} + S_2 \quad .$$

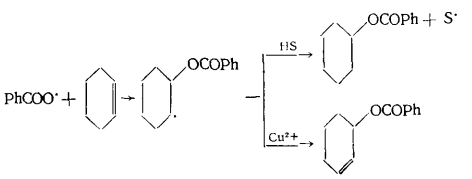
As the carboxylic acid concentration is reduced, the reaction equation becomes

$$RCOOH + S_2O_8^{2-} \xrightarrow{Ag^+} R^+ + H^+ + CO_2 + 2SO_4^{2-} \quad .$$

The yield of alkanes then falls and the yield of alkenes, esters, alcohols, and further-oxidation products (ketones and aldehydes) increases.

Catalytic amounts of copper sulphate cause a sharp increase in the yield of alkenes in the decarboxylation products on treatment with the $Na_2S_2O_8$–Ag^+ system[82]. The effect of Cu^{2+} consists in the trapping and oxidation of intermediate alkyl radicals. Under these conditions, peroxydisulphate interacts with Cu^+, regenerating the initial Cu^{2+} ion. The intermediate formation of benzyl radicals in the decarboxylation of phenylacetic acids by the $Na_2S_2O_8$–Ag^+ system has been demonstrated by their reactions with substituted pyridines, which give rise to 2-benzylpyridines[83]. The alkylation of quinoline, 2-methylquinoline, isoquinoline, acridine, and substituted pyridines with the aid of a radical R· [R = CH_3, C_2H_5, $CH_3(CH_2)_2$, $CH_3(CH_2)_3$, $(CH_3)_2CH$, $(CH_2)_5CH$, or $(CH_3)_3C$], obtained by the oxidative decarboxylation of aliphatic carboxylic acids by the $Na_2S_2O_8$–Ag^+ system, has been investigated[84,85].

The oxidation of sodium benzoate and its derivatives by the $(NH_4)_2S_2O_8$–Cu^{2+} system in the presence of alkenes (cyclohexene and α-pinene)[86] leads to the formation of intermediate benzoyloxy-radicals, which add to the double bond, forming new alkyl radicals. The interaction of alkyl radicals with hydrogen donors leads to the formation of alkanes and their subsequent oxidation by Cu^{2+} ions to the corresponding cations results in the formation of alkenes and alcohols:



Intermediate phenyl radicals were detected in the decarboxylation of PhCOOH under the influence of the $Na_2S_2O_8$–Ag^+ system[87].

An extremely interesting fact is noteworthy: the decarboxylation of benzoic acids by the persulphate–Ag^+ or persulphate–Cu^{2+} system in an aqueous medium proceeds incomparably more readily than the decarboxylation under the influence of transition metal salts in non-aqueous solvents. This may be associated with the easier decarboxylation of carboxylate anions compared with undissociated molecules.

Thermal oxidative decarboxylation of alkane- and arylalkanecarboxylic acids has also been studied by a number of other workers[88-91].

2. Cycloalkanecarboxylic Acids

The decarboxylation of cycloalkanecarboxylic acids has been carried out mainly with lead tetra-acetate or its mixture with Cu^{2+}. Typical products are cycloalkanes and esters, which are believed to be formed[15,16] as a result of the intermediate involvement of carbonium ions.

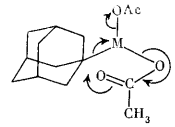
The decarboxylation of cyclopropane-[92] and cyclobutanecarboxylic acids[93] proceeds with partial ring opening and the formation of rearranged acetates, which supports the formation of ionic intermediates.

The intermediate involvement of carbonium ions is believed[54] to be indicated by the results of the decarboxylation of the optically active *endo*- and *exo*-norbornane-2-carboxylic acids by lead tetra-acetate in benzene and acetonitrile. This reaction yields almost exclusively the *exo*-acetates with an appreciable retention of optical activity. The results of the above workers[54] have been explained[94] by the fact that racemic norbornyl acetates are obtained from bridged carbonium ions, while the chiral *exo*-acetates are formed from classical carbonium ions. As a result of a skeletal rearrangement, the reaction of lead tetra-acetate with *exo*- and *endo*-bornane-2-carboxylic acids[95] yields camphene and other products as well as the *exo*- and *endo*-acetates in proportions of 68 : 32. The formation of a mixture of *exo*- and *endo*-acetates in this instance has been explained[94] by the involvement of classical and non-classical carbonium ions in the reaction.

The study of the products of the decarboxylation of bicyclo[3,2,1]octane-2-carboxylic and bicyclo[2,2,2]octane-2-carboxylic acids altered this view, showing that, apart from the pathway with participation of carbonium ions, there is a possibility also of other pathways[94]. The small difference in the proportions of the acetates obtained by the decarboxylation of *exo*- and *endo*-bicyclo[3,2,1]octane-2-carboxylic acids suggests that a radical is formed as a common intermediate. The subsequent formation of the organolead compound $RPb(OAc)_3$ and its heterolysis can lead to a non-classical carbonium ion with its subsequent conversion into an acetate. This is indicated particularly by the similar yields of the acetates in the decarboxylation and acetolysis of the corresponding tosylates[96]. However, the contribution of this reaction pathway is only 50%. Another pathway involves ligand transfer in the organolead compound via the S_Ni mechanism; this pathway is in fact responsible for the partial retention of the stereochemical configuration. In the light of these ideas, it is also possible to account for the results obtained in the decarboxylation of bornane-2-carboxylic[95] and norbornane-2-carboxylic[54] acids.

By analogy with the above data, it has been suggested that, in the decarboxylation of adamantane-2-carboxylic, adamantane-1-carboxylic, and *cis*- and *trans*-decalin-9-carboxylic acids by lead tetra-acetate in benzene in the presence of Cu^{2+} ions (or in their absence), the acetates are formed as a result of heterolysis and ligand transfer (S_Ni substitution) in the organometallic compound obtained by the interaction of the intermediate free radical with lead or copper carboxylate[65].

The high yields of acetates (89 and 93% respectively) in the decarboxylation of adamantane-1-carboxylic acid with $Pb(OAc)_4$ and $Pb(OAc)_4$–$Cu(OAc)_2$ (despite the fact that the oxidation of bridged radicals to carbonium ions should proceed with greater difficulty than the oxidation of related acyclic radicals) may indicate, according to the authors[76], a considerable contribution of the S_Ni mechanism:



M = $Pb(OAc)_2$, or Cu.

The formation of equal amounts of *cis*- and *trans*-decalinyl acetates on decarboxylation of *cis*- and *trans*-decalin-9-carboxylic acids by lead tetra-acetate and $Pb(OAc)_4$–$Cu(OAc)_2$ apparently takes place as a result of the heterolysis of organocopper and organolead compounds.

Finally, the preferred formation of the thermodynamically less stable $\Delta^{1,9}$-octalin compared with $\Delta^{9,10}$-octalin on decarboxylation of *cis*- and *trans*--decalin-9-carboxylic acids suggests, according to the authors[76], that the unsaturated cyclic compounds are obtained as a result of β-elimination from the organometallic compounds and not as a result of the deprotonation of the intermediate carbonium ion.

The products of the oxidative decarboxylation of cycloalkanecarboxylic acids have also been studied in a series of other investigations[97-103].

3. Unsaturated Carboxylic Acids

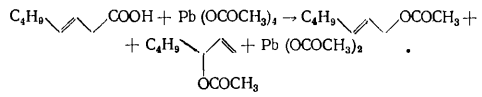
Decarboxylation of unsaturated carboxylic acids has been studied in a series of investigations[104-108]. In the decarboxylation of *trans*- and *cis*-cinnamic acids with lead tetra-acetate in benzene in an atmosphere of nitrogen, it was found unexpectedly that the main product is β-methylstyrene. It is suggested that it is formed as a result of the abstraction of the methyl radical from the intermediate complex formed by the styryl radical and lead tetra-acetate[104,107].

The general validity of this mechanism (differing from the general mechanism proposed by Kochi—see subsection 1 above) is confirmed by data obtained in the decarboxylation of a mixture of cinnamate and β-methylbutyrate salts. This reaction also leads to the formation of a radical recombination product—3-methyl-1-phenylpent-1-ene, which proved to be inactive when the optically active acid was used as the starting material. According to the authors[104], the reaction takes place as a result of the following sequence of transformations:

$$PhCH{=}CHCOOPb^{IV}OCOR \rightarrow CO_2 + [PhCH{=}CH^{\cdot} \ldots Pb^{III}OCOR] \rightarrow 2CO_2 +$$
$$+ [PhCH{=}CH^{\cdot} + R^{\cdot}] + Pb^{II} \rightarrow 2CO_2 + PhCH{=}CHR + Pb^{II} .$$

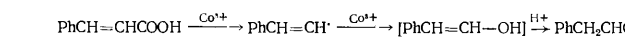
The influence of substituents in the benzene ring of cinnamic acid on the yield of products has been studied[105]. It was found that, in the presence of *p*-NO_2 and *p*-Cl substituents the main product is β-methylstyrene, as for the unsubstituted acid[104]. On the other hand, the decarboxylation of *p*-methoxycinnamic acid gives only traces of β-methylstyrene and the main products are acetates, which are believed to be formed on further oxidation of the unsaturated radical. The oxidative decarboxylation of 3-octenoic acid by lead tetra-acetate in 17% benzene solution of acetic acid leads to the formation of 3-acetoxyhept-1-ene (21%) and 1-acetoxyhept-2-ene

(30%) as the main products[69]:



The reaction is accelerated by a factor of 16 after the addition of 7% Cu^{2+}. Under these conditions, the ratio of the 3-acetoxyhept-1-ene and 1-acetoxyhept-2-ene formed is 85:15. The addition of 0.08 M pyridine increases the rates of reaction by a further factor of 5 and the ratio of the acetates changes to 55:45. The oxidative decarboxylation of vinylacetic acid by lead tetra-acetate gives rise to allyl acetate (70%) and is five times faster than the decarboxylation of 3-octenoic acid. The addition of 0.01M Cu^{2+} increases the yield of esters to 87%, but propene and hexa-1,5-diene are not formed[69]. The authors[69] suggest that the oxidation of aryl radicals by Pb^{4+} and Pb^{4+}–Cu^{2+} with participation of pyridine proceeds via a carbonium ion like the oxidation of benzyl and tertiary radicals.

The kinetics of the oxidation of unsaturated acids by cobalt perchlorate in aqueous acetonitrile in the presence of $HClO_4$ have been investigated[106]. The rate of reaction is directly proportional to the concentrations of the oxidant and the unsaturated acid and is inversely proportional to the acidity of the solution. The study of the reaction products revealed the occurrence of two simultaneous processes: oxidative decarboxylation (5–20%) and oxidation of the double bond (80–95%). The oxidative decarboxylation leads to the formation of mainly aldehydes and ketones, for example:



The main pathway—the oxidation of the double bond—results in the complete cleavage of the latter.

Acids whose double bond is conjugated with a benzene ring are oxidised more readily than acids with an unconjugated double bond. The presence of methyl or phenyl substituents at the double bond of cinnamic acid hinders oxidation. Unsaturated acids are more readily oxidised by tervalent cobalt in an aqueous medium than the corresponding saturated acids[41].

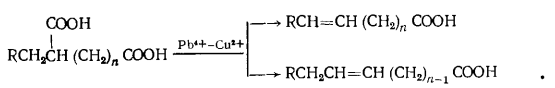
4. Dibasic Carboxylic Acids

The oxidative decarboxylation of dicarboxylic acids is usually carried out with systems containing Pb^{4+} or Pb^{4+}–Cu^{2+}. The rate of decarboxylation of alkanedicarboxylic acids having the general formula $RCH_2CH(CH_2)_nCOOH$, where



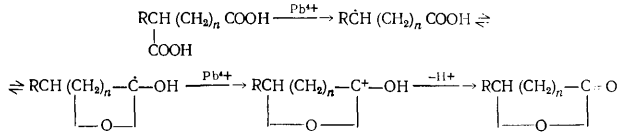
$n = 1$, 2, 3, or 10, and the composition of the reaction products depend significantly on the positions of the carboxy-groups relative to one another[109]. As the COOH groups approach one another, the decarboxylation under the influence of lead tetra-acetate slows down. The decarboxylation of the same acids by the Pb^{4+}–Cu^{2+} system proceeds equally readily for all the acids investigated. At the same time, the structure of R has virtually no influence on the decarboxylation reaction.

When equimolar amounts of the dicarboxylic acid and Pb.$(OAc)_4$ are used in the presence of copper acetate, selective decarboxylation of the carboxy-group at the secondary carbon atom takes place[109,110]. This results in a high yield of alkenoic acids in the *cis*- and *trans*-forms (in approximately equimolar amounts):



The unsaturated carboxylic acids formed can undergo further decarboxylation and conversion into alkadienes and alkenyl acetates.

The oxidation of 1,3- and 1,4-dicarboxylic acids by lead tetra-acetate yields predominantly γ- and δ-lactones[109,111]. It has been suggested that, as in the decarboxylation of monocarboxylic acids, the oxidation of dicarboxylic acids proceeds with the intermediate formation of radicals, which undergo subsequent cyclisation and oxidation:



In addition, unsaturated and saturated monocarboxylic acids are formed in this reaction.

The high yield of lactones in the decarboxylation of 2,3-diphenylglutaric and camphoric acids by lead tetra-acetate has been explained[112] by the ease of elimination of carboxy-groups at the secondary and tertiary carbon atoms respectively. The oxidative decarboxylation of glutaric acid and its monoesters (methyl, ethyl, isopropyl, and benzyl) under the influence of $Na_2S_2O_8$–Ag^+ leads to the formation of butyric acid, alkyl butyrates, and γ-butyrolactones[113]. The oxidative decarboxylation of glutaric and adipic acids by the $Na_2S_2O_8$–$AgNO_3$–$CuSO_4$ system leads to the selective formation of γ-butyrolactone and δ-valerolactone respectively[114].

When cycloalkane-1,2-dicarboxylic acids are treated with $Pb(OAc)_4$,[115–119] bisdecarboxylation takes place and results in 50–80% yields of cycloalkenes. On treatment of α,β-dicarboxylic acids with PbO_2, the yield of olefins is reduced to 25%.[120] The decarboxylation of diphenic acid under the influence of lead tetra-acetate in the acetonitrile–pyridine mixture leads to the formation of 3,4-benzocoumarin (50%); under these conditions, benzoic and phthalic acids are not decarboxylated[121].

The formation of *trans*-stilbene as the main product in the oxidative decarboxylation of *meso*- and d,*l*-1,2-diphenylsuccinic acids under the influence of Pb^{4+} [154] suggests that the bisdecarboxylation is not a synchronous β-elimination process, but includes the formation of an intermediate carbonium ion.

It has been suggested[122] that the oxidative decarboxylation of disubstituted malonic acids by lead tetra-acetate results in the formation of the diacetates $RR'C(OAc)_2$ as intermediates, whose hydrolysis leads to the ketones RR'CO. The decarboxylation of bicyclo[3,2,0]heptane-3,3-dicarboxylic acid apparently proceeds analogously, since it led to the isolation of bicyclo[3,2,0]heptan-3-one.[123]

The study of the reaction of cerium sulphate with dicarboxylic acids in sulphuric acid showed that unsaturated dicarboxylic acids (fumaric and maleic) and succinic acid are not oxidised, while phthalic, tartaric, malonic, and citric acids are oxidised on heating to 95 °C.[124] Oxalic acid readily reacts with cerium sulphate at room temperature, which makes it possible to use this reaction as an analytical method[125].

On treatment with bivalent copper, aminomalonic acid is decarboxylated with formation of glycine[126].

5. α-Hydroxyacids

Carboxylic α-hydroxyacids contain two functional groups, which can be acted upon by oxidants. Oxidative decarboxylation of α-hydroxyacids on treatment with $Pb(OAc)_4$, first investigated by Oeda[127], obeys the stoichiometric equation

$$R_1R_2CCOOH + Pb(OAc)_4 \rightarrow R_1CR_2 + CO_2 + 2CH_3COOH + Pb(OAc)_2 \quad .$$
$$\quad\quad\quad

(up to 10%) in the photodecarboxylation of $Tl(OCOR)_n$, where R is a primary group, indicates, according to the authors[25], that alkenes are formed as a result of the disproportionation of alkyl radicals:

$$2R^{\cdot} \rightarrow R(-H) + RH \quad .$$

The decrease of the yield of alkenes and esters obtained from the acids in the series based on R (tertiary > secondary > primary) shows that the reaction proceeds via the mechanism

$$Tl^{3+} + R^{\cdot} \rightarrow Tl^{2+} + [R^{+}] \text{ etc.}$$

In the presence of Cu^{2+} the mechanism changes:

$$R^{\cdot} + Cu^{2+} \rightarrow R(-H) + Cu^{+} + H^{+} ;$$
$$Cu^{+} + Tl^{3+} \rightarrow Cu^{2+} + Tl^{2+} \quad .$$

The rates of photochemical decarboxylation of the acids RCOOH with primary, secondary, and tertiary groups R on treatment with Ce^{4+} differ little[29]. On treatment with Pb^{4+},[15,57] a significant difference is observed between the rates of decarboxylation in accordance with the sequence pivalic acid > isobutyric acid > butyric acid, which is probably associated with the increase of the activation energy for the homolysis of the bond in the lead carboxylates in this sequence.

In addition to pyridine and lithium acetate and trifluoroacetate in the photochemical oxidative decarboxylation of butyric acid by Ce^{4+} does not have an appreciable influence on the rate of reaction[29], while the addition of strong acids ($HClO_4$, BF_3, CF_3COOH) increases the rate appreciably. In the latter case the yield of alkenes and esters increases and the amount of alkanes falls. Oxygen decreases significantly the rate of reaction and lowers the yield of alkanes in photodecarboxylation by lead tetra-acetate[57]. Under these conditions, products of the oxidation of the radical by oxygen appear:

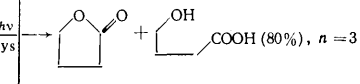
$$(CH_3)_3C^{\cdot} + O_2 \rightarrow (CH_3)_3COO^{\cdot} ;$$
$$2(CH_3)_3COO^{\cdot} \rightarrow O_2 + 2(CH_3)_3CO^{\cdot} \begin{cases} \rightarrow (CH_3)_3COOC(CH_3)_3 \\ \xrightarrow{SH} (CH_3)_3COH + S^{\cdot} \\ \rightarrow (CH_3)_2CO + CH_3^{\cdot} \end{cases} .$$

When pivalic acid interacts with lead tetra-acetate in the presence of oxygen, the formation of di-t-butyl peroxide (3%), acetone (9%), and t-butyl alcohol (78%) is observed.

The formation of free radicals in the photochemical decarboxylation of carboxylic acids by lead tetra-acetate has also been demonstrated by EPR.[57] Irradiation in the cell of the spectrometer of solutions of lead carboxylates in acids, benzene, or pyridine, from which oxygen had not been removed, led to the detection of alkylperoxy-radicals derived from pivalic, 2,2-dimethylbutyric, 2,2-dimethylvaleric, and 2,2-dimethyloctanoic acids (singlet, $g = 2.0152$).

The chain mechanism of the photochemical decarboxylation of carboxylic acids has been demonstrated in the determination of the quantum yield. In the oxidation of pivalic and dimethylbutyric acid by lead tetra-acetate the exact quantum yield could not be measured, but, according to a preliminary estimate, the chain length is approximately 200.[57] The quantum yield in the photochemical decarboxylation of acids by Ce^{4+} depends on the concentration of the latter and on the type of acid. At a 0.1M concentration of cerium acetate and 3500 Å a quantum yield is 1.11 ± 0.07 for pivalic acid, 0.81 ± 0.05 for isobutyric acid, and 0.52 ± 0.05 for butyric acid.

The photochemical decarboxylation of dibasic acids (succinic, glutaric, and adipic) on treatment with a 0.02M $FeCl_3$ solution (3500 Å, 38 °C) proceeds

$$HOOC(CH_2)_nCOOH \xrightarrow[2\text{-}6\ \text{days}]{FeCl_3, h\nu} \begin{cases} \rightarrow Cl(CH_2)_2COOH\ (78\%),\ n=2 \\ \rightarrow \text{  }\ (80\%),\ n=3 \\ \rightarrow Cl(CH_2)_4COOH\ (70\%),\ n=4 \end{cases} .$$

As a result of the reaction, chloro-substituted monobasic acids are formed from succinic and adipic acids, while glutaric acid leads mainly to γ-butyrolactone and a certain amount of a hydroxyacid. In the absence of $FeCl_3$ and in the dark the reaction does not take place. Special experiments have shown that neither β-hydroxypropionic nor γ-chlorobutyric acid are intermediates.

The decarboxylation of metal acetates, mainly mercury acetates, which proceeds with formation of organometallic compounds, has been considered in detail in a monograph[19]. The most probable mechanism of the photodecarboxylation of mercury salts of carboxylic acids (in benzene and acetic acid as solvents) is described by the following equations.

$$(RCOO)_2Hg \rightarrow RCOO^{\cdot} + {}^{\cdot}HgOCOR ;$$
$$RCOO^{\cdot} \rightarrow R^{\cdot} + CO_2 ;$$
$$R^{\cdot} + {}^{\cdot}HgOCOR \rightarrow RHgOCOR ;$$
$$R^{\cdot} + (RCOO)_2Hg \rightarrow RHgOCOR + RCOO^{\cdot} ;$$
$$2\,HgOCOR \rightarrow Hg_2(OCOR)_2 ;$$
$$Hg_2(OCOR)_2 \rightarrow Hg + (RCOO)_2Hg .$$

In this mechanism the $R^{\cdot} + (RCOO)_2Hg + RHgOCOR + RCOO^{\cdot}$ state, which presupposes a chain reaction mechanism, has not been supported by direct evidence. The photochemical reaction leads to the formation of a considerable amount of mercury(I) salts and organomercury compounds. In addition, similar reactions of free radicals result in the formation of saturated and unsaturated hydrocarbons [Eqn.(2)] as well as metallic mercury. The reaction is of preparative interest for the synthesis of alkylmercury salts. Mercury salts of aromatic acids are decarboxylated with much greater difficulty than the salts of aliphatic acids.

The decomposition of lead tetracarboxylates $(RCOO)_4Pb$ ($R = C_6H_5$, $o\text{-}CH_3C_6H_4$, $p\text{-}CH_3C_6H_4$, $o\text{-}O_2NC_6H_4$, $p\text{-}O_2NC_6H_4$, C_6H_{11}, or C_5H_9) in benzene by ultraviolet light or peroxides[140] is hindered when a substituent is present in the benzene ring of the arenecarboxylic acid. The radicals $RCOO^{\cdot}$, generated in the reaction, react with one another: $2RCOO^{\cdot} \rightarrow RCOOR + CO_2$, or decompose into CO_2 and radicals $R^{\cdot}$, which interact with benzene, leading to the formation of biaryls and disproportionation products.

IV. INITIATED DECARBOXYLATION

The initiated decarboxylation of aromatic acids (benzoic and toluic) in aprotic solvents (*o*-dichlorobenzene, nitrobenzene) takes place in the presence of oxygen and t-butyl peroxide or t-butyl hydroperoxide at temperatures sufficiently high to cause the homolysis of the peroxide (125 to 200 °C).[141,142] It has been suggested that the reaction mechanism involves the formation of aroyloxy-radicals when the acid interacts with a radical:

$$ArCOOH + X^{\cdot} \rightarrow ArCOO^{\cdot} + HX \quad .$$

Since the reaction does not take place in the absence of oxygen, it has been postulated that the radicals obtained from the initiator (methyl and t-butoxy-radicals, etc.) do not abstract hydrogen from the carboxy-group. Peroxy- and hydroxy-radicals (X = RCOO· or HO·) are apparently reactive. The aroyloxy-radicals are readily decomposed into CO_2 and an aryl radical, which interacts with the molecules of the aromatic solvent to form biphenyls. The initiated decarboxylation is catalysed by cobalt(III) naphthenates probably as a result of the direct oxidation of the acid by metal ions. The yield of biphenyl reaches 50% in this case.

Mercury salts of carboxylic acids are decarboxylated by acetyl, di-t-butyl, benzoyl, etc. peroxides or ultraviolet light with formation of organomercury compounds[19,143]. The reaction is carried out in acetic acid, benzene, and their mixtures at 80–98 °C:

$$RCOOHgOOCR + R'^{\cdot} \rightarrow R'HgOCOR + RCOO^{\cdot} \; ;$$
$$RCOO^{\cdot} \rightarrow R^{\cdot} + CO_2 \quad .$$

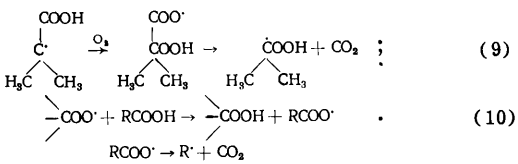
It has a radical chain mechanism, as shown by the virtually quantitative conversion of the mercury salts of carboxylic acids for comparatively small amounts of peroxy-compounds (molar ratio mercury carboxylate : peroxide ≅ 6 : 1) and also by the presence of small amounts of alkanes and alkenes in the reaction products. The mercury salts of lower representatives of homologous series of alkanecarboxylic acids react more readily than the salts of the higher and aromatic acids. The introduction of substituents into the aromatic ring prevents the decarboxylation of the mercury salts of aromatic carboxylic acids. The introduction of electronegative substituents into the molecule of an aliphatic mercury carboxylate also hinders the initiated decarboxylation reaction, the magnitude of the effect diminishing as the substituent becomes more remote from the carboxy-group[19].

Mercury(I) salts also react with diacyl peroxides, forming organomercury compounds:

$$RCOOHg-HgOOCR + (R'COO)_2 \rightarrow 2R'HgOCOR + 2CO_2 \quad .$$

A series of organomercury compounds have been obtained with the aid of these reactions: the salts of aryl-, methyl-, ethyl-, and propyl-mercury[143], cyclopropyl- and cycloheptyl-mercury[144], cyclohexyl- and cyclopentyl-mercury[145], n-butyl-, n-pentyl-, and n-nonyl-mercury[146], and α-naphthylmercury[147].

The decarboxylation of carboxylic acids is frequently accompanied by the liquid-phase oxidation of organic compounds. Data for this process, which is called "decarboxylation coupled with oxidation" or "oxidative decarboxylation", have already been surveyed[20,148] and will not be considered in this review. One should note that such reactions can also be classified as initiated decarboxylation, since the decarboxylation takes place under the influence of radicals obtained by the oxidation of organic admixtures or the carboxylic acids themselves. The mechanism of reactions of this kind can include intramolecular decarboxylation [reaction (9)], when the molecules being oxidised are also decarboxylated, and intermolecular decarboxylation [reaction (10)], when molecules of one type are oxidised and those of another are decarboxylated:



$$\xrightarrow{O_2} \quad \text{(9)}$$

$$\text{(10)}$$

$$RCOO^{\cdot} \rightarrow R^{\cdot} + CO_2$$

V. THE EFFECT OF LIGANDS IN THE OXIDATIVE DECARBOXYLATION OF CARBOXYLIC ACIDS

Strong acids accelerate the decarboxylation of carboxylic acids under the influence of Pb^4,[32,57] Mn^{3+},[28] Co^3,[27] and Tl^{3+}[25] ions. This effect is attributed to the formation of cationic complexes, which are stronger oxidants than their neutral analogues:

$$M(O_2CR)_n + H^+ \rightleftarrows M(O_2CR)^+_{n-1} + RCO_2H \quad .$$

The decarboxylation of alkanecarboxylic[15,31] and dicarboxylic[109] acids by lead tetra-acetate in benzene is appreciably accelerated in the presence of pyridine. The acceleration of the reaction in the presence of acetate and trifluoroacetate has been observed in the decarboxylation of acids by Co^{3+},[27] and Mn^{3+}[28] ions. The influence of acetate ions on the rate of reaction has been explained by the formation of labile complexes of the type $[Pb^{IV}(OAc)_6^{2-}$,[149] $[Co^{III}_2 \cdot (O_2CR)_7^-]$, and $[Co^{III}(O_2CR)_4^-]$.[27] Spectrophotometric measurements have shown that the addition of 3 M $LiOCOCH_3$ to lead tetra-acetate in acetic acid causes a hypsochromic shift in the ultraviolet spectrum (there is a shoulder at 280 nm), which increases after the addition of small amounts of triethylamine.

Certain complexes of lead carboxylates with pyridine have been isolated and investigated[149]:

$$Pb(OAc)_{4-n}(O_2CR)_n + m\,Py \rightleftarrows Pb(OAc)_{4-n}(O_2CR)_n Py_m \quad .$$

There exists a view[15] that the accelerating influence of pyridine is associated with the fact that the formation of metal carboxylates is facilitated in the pre-equilibrium stages:

$$Pb(OAc)_4 + n\,RCO_2H \rightleftharpoons Pb(OAc)_4HOCOR\ ;$$
$$Py + Pb(OAc)_4HOCOR \rightleftharpoons PyH^+ + Pb(OAc)_4OCOR^-\ ;$$
$$Pb(OAc)_4OCOR^- \rightleftharpoons OAc^- + Pb(OAc)_3OCOR\ .$$

The oxidative decarboxylation of mandelic acid by lead tetra-acetate in acetic acid is catalysed by different basic compounds such as water, methanol, DMF, 2,6-lutidine, 2,4-lutidine, triethylamine, and acetate salts[133]. The process consists of two fluxes, one of which constitutes the non-catalytic reaction and the other the base-catalysed reaction. In the range of concentrations up to 3M for methanol and up to 1M for water, the reaction is of first order with respect to methanol and water. At higher concentrations of the additives the reaction order increases to two. The concentrations of acetate salts and amines are included in the kinetic equation with an exponent close to unity. In terms of their catalytic effect, the additives can be arranged in the following sequence [the values of k_2 (litre mol^{-1} s^{-1}) are indicated in brackets]: H_2O (0.065) < CH_3OH (0.13) < LiOAc (73.5) < NaOAc (193) < KOAc (263). The catalytic action of bases is explained by the modification of the oxidant as a result of the change in the ligand environment of the lead ion. Apart from kinetic relations, this is indicated by a series of physicochemical measurements. When lead tetra-acetate is dissolved in methanol, the brown-red colour of the complex appears and then vanishes after the addition of 5% acetic acid without loss of the oxidising properties of the oxidant. Furthermore, the complex $Pb(OAc)_2(OCH_3)OH$ has been isolated from methanol and characterised. The relative catalytic activities of acetate salts decrease in the sequence KOAc > NaOAc > LiOAc, i.e. with decrease of the degree of dissociation of the ion pairs into ions[150,151]. However, it has been suggested that, apart from ions, ion pairs also exhibit a catalytic effect in the reaction. Since amines can participate in the formation of acetate ions (in accordance with the equation $Py + HOAc \rightleftharpoons PyH^+OAc^-$), which accelerate the reaction, their catalytic effect is difficult to isolate in a pure form. Acrylonitrile accelerates the reaction to a greater extent than acetonitrile, which indicates a specific effect of bidentate ligands.

The catalytic decarboxylation of dicarboxylic β-ketoacids has been reviewed[152-154]; in view of its specificity, this reaction will not be considered here. It is also characterised by catalytic effects of basic ligands (pyridine, quinoline, bipyridyl, phenanthroline, etc.). The explanation of the catalytic effects in these reactions given by Bonchev[155] can also be applied to the oxidative decarboxylation of carboxylic acids with the aid of transition metal ions. The accelerating effects of π-ligands have been explained[155] by the presence of a reverse π-dative bond between the metal and the ligand (M → L), which increases the positive charge of the metal ion and hence increases its catalytic activity. The interaction of the metal ion with the ligand has been confirmed experimentally by NMR and also by absorption spectroscopy and EPR.

The effect of ligands should be significant also in the second stage of the decarboxylation involving successive oxidation of the free radicals formed in the first stage of the reaction. This is indicated particularly by Kochi's study[156] of the oxidation of alkyl radicals by copper(II) salts. The replacement of the acetate ligand by the weakly coordinated perchlorate and triflate ligands in the oxidation of radicals in acetic acid results in a sharp decrease of the yield of alkenes. When the n-butyl radical is oxidised by $Cu(ClO_4)_2$ and $Cu(O_3SCF_3)_2$, the amount of alkenes falls to 34.1% (compared with the 94% yield of alkenes in the oxidation by copper acetate) with a simultaneous increase of the yield of alkyl acetates. Analysis of the composition of the products of the oxidation of radicals by various copper(II) salts led the authors[156] to the conclusion that the acetate ligand promotes oxidative elimination, which increases the yield of alkenes; on the other hand, the capacity for oxidative solvolysis increases with increase of the stability of the carbonium intermediate, which is also promoted by weakly coordinated ligands such as perchlorate and triflate.

REFERENCES

1. B.C.L.Weedon, Quart.Rev., **6**, 380 (1952).
2. N.L.Weinberg and H.R.Weinberg, Chem.Rev., **68**, 449 (1968).
3. G.E.Svadkovskaya and S.A.Voitkevich, Uspekhi Khim., **29**, 364 (1960) [Russ.Chem.Rev., No.3 (1960)].
4. L.Eberson, Symposium, "Elektrokhimiya Organicheskikh Soedinenii" (Electrochemistry of Organic Compounds) (Translated into Russian), Izd.Mir, Moscow, 1976, p.334.
5. J.Jacques, C.Weidmann, and H.Horeau, Bull.Soc. chim.France, 424 (1959).
6. K.Kitahonoki and Y.Takano, Tetrahedron Letters, 1597 (1963).
7. G.Büchi, R.E.Erickson, and N.Wakabayoshi, J. Amer.Chem.Soc., **83**, 927 (1961).
8. E.Grovenstein, D.V.Rao, and J.W.Taylor, J.Amer. Chem.Soc., **83**, 1705 (1961).
9. A.C.Cope, C.H.Park, and P.Sheiner, J.Amer. Chem.Soc., **84**, 4862 (1962).
10. L.R.C.Barclay, C.E.Milligan, and N.D.Hall, Canad.J.Chem., **40**, 1664 (1962).

11. E.E.van Tamelen and S.P.Pappas, J.Amer.Chem. Soc., **85**, 3297 (1963).
12. W.H.Starnes, J.Amer.Chem.Soc., **86**, 5603
13. L.H.Zalkow and N.N.Girotra, Chem.Ind.(London), 704 (1964).
(1964).
14. A.A.Clifford and W.A.Waters, J.Chem.Soc., 2796 (1965).
15. J.K.Kochi, J.Amer.Chem.Soc., **87**, 1811, 2500, 3609 (1965).
16. J.K.Kochi, Science, **155**, 415 (1967).
17. H.Taube, Adv.Inorg.Radiochem., **1**, 1 (1959).
18. R.G.Johnson and R.K.Ingham, Chem.Rev., **56**, 219 (1956).
19. Yu.A.Ol'dekop and N.A.Maier, "Sintez Metalloorganicheskikh Soedinenii Dekarboksilirovaniem Atsilatov Metallov" (The Synthesis of Organometallic Compounds by the Decarboxylation of Metal Acylates), Izd.Nauka i Tekhnika, Minsk, 1970.
20. N.I.Mitskevich and B.V.Erofeev, "Sopryazhennoe s Okisleniem Dekarboksilirovanie Karbonovykh Kislot" (Decarboxylation of Carboxylic Acids Coupled with Oxidation), Izd.Nauka i Tekhnika, Minsk, 1970.
21. K.Hensler and H.Loeliger, Helv.Chim.Acta, **52**, 1495 (1969).
22. N.Hay and J.K.Kochi, J.Inorg.Nuclear Chem., **30**, 884 (1968).
23. J.M.Mathai and R.Vasudevan, J.Chem.Soc., B, 1361 (1970).
24. K.B.Wiberg and P.C.Ford, Inorg.Chem., **7**, 369 (1968).
25. J.K.Kochi and T.W.Bethea, J.Org.Chem., **33**, 75 (1968).
26. A.T.T.Hsien, A.G.Lee, and P.L.Sears, J.Org. Chem., **37**, 2637 (1972).
27. S.S.Lande and J.K.Kochi, J.Amer.Chem.Soc., 90, 5196 (1968).
28. L.M.Anderson and J.K.Kochi, J.Amer.Chem.Soc., **92**, 2450 (1970).
29. R.A.Sheldon and J.K.Kochi, J.Amer.Chem.Soc., **90**, 6688 (1968).
30. L.M.Anderson and J.K.Kochi, J.Org.Chem., **35**, 986 (1970).
31. J.D.Bacha and J.K.Kochi, Tetrahedron, **24**, 2215 (1968).
32. M.Adinarayana, B.Sethuram, and R.T.Navaneeth, Current Sci., **44**, 581 (1975).
33. M.Adinarayana, P.K.Saiprakash, B.Sethuram, and T.N.Rao, J.Indian Chem.Soc., **53**, 255 (1976).
34. B.Singh, K.M.M.Richards, R.K.Shukla, and B.Krishna, J.Indian Chem.Soc., **53**, 751 (1976).
35. S.B.Hanna and S.A.Sarac, J.Org.Chem., **42**, 2069 (1977).
36. S.B.Hanna and S.A.Sarac, J.Org.Chem., **42**, 2063 (1977).
37. M.Adinarayana, B.Sethuram, and T.Rao, J.Indian Chem.Soc., **53**, 877 (1976).
38. E.Mentasti, E.Pelizzetti, and C.Baiocchi, J.Chem. Soc., Perkin Trans., II, 1841 (1976).
39. L.B.Yong and W.S.Trahanowsky, J.Amer.Chem. Soc., **91**, 5060 (1969).
40. W.S.Trahanowsky, J.Cramer, and D.W.Brixus, J.Amer.Chem.Soc., **96**, 1077 (1974).
41. P.R.Sharan, P.Smith, and W.A.Water, J.Chem. Soc., B, 1322 (1968).
42. R.M.Dessau and E.J.Heiba, J.Org.Chem., **40**, 3647 (1975).
43. E.Pelizzetti and E.Mentasti, J.Chem.Soc., Dalton Trans., 2086 (1975).
44. C.F.Wells and D.Whatley, J.Chem.Soc.Faraday Trans.I, 434 (1972).
45. H.N.Halvorson and J.Halpern, J.Amer.Chem.Soc., **78**, 5462 (1956).
46. J.Halpern and S.M.Taylor, Disc.Faraday Soc., **29**, 174 (1960).
47. J.P.Coleman, J.H.P.Utley, and B.C.L.Weedon, Chem.Comm., 438 (1971).
48. J.P.Coleman, R.Lines, J.H.P.Utley, and B.C.L.Weedon, J.Chem.Soc., Perkin Trans.II, 1064 (1974).
49. J.P.Coleman and L.Eberson, Chem.Comm., 1300 (1971).
50. C.F.Wells and M.Husain, J.Chem.Soc., A,380 (1971).
51. R.A.Sheldon and J.K.Kochi, Org.React., **19**, 279 (1972).
52. J.K.Kochi, R.A.Sheldon, and S.S.Lande, Tetrahedron, **25**, 1197 (1969).
53. W.A.Mosher and C.L.Kehr, J.Amer.Chem.Soc., 75, 3172 (1953).
54. E.J.Corey and J.Casanova, J.Amer.Chem.Soc., **85**, 165 (1963).
55. D.J.Davies and C.Waring, J.Chem.Soc., **C**, 1639 (1967).
56. H.Loeliger, Helv.Chim.Acta, **52**, 1516 (1969).
57. J.K.Kochi, J.D.Bacha, and T.W.Bethea, J.Amer. Chem.Soc., **89**, 6538 (1967).
58. D.Benson, P.Proll, L.Sutceiffe, and J.Walkley, Disc.Faraday Soc., **29**, 60 (1960); Trans.Faraday Soc., **56**, 246 (1960).
59. S.Forshult, C.Lagercrantz, and K.Torssell, Acta Chem.Scand., **23**, 522 (1969).
60. J.C.Chottard, M.Julia, and J.M.Salard, Tetrahedron, **25**, 4967 (1969).
61. D.J.Davies and C.Waring, Chem.Comm., 263 (1965).
62. D.J.Davies and C.Waring, J.Chem.Soc., **C**, 1865 (1968).
63. D.J.Davies and C.Waring, J.Chem.Soc., 2337 (1968).
64. K.Torssell, Ark.Kemi, **31**, 401 (1970).
65. A.L.J.Beckwith, R.T.Cross, and G.E.Gream, Austral.Chem., 27, 1673, 1693 (1974).
66. D.J.Davies and C.Waring, J.Chem.Soc., **C**, 2332 (1968).
67. J.K.Kochi, J.Org.Chem., **30**, 3265 (1965).
68. A.T.Sister and J.G.Traynham, J.Org.Chem., **39**, 153 (1974).
69. J.D.Bacha and J.K.Kochi, J.Org.Chem., **33**, 83 (1968).
70. W.H.Richardson and W.C.Koskinen, J.Org.Chem., **41**, 3188 (1976).
71. C.L.Jenkins and K.J.Kochi, J.Amer.Chem.Soc., **94**, 843 (1972).
72. J.K.Kochi and R.V.S.Subramanian, J.Amer.Chem. Soc., **87**, 4855 (1965).
73. A.L.J.Beckwith, G.E.Gream, and D.L.Struble, Austral.J.Chem., **25**, 1081 (1972).
74. F.Fichter and J.Hees, Helv.Chim.Acta, **18**, 704 (1935); **19**, 149 (1936).
75. F.Fichter and H.Lapin, Helv.Chim.Acta, **12**, 993 (1929).
76. F.Fichter and H.E.Suenderhauf, Helv.Chim.Acta, **16**, 338 (1933).
77. F.Fichter and L.Panizza, Helv.Chim.Acta, **15**, 996 (1932).

78. R.O.C.Norman, P.M.Storey, and P.R.West, J. Chem.Soc., **B**,1087 (1970).
79. J.Russell and R.H.Thomson, J.Chem.Soc., 3379 (1962).
80. D.A.House, Chem.Rev., **62**, 185 (1962).
81. D.D.Tanner and S.A.A.Osman, J.Amer.Chem.Soc., **90**, 6572 (1968).
82. J.M.Anderson and J.K.Kochi, J.Amer.Chem.Soc., **92**, 1651 (1970).
83. A.Clerici, F.Minisci, and O.Porta, Tetrahedron, **29**, 2775 (1973).
84. F.Minisci, R.Bernardi, F.Bertini, R.Golli, and M.Perchinummo, Tetrahedron, **27**, 3575 (1971).
85. F.Minisci, R.Mondelli, G.P.Cardini, and O.Porta, Tetrahedron, **28**, 2403 (1972).
86. M.Julia and D.Mansuy, Bull.Soc.chim.France, 1678 (1974).
87. A.Clerici and F.Minisci, Gazz chim.Ital., **103**, 171 (1973); Chem.Abs., **79**, 41 645 (1973).
88. R.G.R.Bacon and J.R.Doggart, J.Chem.Soc., 1332 (1960).
89. Yu.N.Ogibin, M.I.Katsin, and G.I.Nikishin, Izv. Akad.Nauk SSSR, Ser.Khim., 587 (1973).
90. J.S.Kiely, L.L.Nelson, and P.Boudyouk, J.Org. Chem., **42**, 1480 (1977).
91. J.C.Chottard and M.Jullia, Tetrahedron, **28**,5615 (1972).
92. T.Shono, J.Nishiguchi, and R.Oda, Tetrahedron Letters, 379 (1970).
93. J.D.Bacha and J.K.Kochi, J.Org.Chem., **33**, 2746 (1968).
94. B.C.C.Cantello, J.M.Mellor, and G.Scholes, J. Chem.Soc., Perkin Trans, II, 348 (1974).
95. G.E.Gream and D.Wege, Tetrahedron Letters, 503 (1967).
96. H.L.Goering and G.N.Fickes, J.Amer.Chem.Soc., **90**, 2848, 2856, 2862 (1968).
97. C.Descoins and M.Julia Huynh Van Sang, Bull. Soc.chim.France, 2037 (1972).
98. S.D.Elakovich and J.G.Traynham, J.Org.Chem., **38**, 873 (1973).
99. A.S.Vaidya, P.N.Choudhari, and A.S.Rao, Indian J.Chem., **11**, 645 (1973).
100. A.J.Birch and J.Stoble, Tetrahedron letters, 2079 (1976).
101. J.B.Stothers and K.C.Teo, Canad.J.Chem., **54**, 1222 (1976).
102. P.K.Jadhav and U.R.Nayak, Tetrahedron Letters, 1533 (1977).
103. C.R.Bennett and R.C.Cambie, Tetrahedron, **23**, 927 (1967).
104. D.Danielli, P.Manitto, F.Ronchetti, and G.Russo, Chem.Ind.(London), 430 (1973).
105. B.Danielli, F.Ronchetti, and G.Russo, Chem.Ind. (London), 1067 (1973).
106. P.Smith and W.A.Waters, J.Chem.Soc., **B**, 462 (1969).
107. B.Danielli, P.Manitto, and G.Russo, Chim.Ind., **51**, 609 (1969).
108. D.N.Vyas, S.B.Mehta, and S.H.Mehta, Chem.Era, **11**, 14 (1976).
109. Yu.N.Ogibin, M.I.Katsin, and G.I.Nikishin, Izv. Akad.Nauk SSSR, Ser.Khim., 1345 (1975).
110. Yu.N.Ogibin, M.I.Katsin, and G.I.Nikishin, Izv. Akad.Nauk SSSR, Ser.Khim., 1225 (1972).
111. L.R.Barclay, C.E.Milligan, and N.D.Hall, Canad. J.Chem., **40**, 1664 (1962).
112. L.L.McCoy and A.Zagalo, J.Org.Chem., **25**, 924 (1960).
113. Yu.N.Ogibin, E.I.Troyanskii, and G.I.Nikishin, Izv.Akad.Nauk SSSR, Ser.Khim., 2239 (1974).
114. Yu.N.Ogibin, E.I.Troyanskii, and G.I.Nikishin, Izv.Akad.Nauk SSSR, Ser.Khim., 2522 (1974).
115. C.A.Grob, M.Ohta, and A.Weiss, Angew.Chem., **70**, 343 (1958).
116. C.A.Grob, M.Ohta, E.Renk, and A.Weiss, Helv. Chim.Acta, **41**, 1191 (1958).
117. C.M.Cimarusti and J.Malinski, J.Amer.Chem.Soc., **90**, 113 (1968).
118. N.B.Chapman, S.Sotheesivaran, and K.J.Toyne, Chem.Comm., 214 (1965).
119. L.H.Zalkow and D.R.Brannon, J.Chem.Soc., 5497 (1964).
120. W. von E. Doering, M.Farber, and A.Sayigh, J. Amer.Chem.Soc., **70**, 4370 (1952).
121. W.R.Moore and H.Arzoumanian, J.Org.Chem., **27**, 4667 (1962).
122. J.J.Tufariello and W.J.Kissel, Tetrahedron Letters, 6145 (1966).
123. J.Meinwald, J.J.Tufariello, and J.J.Hurst, J.Org. Chem., **29**, 2914 (1964).
124. H.Willard and P.Young, J.Amer.Chem.Soc., **52**, 132 (1930).
125. N.Furman, J.Amer.Chem.Soc., 50, 755 (1928).
126. J.H.Fitzpatrick and D.Hapgood, Inorg.Chem., 13, 568 (1974).
127. H.Oeda, Bull.Chem.Soc.Japan, 9, 8 (1934).
128. J.R.Jones, W.A.Waters, and J.S.Littler, J.Chem. Soc., 630 (1961).
129. P.Levesley and W.A.Waters, J.Chem.Soc., 217 (1955).
130. T.J.Kemp and W.A.Waters, J.Chem.Soc., 1192 (1964).
131. K.K.Baneryi, Tetrahedron, **29**, 1401 (1973).
132. Y.Pocker and B.C.Davis, J.Amer.Chem.Soc., **95**, 6216 (1973).
133. Y.Pocker and B.C.Davis, J.Org.Chem., **40**, 1625 (1975).
134. S.D.Paul and D.G.Pradham, Indian J.Chem., 11, 1155 (1973).
135. R.Dayal and G.V.Bakore, Indian J.Chem., 10, 1165 (1972).
136. D.C.Nonhebel and J.C.Walton, "Free-Radical Chemistry: Structure and Mechanism" (Translated into Russian), Izd.Mir, Moscow, 1977.
137. R.E.Schwerzell, R.G.Lawler, and G.T.Evans, Chem. Phys.Letters, 29, 106 (1974).
138. O.Farver and G.Nord, Chem.Comm., 736 (1967).
139. J.A.Kuhnle, R.E.Lundin, and A.C.Waiss, Chem. Comm., 287 (1972).
140. N.A.Maier and Yu.A.Ol'dekop, Vests.Akad.Nauk Beloruss.SSR, Ser.Khim., No.4, 74 (1971).
141. W.H.Starnes, J.Amer.Chem.Soc., **84**, 2270 (1962).
142. W.H.Starnes, J.Org.Chem., **31**, 1436 (1966).
143. Yu.A.Ol'dekop and N.A.Maier, Izv.Akad.Nauk SSSR, Ser.Khim., 1171 (1966).
144. Yu.A.Ol'dekop, N.A.Maier, and Yu.D.But'ko, Zhur. Obshch.Khim., **41**, 2253 (1971).
145. Yu.A.Ol'dekop, N.A.Maier, and Yu.D.But'ko, Zhur. Obshch.Khim., **40**, 641 (1970).
146. Yu.A.Ol'dekop, N.A.Maier, A.A.Erdman, and Yu.A.Dzomidava, Zhur.Obshch.Khim., **40**, 637 (1970).
147. N.A.Maier, V.I.Gesel'berg, and Yu.A.Ol'dekop, Zhur.Obshch.Khim., **32**, 2030 (1960).

148. I.V.Berezin and A.M.Ragimova, Zhur.Fiz.Khim., **36**, 581 (1962) [Russ.J.Phys.Chem., No.3 (1962)].
149. J.P.Fackler, J.Amer.Chem.Soc., **84**, 24 (1962); **86**, 5132 (1964).
150. J.M.Kolthoff and S.Bruckenstein, J.Amer.Chem.Soc., **78**, 1 (1956).
151. S.Bruckenstein and J.M.Kolthoff, J.Amer.Chem.Soc., **78**, 10 (1956).
152. F.H.Westheimer, Trans.New York Acad.Sci., **18**, 15 (1955).
153. Q.Fernando, Adv.Inorg.Radiochem., **7**, 185 (1965).
154. E.Ochiai, Coordin.Chem.Rev., **3**, 49 (1968).
155. P.Bonchev, "Complex Formation and Catalytic Activity" (Translated into Russian), Izd.Mir, Moscow, 1975.
156. C.L.Jenkins and J.K.Kochi, J.Amer.Chem.Soc., **94**, 843 (1972)..

Institute of Organic Chemistry
of the Academy of Sciences of
Ukrainian SSR

Lomonosov Moscow State University

Translated from *Uspekhi Khimii*, **49**, 2286 - 2313 (1980) U.D.C. 547.914

The Synthesis of Polymers by Modification Methods

V.V.Korshak

The present state of the syntheses of polymers by modification methods is considered and the characteristics of the polymer modification reactions, determined by the specific macromolecular features of the polymers, are discussed. The applicability of the concept of the heterounit structure to polymers obtained by the modification procedure is demonstrated. Typical groups of reactions modifying natural and synthetic polymers and their features are specified and the characteristics of such reactions, involving substitution, structure formation, degradation, addition, elimination, isomerisation, and exchange, are considered. The prospects for the development of modification processes as a leading trend in the field of the synthesis of polymers are described.
The bibliography includes 130 references.

CONTENTS

I. Introduction 1135
II. Characteristics of polymer modification reactions 1135
III. The heterounit structure of polymers obtained by the modification procedure 1138
IV. Typical chemical polymer modification reactions 1138

I. INTRODUCTION

The modification of polymers is one of the ways of synthesising high-molecular-weight compounds, which, together with polymerisation and polycondensation, has been used for a long time to synthesise polymers.

Whereas the polymerisation and polycondensation reactions are processes based on the conversion of monomers into polymers, the third procedure (modification) is a process based on the interconversion of polymers (Fig.1).

Consequently, *chemical modification of polymers is a process in which the initial polymer is subjected to physical or chemical influences, as a result of which it is converted into a new polymer with a different chemical structure*†.

The polymer modification reaction was first achieved by the French worker Braconnot, who obtained nitrocellulose in 1833 by treating cellulose with nitric acid[1]. Similar reactions were later carried out on a series of natural polymers. Different derivatives of cellulose, starch, proteins, rubber, and other natural polymers were obtained[2]. Subsequently synthetic polymers such as poly(vinyl chloride), polystyrene, polyethylene, and others began to be subjected to modification reactions at an increasing frequency[2].

Such wide-scale use of the modification reactions is due to the fact that the initial polymers do not meet all the practical requirements as regards their properties. Thus many insoluble polymers can be converted by modification into soluble high-molecular-weight compounds. A striking example of this kind is provided by cellulose, whose esters are readily soluble in organic solvents; chlorinated poly(vinyl chloride) and polyethylene become readily soluble. The introduction of carboxy- and amino-groups into polystyrene imparts to it acid and basic properties respectively, which are essential for ion-exchange resins. The introduction of nitrate ester groups into cellulose imparts explosive properties to the latter. The introduction of phosphate groups as well as chlorine, fluorine, bromine, and certain other elements into polymers renders them incombustible.

† According to this definition, the copolymerisation of monomers should not be classified as chemical modification of polymers.

Thus the modification of polymers constitutes an extremely universal method whereby it is possible to vary within a wide range their physical and chemical properties in the desired direction. Because of this, the modification of polymers has now become one of the most important procedures whereby a large number of polymers are synthesised both in the laboratory and in industry. In industry modification processes have found extensive applications in the synthesis of many polymers, produced on a large scale, such as nitrocellulose, acetylcellulose, other cellulose esters and ethers, poly(vinyl alcohol), acetals of poly(vinyl alcohol), chlorinated poly(vinyl chloride), chlorinated and sulphochlorinated polyethylene, and others. There is no doubt that in the future modification will acquire still greater importance in industry.

The aim of the present review is to outline the present state of the modification processes and the likely prospects for their utilisation. The characteristics of the polymer modification reactions, determined primarily by their macromolecular nature, are considered at the beginning of the review. A feature of polymers such as their heterochain structure, which in many respects determined their characteristic set of physical and chemical properties, merits particular attention. Next, typical reactions used at present for the modification of polymers are described.

II. CHARACTERISTICS OF POLYMER MODIFICATION REACTIONS

A characteristic feature of the polymer modification processes is the fact that all reactions of this kind do not as a rule go to completion and are accompanied by side reactions, which has a significant influence on the course of the process and its results. This is caused by the influence of a number of significant physical and chemical factors, manifested in a specific manner in various polymer modification reactions. Such factors include the influence of the nature of the reagents and catalysts, the structure and degree of crystallinity of polymers, temperature, the nature of the solvent, and others. Ultimately, the reactions therefore result in a mixture of macromolecules of different structure, each of which contains different units in a wide variety of combinations. The final polymer is chemically inhomogeneous, i.e. has a heterounit structure[3].

Consequently reactions in the polymer chain obey much more complex rules than the analogous reactions of low-molecular-weight compounds. The explanation is that not only the structure of the reacting groups but also a number of specific influences, determined by the macromolecular nature of one or both reactants, play a significant role here. The chain effect, the effect of the neighbouring group, and configurational, conformational, electrostatic, and supermolecular effects are usually isolated from such influences as the most significant[3-5].

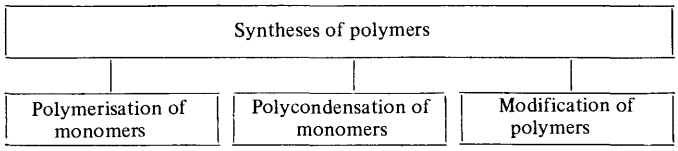
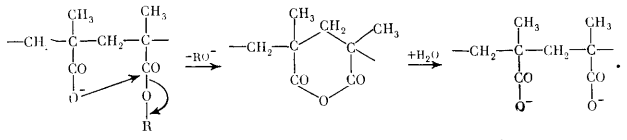


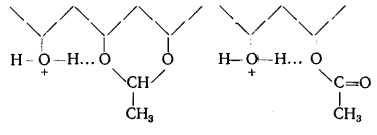
Figure 1. Different processes leading to the synthesis of polymers.

The relative steric disposition of different groups in the polymer chain has a significant steric or electrostatic (polar) influence on their reactivity. This influence can be shown both in the activation and passivation of neighbouring groups. The increase of the rate of reaction under the influence of a neighbouring group, known as "anchimeric assistance", is exhibited mainly when five- or six-membered rings can be formed. Thus it is observed for succinate esters. In exactly the same way, owing to the steric proximity of a neighbouring group, isotactic poly(methyl methacrylate) hydrolyses faster than the syndiotactic and atactic polymers, because in the isotactic polymer the neighbouring functional groups are distributed more favourably for their interaction with one another, leading to the formation of an intermediate cyclic anhydride[6,7]. The distribution function of the compositions of polymers has been considered in a number of investigations[8,9].

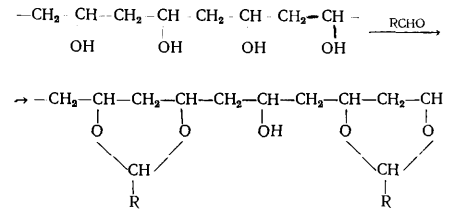
As already stated, one of the causes of the formation of anomalous units in polymer modification processes is the influence of neighbouring units which have already reacted (the "neighbour effect")[10]. A characteristic example of the acceleration of the reaction by the "neighbour effect" is the hydrolysis of the methacrylate–methacrylic acid copolymer[11]:



In the case of the partially hydrolysed poly(vinyl acetate) or polyvinylacetal this interaction takes place via the formation of a hydrogen-bonded ring[12], which facilitates the hydrolysis of acetals and acetates by increasing their reactivity[13] via the mechanism



As a result of the "neighbour effect", not all the initial hydroxyls in poly(vinyl alcohol) are converted into the acetal by treatment with aldehydes. According to Flory's calculations[14], approximately 13.53% of the hydroxyls should remain unsubstituted:



As another example, one may take polyethylene, which is readily chlorinated up to a chlorine content of 60%, whereupon the reaction slows down and, after the attainment of a chlorine content of 73%, ceases, although theoretically the chlorine content could reach 85.5%.[15] The explanation is that CCl_2 groups are not formed and the first stage proceeds with formation of the $-CH_2CHCl-$ groups up to a chlorine content of 56.8%. The next stage consists in the formation of the $-CHClCHCl-$ groups up to a chlorine content of 73.2%, whereupon the chlorination reaction stops. The retarding effect of the chlorine atoms in the $-CHCl-$groups on the chlorination of neighbouring CH groups can be accounted for by the inductive effect[13,16].

Thus in substitution reactions the "neighbour effect" as well as the steric and electrostatic influence of the initial side groups play a significant role[13].

Examples are known in which different effects are superimposed. Thus the alkaline hydrolysis of polymethacrylamide does not go to completion[17] and the methacrylamide–methacrylic acid copolymer hydrolyses with greater difficulty the smaller its methacrylamide content[18]. The loss of reactivity by the amide groups in these cases occurs both as a consequence of their being blocked by two ionised carboxy-groups and as a result of the electrostatic repulsion by the latter of hydroxide ions which catalyse the hydrolysis[19].

Attention should be drawn to the fact that, in order to characterise fully the polymer formed as a result of chemical modification, it is important to establish not only the presence of anomalous units and their number but also their sequence in the polymer macromolecule. Thus the frost resistance and physical properties of vulcanised rubbers are determined not only by the ratio of the *cis*- and *trans*-units but also by their sequence in the macromolecules[20]. Yet another example is provided by chlorinated polyethylene containing 56% of chlorine, the properties of which differ appreciably from those of poly(vinyl chloride) with the same chlorine content[21]. In the former case we have an irregular and in the latter a regular arrangement of chlorine atoms, as can be seen from the formulae of these polymers:

$$-CH_2-CH_2-CHCl-CHCl-CH_2-CH_2-;\ (-CH_2-CHCl-)_x.$$

Polyethylene chlorinated in solution in carbon tetrachloride and in an aqueous suspension has different arrangements of chlorine atoms and, for the same content of the latter, these two types of polymers have appreciably different properties[22].

It has been found that the hydrolysis of isotactic polyacrylonitrile converts it into an atactic polymer[23], while polymethacrylate esters hydrolyse without change of configuration[24], which constitutes a specific illustration of the influence of the steric structure on the chemical properties of these polymers and particularly on the structure of their reaction products.

When the causes responsible for the chemical inhomogeneity of the products, i.e. the formation of heterounit polymers, are considered, one should bear in mind that the physical structure of the initial polymer plays a by no means subsidiary role[25,26]. Its role is particularly significant when the reaction takes place in a heterogeneous system. This is necessary when there is no suitable solvent for the reaction or when one has to retain the initial form of the polymer, as, for example, in the treatment of fibres and films. Finally, the tendency towards the manufacture of polymers with the greatest possible elimination of all solvents has been recently assuming an increasing importance. Together with economical and ecological causes, this is associated with the fact that reactions in solution are sensitive to the nature of the solvent and to the properties of the solution, which can be significantly reflected in the degree of conversion and in the structure of the modification products formed.

The compatibility of the polymers is also significant, because, as the reaction proceeds, their composition changes very considerably with a corresponding alteration of their properties. Incompatibility can cause phase separation or coiling of the chains. As a result of the latter, the reaction is localised on the surfaces of compact coils or becomes diffusion-controlled. The accessibility of the functional groups of the polymer to the low-molecular-weight reagent is thus altered, which affects the degree of the modification reaction and the structure of the product[27].

Factors such as the supermolecular structure of the polymers, the orientation of the macromolecules in solution, and the solubility and compatibility of the polymers and reagents in solutions also exert a considerable influence on the result of reactions involving substitution in macromolecules. The influence of the supermolecular structure of the polymer in a reaction carried out in a heterogeneous system, where the solid polymer is acted upon by liquid reagents, is associated with the fact that the rate and degree of conversion depend on the rate of diffusion of the liquid reagent into the bulk of the polymer structure. This diffusion takes place more readily in an amorphous polymer and in the amorphous regions of crystalline polymers. Macromolecules in the amorphous regions react faster and are more fully acted upon by chemicals than macromolecules in the ordered crystalline state.

The hydrolysis of poly(ethylene terephthalate)[28], the chlorination[29] and oxidation[30] of polyethylene, the grafting of styrene onto polyamides[31], and the heterocyclisation of polyhydrazides to polyoxadiazoles[32] proceed much more readily in the amorphous regions than in the crystalline regions, since the orientation of polymer chains in the latter hinders both the accessibility of the macromolecules to the reagents and the interaction of the functional groups of the macromolecules with one another.

It has been shown for the sulphochlorination of polyethylene that the number of sulpho-groups which have entered the polymer corresponds to the degree of crystallinity of the latter determined by X-ray diffraction[33]. It has been found that the degree of acetylation of cellulose also depends markedly on the supermolecular and morphological structures of the initial cellulose[25,34]. The degree of crystallinity of cellulose affects not only the distribution of the substituted groups along the chain of the macromolecule but also the mode of substitution in the glucose residues. Thus, although the primary hydroxy-group at the sixth carbon atom is more reactive, the heterogeneous xanthate substitution reaction takes place preferentially at the less reactive secondary hydroxyls attached to the second or third carbon atoms. The explanation is that the hydroxyl at the sixth carbon atom is blocked by intramolecular and intermolecular hydrogen bonds[35,36].

The study of the oxidation and chlorination of isotactic poly-4-methylpentene showed that these processes take place preferentially at the bends in the chains, since the lowest activation energy is required at these sites as a consequence of internal stresses[37].

The nature of the reagents is also very important. Thus acetic anhydride and nitric acid react with all the hydroxy-groups of cellulose, while trityl chloride reacts only with the primary groups[38]. The reaction temperature also plays a significant role. All possible polymer modification reactions take place more readily at temperatures above the glass point of the polymer[39].

In view of the above characteristics of the reactions in heterogeneous systems, in chemical modification reactions an attempt is made to dissolve the polymers or at least to obtain them in a gel, i.e. in a swollen state, which facilitates the substitution process[40–42].

Substitution reactions in solution, i.e. in a homogeneous system, take place faster and result in a more complete substitution of the functional groups and a more uniform disposition of the substituting groups along the chain than in a heterogeneous system. Thus acetylation of poly(vinyl alcohol) in a homogeneous solution makes it possible to obtain a virtually fully substituted product, while a considerable number of unsubstituted hydroxy-groups remain after acetylation in a heterogeneous system[42]. The distribution of free hydroxy-groups and correspondingly acetyl groups in the cellulose acetate obtained under homogeneous conditions is more regular than in the acetate obtained under heterogeneous conditions[43]. Since a single treatment of the polymer with the reagent does not lead to complete substitution, the treatment must be frequently repeated. Fig.2 shows how the content of methoxy-groups in methylated cellulose depends on the number of repeated treatments[44].

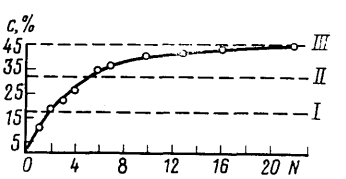


Figure 2. Dependence of the content of methoxy-groups (c) in methylated cellulose on the number of repeated treatments: I) monomethylcellulose; II) dimethylcellulose; III) trimethylcellulose. The continuous curve represents the variation of the content of methoxy-groups in the specimen.

As already mentioned, the polymer modification reactions never go to completion and they therefore lead to heterounit polymers containing the initial units as well as the final and intermediate units. The study of the resulting polymers shows that the substituents are usually distributed at random along the polymer chain. Fig.3 illustrated the distribution of substituents for different degrees of substitution.

III. THE HETEROUNIT STRUCTURE OF POLYMERS OBTAINED BY THE MODIFICATION PROCEDURE

One of the characteristic features of the modification reactions is their failure to reach completion, as a consequence of which some of the initial functional groups do not react and remain in the unchanged state. At the same time there is a possibility of a wide variety of side reactions, which also lead to the formation of units of a different chemical type and give rise to chemical heterogeneity in the macromolecules, referred to as the heterounit structure of polymers[45–48].

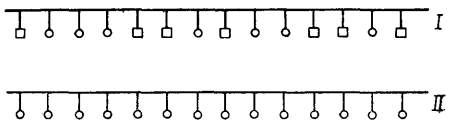


Figure 3. Distribution of substituents in the macromolecule for different degrees of substitution of the functional groups: I) partial, irregular substitution in heterounit polymers; II) complete substitution.

The heterounit polymers obtained as a result of various modification reactions differ by the presence of anomalous units in the macromolecule, i.e. are chemically heterogeneous. Whereas the structure of a normal homounit polymer can be represented by the usual formula $-(-M-)_x-$, the macromolecule of a heterounit polymer contains anomalous A units:

$$-M-M-M-A-M-M- \quad .$$

Consequently the structure of a heterounit polymer can be represented by the following formula in the general case:

$$-[-(-M-)_{\overline{[m]}}-(-A-)_{\overline{[n]}}-]_x$$

where M are normal units, A are anomalous units, and $[\overline{m}]$ and $[\overline{n}]$ are coefficients indicating a statistical distribution of the units in the macromolecule of the heterounit polymer obtained by one of the modification methods[45–48].

As an example, one may quote the formula of heterounit cellulose nitrate[49]:

$$-[-C_6H_7O_2(OH)_3-]_{\overline{[m]}}-[-C_6H_7O_2(OH)_2(ONO_2)-]_{\overline{[n]}}$$
$$-[-C_6H_7O_2(OH)(ONO_2)_2-]_{\overline{[p]}}-[-C_6H_7O_2(ONO_2)_3-]_{\overline{[q]}} \quad .$$

Thus we may expect the presence of units of at least four different types in the macromolecules of this cellulose ester, disregarding the anomalous units which might have been present in the initial cellulose.

Yet another example of a heterounit polymer is provided by chlorinated polyethylene, the general structure of which can be expressed by the following formula:

$$-(-CH_2-CHCl-)_{\overline{[m]}}(-CH_2-CH_2-)_{\overline{[n]}}-(-CHCl-CHCl-)_{\overline{[p]}} \quad .$$

Naturally the coefficients depend on the degree of the modification and its conditions.

Fig. 4 illustrates the fundamental reactions—both normal reactions and secondary reactions—which can occur in the modification of polymers and which we designate as the "set of modifying reactions". The data in Fig. 4 readily lead to the conclusion that the causes responsible for the heterounit structure of the products of the modifying reactions are fairly numerous. It is therefore not surprising that all the modification methods lead to the formation of chemically heterogeneous heterounit polymers. This conclusion is very significant, because it relates the structure of polymers to their properties[50].

It had been shown earlier for a large number of polymers that the heterounit structure is a factor which exerts a very significant influence on the entire set of physical and chemical properties of heterounit polymers[45]. Thus a statistical distribution of units of different chemical types in the macromolecules of heterounit polymers is frequently responsible for their ready solubility, a decrease of the melting point and thermal stability, an increase of elasticity, and the simultaneous decrease of strength[46].

On the basis of the concept of the heterounit structure, the modification reactions must be represented with allowance for the formation of anomalous units. For example, the nitration of cellulose can be represented thus:

$$-[-C_6H_7O_2(OH)_3-]_x \xrightarrow{HNO_3}$$
$$\rightarrow -[-C_6H_7O_2(OH)_3-]_{\overline{[m]}}-[-C_6H_7O_2(OH)_2(ONO_2)-]_{\overline{[n]}}$$
$$-[-C_6H_7O_2(OH)(ONO_2)_3-]_{\overline{[p]}}-[-C_6H_7O_2(ONO_2)_3-]_{\overline{[q]}} \quad .$$
$$x = m + n + p + q$$

The hydrolysis of poly(vinyl acetate) can be represented by the equation

$$-\left[-CH_2-\underset{OCOCH_3}{CH}-\right]_x- \xrightarrow{H_2O} -\left[-CH_2-\underset{OCOCH_3}{CH}-\right]_{\overline{[m]}}-\left[-CH_2-\underset{OH}{CH}-\right]_{\overline{[n]}} \quad .$$
$$x = m + n$$

The chlorination of polyethylene is described schematically by the following equation:

$$-[-CH_2-CH_2-]_x \xrightarrow{Cl_2}$$
$$\rightarrow -[-CH_2-CH_2-]_{\overline{[m]}}-[-CH_2-CHCl-]_{\overline{[n]}}-[-CHCl-CHCl-]_{\overline{[p]}} \quad .$$
$$x = m + n + p$$

Naturally, this type of expanded representation of the modification reactions requires much space and for the sake of economy we shall henceforth represent only the extreme units in the chain of transformations occurring in the modification processes.

IV. TYPICAL CHEMICAL POLYMER MODIFICATION REACTIONS

Polymer modification processes are based on the use of a series of chemical reactions. In considering the polymer modification reactions known at the present time, one should note their large number and wide variety. Among these reactions, there are both processes based on the interactions of polymers with low-molecular-weight reagents and reactions of polymers with polymers. To facilitate the discussion of these reactions, we combined them into seven groups in terms of their chemical similarity. Examples of typical reactions in each group are given in Table 1, which shows that a series of different reactions are widely used in polymer modification processes. Here we encounter both substitution and elimination reactions, on the one hand, and reactions involving addition to multiple bonds, structure formation, and degradation of polymers, on the other. In addition, reactions involving the isomerisation of macromolecules and extremely unusual exchange type reactions of heterochain polymers are used for this purpose.

An interesting feature of all these reactions is that each has a specific influence on the structure of the polymer

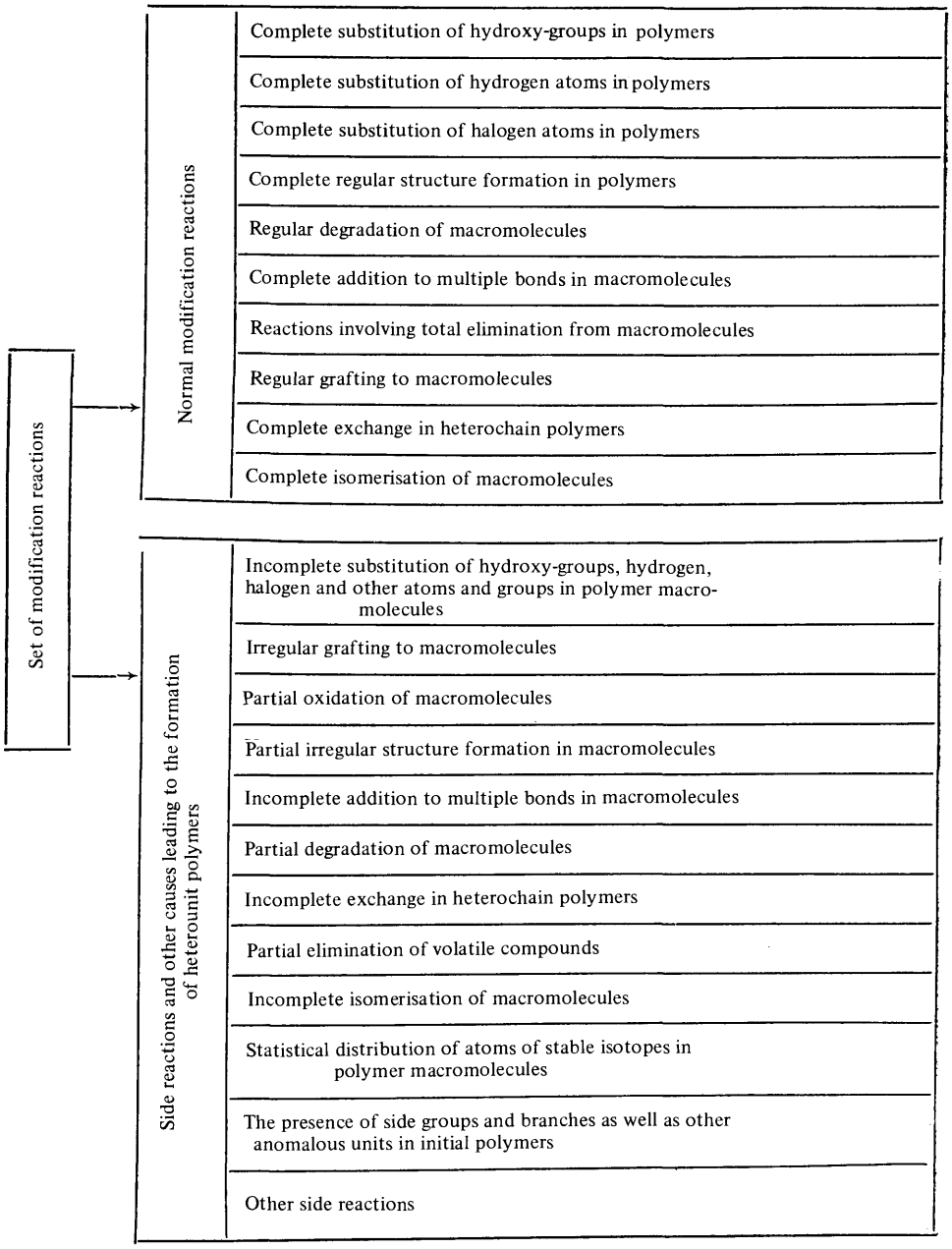


Figure 4. The set of modification reactions.

macromolecule formed as a result of the modification. Fig. 5 illustrates schematically the changes in the structure of macromolecules occurring as a result of the modification processes. It shows that in reactions of type (1) the structure of the polymer chain is retained, as in fact should have been the case in reactions of the polymer-analogue type to which these processes belong. In all the remaining types of reactions the structure of the macromolecule changes significantly. The remaining modification reactions cannot therefore be included in the class of polymer-analogue transformations.

In considering the modification reactions, one must bear in mind not only their chemical nature but also the way in which they are carried out (in solution, in the melt, in an emulsion, and in the solid), since the result of the process depends significantly on its conditions.

1. Polymer Modification Reactions Involving Substitution

We shall now consider in detail reactions of each type, examples of which are given in Table 1. We shall begin their consideration with the widely used substitution reactions.

The substitution reactions in Table 2 can be subdivided into the following subgroups: (1) substitution of a hydroxy-group by acyl and alkyl groups as well as inorganic acid residues; (2) substitution of a hydrogen atom by deuterium, a halogen, halogeno-, nitro-, phosphino-, and sulpho-groups, as well as alkyl groups in grafting reactions; (3) hydrolysis of derivatives of polymeric carboxylic acids; (4) substitution of a halogen and other groups for a hydroxy- or amino-group; (5) oxidation of side groups.

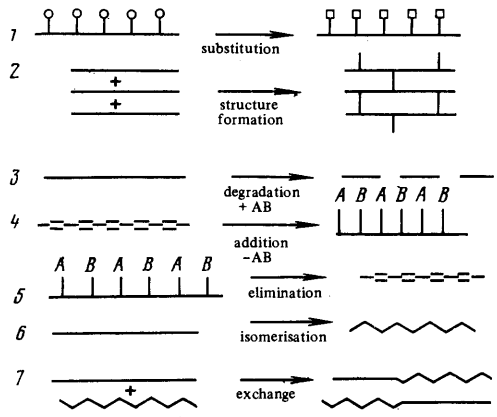


Figure 5. The change in the structure of macromolecules as a result of the modification reaction (the numbers of the reactions have the same significance as in Table 1).

Table 1. Examples of typical chemical polymer modification reactions.

Name and equation of modification reaction	References
Substitution of atoms and groups in macromolecule $-[-C_6H_7O_2(OH)_3-]_x- \xrightarrow{HNO_3} -[-C_6H_7O_2(ONO_2)_3-)_x-$	1
Structure formation in polymers $-CH_2-CH_2-CH_2- \xrightarrow{h\nu} -CH_2-\underset{\displaystyle CH_2-CH-CH_2-}{\overset{\displaystyle |}{CH}}-CH_2-$	51
Degradation of macromolecules $-[-CH_2-CH=CH-CH_2-CH_2-]_x- \xrightarrow{WCl_6(CH_3)_2Si(CH_2)_2Si(CH_3)_3}$ $\rightarrow -[-CH_2-CH=CH-CH_2-CH_2-]_{x/n}-$	52
Reactions involving addition to multiple bonds in macromolecule $-[-CH_2-CH=CH-CH_2-]_m- \xrightarrow{+Cl_2} -[-CH_2-\underset{Cl}{\overset{|}{CH}}-\underset{Cl}{\overset{|}{CH}}-CH_2-]_m-$	53
Reactions involving elimination from macromolecules $-(-CH_2-CCl_2-)_x- \xrightarrow{-HCl} -(-C\equiv C-)_x-$	54
Isomerisation reactions of macromolecules $-[-C\equiv C-C\equiv C-]_x- \rightarrow =[=C=C=C=C=]_x=$	55
Exchange reactions of heterochain polymers $-R-\overset{+}{COO}-R- \quad -R-\overset{+}{COO}-R'$ $-R'-\overset{+}{COO}-R'- \rightarrow -R'-\overset{+}{COO}-R-$	56

These reactions have certain common features consisting in the nature of the alteration of the structure and the properties of the resulting polymers. We may note that the replacement of a hydroxy-group in the polymer by an acid residue or an alkyl group makes the polymer soluble in inorganic solvents; the substitution of hydrogen by a halogen has a similar influence. In contrast, the substitution of an alkyl group in an ether by a hydroxy group impairs the solubility of such a polymer in organic solvents.

Table 2. Examples of polymer modification reactions by substitution.

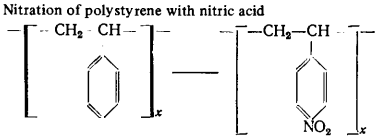
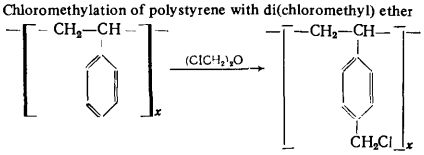
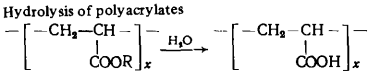
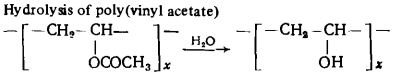
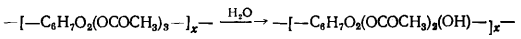
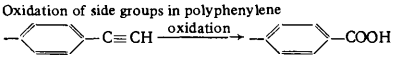
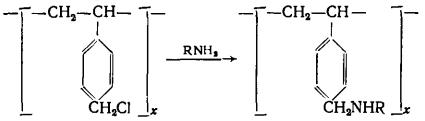
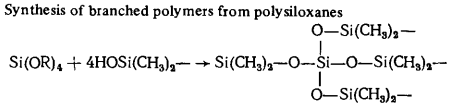
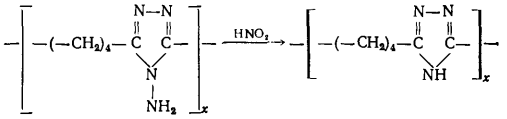
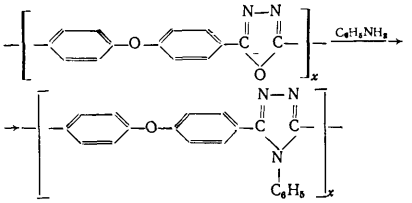
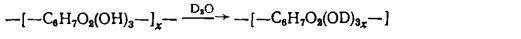
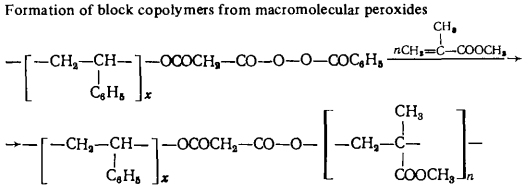
Name and equation of modification reaction	Refs.
Nitration of cellulose with nitric acid $-[-C_6H_7O_2(OH)_3-]_x- \xrightarrow{HNO_3} -[-C_6H_7O_2(ONO_2)_3-]_x-$	1
Acetylation of cellulose with acetic anhydride $-[-C_6H_7O_2(OH)_3-]_x- \xrightarrow{(CH_3CO)_2O} -[-C_6H_7O_2(OCOCH_3)_3-]_x-$	57
Acetylation of poly(vinyl alcohol) with acetic anhydride $-\left[-CH_2-\underset{OH}{\overset{|}{CH}}-\right]_x- \xrightarrow{(CH_3CO)_2O} -\left[-CH_2-\underset{OCOCH_3}{\overset{|}{CH}}-\right]_x-$	58
Acetylation of poly(vinyl alcohol) with aldehydes $-\left[-CH_2-\underset{OH}{\overset{|}{CH}}-CH_2-\underset{OH}{\overset{|}{CH}}-\right]_x- \xrightarrow{RCHO} -\left[-CH_2-\underset{\displaystyle O\quad O}{\overset{\displaystyle |}{CH}}-CH_2-\underset{\displaystyle R}{\overset{\displaystyle |}{CH}}-\right]_x-$	59
Nitration of poly(vinyl alcohol) with nitric acid $-\left[-CH_2-\underset{OH}{\overset{|}{CH}}-\right]_x- \xrightarrow{HNO_3} -\left[-CH_2-\underset{ONO_2}{\overset{|}{CH}}-\right]_x-$	60
Chlorination of poly(vinyl chloride) with elemental chlorine $-[-CH_2-CHCl-]_x- \xrightarrow{Cl_2} -[-CHCl-CHCl-]_x-$	61
Chlorination of polyethylene with elemental chlorine $-[-CH_2-CH_2-]_x- \xrightarrow{Cl_2} -[-CHCl-CH_2-]_x-$	62
Nitration of polystyrene with nitric acid 	63
Chloromethylation of polystyrene with di(chloromethyl) ether 	64
Sulphochlorination of polyethylene with sulphur dioxide and chlorine $-[-CH_2-CH_2-]_x- \xrightarrow{SO_2+Cl_2} -\left[-CHCl-\underset{SO_2Cl}{\overset{|}{CH}}-\right]_x-$	65
Grafting by chain transfer in the presence of peroxides $-[-CH_2-CH_2-]_x- \xrightarrow{R^\cdot} -[CH_2-\dot{C}H-]_x- \xrightarrow{H_2C=CHX}$ $\rightarrow -\left[\begin{matrix}CH_2-CHX-\\ -CH_2-CH-\end{matrix}\right]_x-$	66
Repeated grafting of polyamides under the influence of ozone to obtain "pemosors" (multiple grafted copolymers) $-(-CH_2-)_4-CONH- \xrightarrow{O_3} -CH_2-\dot{C}H-CH_2-CH_2-CONH- \xrightarrow{H_2C=CHX}$ $\begin{matrix}CH_2-CHX-CH_2-CHX-\\ -CH_2-CH-CH_2-CH_2-CONH-\end{matrix} \xrightarrow{O_3} \begin{matrix}CH_2-CHX-\dot{C}H-CHX\\ -CH_2-CH-CH-CH_2-CONH-\end{matrix} \xrightarrow{H_2C=CHY}$ $\begin{matrix}CH_2-CHY-CH_2-CHY-\\ CH_2-CHX-CH-CHX-\\ \rightarrow -CH_2-CH-CH-CH_2-CONH-\\ CH_2-CHY-CH_2-CHY-\end{matrix}$	67
Grafting by addition of epoxyalkanes to polyamide $-R-CO-NH-R'- \xrightarrow{CH_2-CH_2\ (O)} -R-CO-\underset{\displaystyle CH_2-CH_2-O-}{\overset{\displaystyle |}{N}}-R'-$	68

Table 2 (cont'd).

Name and equation of modification reaction	Refs.
Hydrolysis of polyacrylates 	69
Hydrolysis of poly(vinyl acetate) 	70
Hydrolysis of cellulose triacetate 	71
Oxidation of side groups in polyphenylene 	72
Amination of polychloromethylstyrene by amines 	73
Synthesis of branched polymers from polysiloxanes 	75
Conversion of polyaminotriazoles into polytriazoles by treatment with nitrous acid 	76
Conversion of polyoxadiazoles into polytriazoles by treatment with aniline 	77
Deuteration of cellulose with heavy water 	78
Formation of block copolymers from macromolecular peroxides 	79

The majority of polymer modification reactions involving substitution belong to the type designated as polymer-analogue reactions. Their characteristic feature is retention of the main macromolecular skeleton, only the nature of the substituents surrounding the main chain being altered. The specific features of reactions of this type were considered previously.

2. Polymer Modification Reactions Involving Structure Formation

The modification of polymers by structure formation is a process in which the macromolecules pass through a stage with branched structures and are ultimately converted into infusible and insoluble three-dimensional structures. In the first stage of this process the polymer interacts with the cross-linking agent, which leads to the formation of bonds between the macromolecules. An industrial structure formation process, known as vulcanisation, is widely used in the processing of polymers, particularly elastomers. Vulcanisation imparts to rubbers resistance to wear and other mechanical influences and resistance to oxidation and the action of solvents.

Table 3. Examples of polymer modification reactions by structure formation.

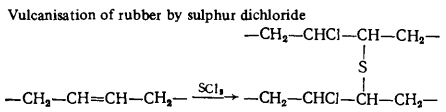
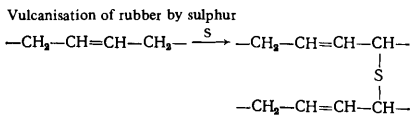
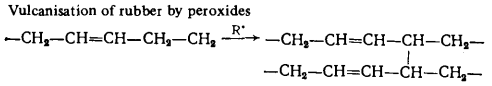
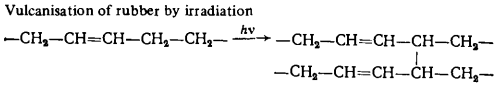
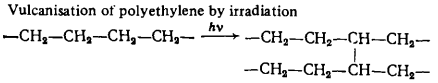
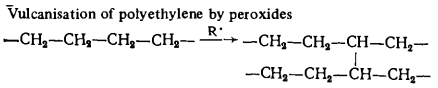
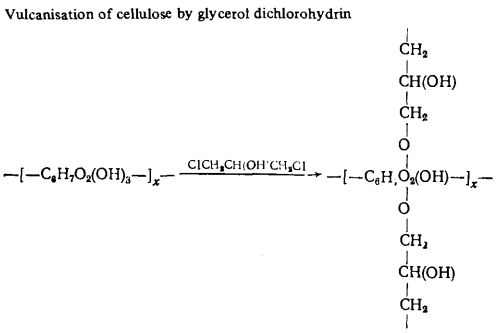
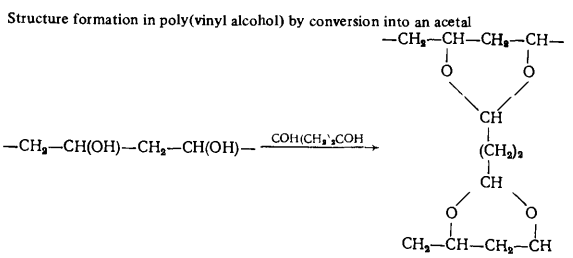
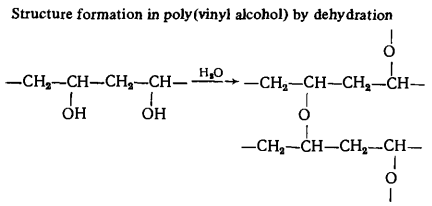
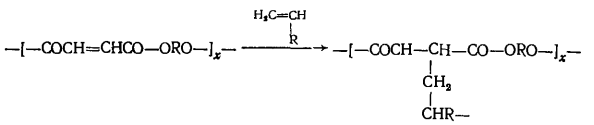
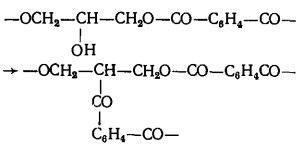
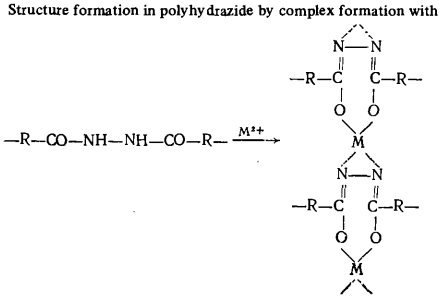
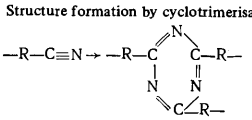
Name and equation of structure formation reaction	Refs.
Vulcanisation of rubber by sulphur dichloride 	80
Vulcanisation of rubber by sulphur 	80
Vulcanisation of rubber by peroxides 	81
Vulcanisation of rubber by irradiation 	82
Vulcanisation of polyethylene by irradiation 	83
Vulcanisation of polyethylene by peroxides 	84
Vulcanisation of cellulose by glycerol dichlorohydrin 	85
Structure formation in poly(vinyl alcohol) by conversion into an acetal 	86

Table 3 (cont'd).

Name of equation of structure formation reaction	Refs.
Structure formation in poly(vinyl alcohol) by dehydration 	58
Structure formation in unsaturated polyesters by copolymerisation with monomers 	87
Structure formation in Glyptals by treatment with dicarboxylic acids or their derivatives 	88
Structure formation in polyhydrazide by complex formation with metal ions 	89, 106
Structure formation by cyclotrimerisation of nitriles 	90

Examples of reactions involving structure formation in polymers are presented in Table 3, which shows that peroxide and radiation vulcanisations are widely used for modification by structure formation. In addition, in the case of rubbers vulcanisation by sulphur and its derivatives is used.

The cross-linking effect of bifunctional reagents and reagents with a larger number of functional groups is used for cellulose, poly(vinyl alcohol), and other polymers. As a result of these reactions, branching takes place initially and is followed by structure formation in polymers with different degrees of cross-linking, determined by the number of links between branching nodes (a), as shown below in Fig.6. Each branching node can then contain between three and eight and more branches (Fig.7).

In the limit the structured polymer has a molecular weight equal to that in the entire volume which it occupies. However, there is a possibility also of another type of structure formation, where the initial macromolecule contains in each unit a group capable of combining, as a result of the reaction, with one end of another macromolecule. A branched polymer, also occupying the entire space, is then formed. The structure of such a polymer branched to the maximum extent is illustrated in Fig.8. It is in essence a regularly grafted copolymer.

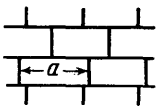


Figure 6. Schematic representation of a three-dimensional polymer.

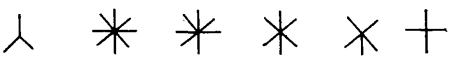


Figure 7. Schematic representation of the possible branching.

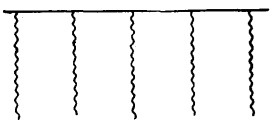


Figure 8. Schematic representation of a regularly branched polymer.

The data in Table 3 show that the structure formation reaction is used to modify different polymers as a procedure involving the conversion of linear polymers into three-dimensional structures. The cross-linked three-dimensional polymers formed are stronger, are insoluble, and exhibit a greater thermal stability than the initial linear polymer: this accounts for the wide-scale employment of this modification method, particularly in the rubber industry.

3. Polymer Modification Reactions Involving Degradation

Degradation is a process directly opposed to structure formation and is used to decrease the molecular weight of polymers. Degradation is widely used as a polymer modification method, particularly in the processing of natural polymers such as rubber and cellulose. With the aid of degradation by mechanochemical and oxidative methods, one obtains polymers with the optimum size of the macromolecules. Table 4 presents examples of certain polymer degradation reactions.

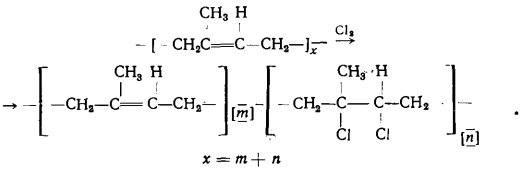
The degradation of carbochain polymers is carried out by a mechanical procedure (on rollers or other machines). In the case of cellulose oxidative degradation by atmospheric oxygen is used. In metathetical reactions in the presence of tungsten- or molybdenum-containing catalysts the carbon–carbon double bonds also become extremely labile and capable of degradative transformations[52].

The data in Table 4 show that hydrolysis, acidolysis, and aminolysis are widely used degradation reactions of heterochain polymers, which lead to the rupture of polar bonds such as ether, amide, acetal, etc. bonds.

4. Polymer Modification Reactions Involving Addition

Addition reactions are used as a procedure for the modification of polymers. When polymers contain multiple carbon–carbon bonds, halogens, oxidants, hydrogen, and other reagents can add to them. At the same time, there also exist metathetical reactions via the addition to carbon–carbon double bonds in unsaturated cyclo-olefins as well as the addition of epoxyalkanes to ester linkages.

As an example of the formation of a heterounit polymer, we may quote the rubber chlorination reaction:



$x = m + n$

An analogous process occurs in the synthesis of block copolymers from polyethers, having terminal hydroxy-groups, and di-isocyanates. In this case the addition involves the double bonds of the di-isocyanates.

Table 4. Examples of polymer modification reactions by degradation.

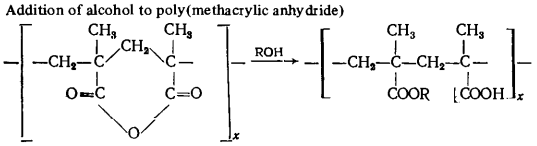
Name and equation of degradation reaction	Refs.
Mechanical degradation of polyethylene $-CH_2-CH_2-CH_2-CH_2-CH_2- \rightarrow -CH_2-CH_3+CH_2=CH-CH_2-$	91
Mechanical degradation of rubber $-[-CH_2-CH=CH-CH_2-]_x- \rightarrow -[-CH_2-CH=CH-CH_2-]_{x/n}-$	92
Oxidative degradation of cellulose $-[-C_6H_7O_2(OH)_3-]_x- \xrightarrow{O_2} -[-C_6H_7O_2(OH)_3-]_{x/n}-$	93
Acidolysis of polyesters $-R-COO-R'- \xrightarrow{R''COOH} -R-COOH+R''-COOR'-$	94
Acidolysis of polyamides $-R-CO-NH-R'- \xrightarrow{R''COOH} -R-COOH+R''-CONH-R'-$	95
Aminolysis of polyesters $-R-COO-R' \xrightarrow{R''NH_2} -R-CONH-R''+HOR'-$	94
Aminolysis of polyamides $-R-CONH-R'- \xrightarrow{R''NH_2} -R-CONHR''+H_2N-R'$	95
Esterolysis of polyesters $-R-COO-R'- \xrightarrow{R''-COO-R'''} -R-COO-R'''+R''-COO-R'-$	94
Hydrolysis of cellulose $-[-C_6H_7O_2(OH)_3-]_x- \xrightarrow{H_2O} -[-C_6H_7O_2(OH)_3-]_{x/n}-$	93
Hydrolysis of polyesters $-R-COO-R'- \xrightarrow{H_2O} -RCOOH + HOR'-$	94
Hydrolysis of polyamides $-R-CONH-R'- \xrightarrow{H_2O} -R-COOH + H_2N-R'-$	95
Depolymerisation of unsaturated polymers under the influence of catalysts of metathetical reactions $-[-CH_2-CH=CH-CH_2-CH_2-]_x \xrightarrow{WCl_6(CH_3)_2Si(CH_2)_2Si(CH_3)_2} \rightarrow -[-CH_2-CH=CH-CH_2-CH_2-]_{x/n}-$	52
Hydrolytic degradation of β-propiolactone copolymers $\ldots-CH_2-\underset{\displaystyle CH_2Cl}{\overset{\displaystyle CH_2Cl}{\overset{|}{C}}}-CH_2-OCH_2-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-(OCH_2-CH_2-\overset{\displaystyle O}{\overset{\|}{C}})_n-OCH_2-\ldots \xrightarrow{H_2O}$ $\rightarrow \ldots-CH_2-\underset{\displaystyle CH_2Cl}{\overset{\displaystyle CH_2Cl}{\overset{|}{C}}}-CH_2-OCH_2-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-OH+H[OCH_2CH_2COO]H+HOCH_2-\ldots$	96

Table 5 presents examples of different reactions involving addition to polymers. Polymers modified by the addition of halogens usually become more soluble and chemically stable. The data in Table 5 show that the addition of halogens, hydrogen, or oxygen to polymers having double bonds in the macromolecule is one of the most important modification methods. Such addition leads to heterounit polymers.

Table 5. Examples of polymer modification reactions by addition.

Name and equation of addition reaction	Refs.
Chlorination of rubber with elemental chlorine $-CH_2-CH=CH-CH_2- \xrightarrow{Cl_2} -CH_2-CHCl-CHCl-CH_2-$	53
Addition of epoxyalkanes to polyesters $-R-COO-R- \xrightarrow{H_2C-CHR'\ (O)} -R-CO-OCH_2-\underset{\displaystyle R'}{\overset{|}{C}}H-O-R-$	97
Addition of cyclo-olefins to polydienes in a metathetical reaction $-CH_2-CH=CH-CH_2- \xrightarrow{WCl_6(CH_3)_2Si(CH_2)_2Si(CH_3)_2} -CH_2-CH \underset{\displaystyle CH-(CH_2)_n}{\overset{\displaystyle \|}{\overset{\displaystyle \|}{CH}}} CH-CH_2-$ $-CH=CH-(CH_2)_n-$	98
Addition of trioxan to polydioxolan $-CH_2-O-CH_2-CH_2-O- \xrightarrow{(CH_2O)_3} (-CH_2O-)_4-CH_2-CH_2-O-$	99
Hydrogenation of polyphenylene-ethylene $-[-CH_2-CH_2-C_6H_4-]_x- \xrightarrow{H_2} -[-CH_2-CH_2-C_6H_{10}-]_x-$	100
Addition of di-isocyanates to polyesters $-COR'CO-ORO-H \xrightarrow{O=C=N-R''-N=C=O} -COR'C-ORO-CO-NHR''-NH-CO-ORO-COR'CO-$	101
Introduction of xanthate groups into cellulose by treatment with carbon disulphide $-[-C_6H_7OH)_2(ONa)-]- \xrightarrow{xCS_2} -\left[-C_6H_7O_2(OH)_2-OC(=S)SNa-\right]_x-$	102
Addition of cuoxam to cellulose $-[-C_6H_7O_2(OH)_3-]_x- \xrightarrow{[Cu(NH_3)_4(OH)_2]} -\left[-C_6H_7O_2-OH\rightarrow Cu^{2+}\leftarrow \begin{matrix} OH \\ OH \end{matrix}, \begin{matrix} NH_3 \\ NH_3 \end{matrix}\ 2HO^- -\right]_x-$	103
Quaternisation of poly-4-vinylpyridine by treatment with alkyl halides $-[-CH_2-CH(C_5H_4N)-]- \xrightarrow{RBr} -[-CH_2-CH(C_5H_4{}^+NRBr^-)-]-$	104
Epoxidation of polyisoprene by treatment with perbenzoic acid $-CH=C(CH_3)-CH_2- \xrightarrow{R-C(=O)-O-O-H} -CH(O)C(CH_3)-CH_2-$	105
Ozonisation of rubbers $-CH_2-CH=CH-CH_2- \xrightarrow{O_2} -CH_2-CH(O_2)-CH-CH_2-$	107

Table 5 (cont'd).

Name and equation of addition reaction	Refs.
Addition of alcohol to poly(methacrylic anhydride) 	108

The modification of heterochain polyesters by the addition of epoxyalkanes to the latter, which results in the formation of polyesters containing ether linkages, is very unusual[97]. The reactions involving the formation of various complexes of cellulose, polyhydrazides, and other polymers with different metals are very interesting. The ozonisation of rubbers, leading to the formation of unstable ozonides, is widely used in the analysis of rubbers.

Table 6. Examples of the modification of polymers by elimination reactions.

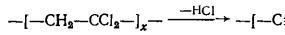
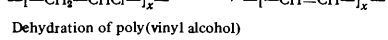
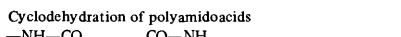
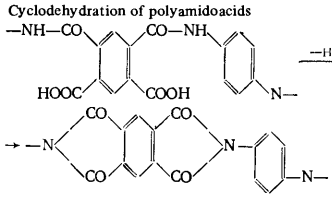
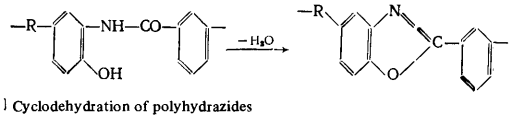
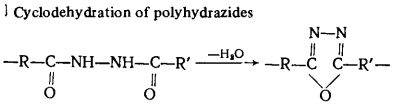
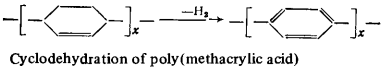
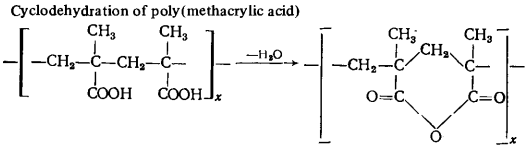
Name and equation of elimination reaction	Refs.
Dehydrochlorination of poly(vinylidene chloride) 	54
Dehydrochlorination of poly(vinyl chloride) 	106
Dehydration of poly(vinyl alcohol) 	42
Cyclodehydration of polyamidoacids 	107
Cyclodehydration of polyoxyamides 	108
Cyclodehydration of polyhydrazides 	109
Dehydrogenation of polycyclohexadiene 	110
Cyclodehydration of poly(methacrylic acid) 	111

Table 6 (cont'd).

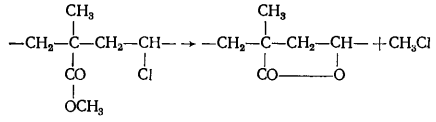
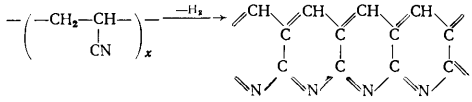
Name and equation of elimination reaction	Refs.
Thermolysis of methyl methacrylate–vinyl chloride copolymer 	112
Pyrolysis of polyacrylonitrile 	113
Pyrolysis of cellulose in order to obtain carbon and graphite fibre $-[-C_6H_7O_2(OH)_3-]_x- \xrightarrow{-H_2O} -[-C_6-]_x-$	114
Pyrolysis of phenol-formaldehyde polymer in order to obtain glassy carbon $-[-C_6H_3(OH)(CH_2)_2-]_x- \xrightarrow{-H_2O} -[-C_8-]_x-$	115

Table 7. Examples of isomerisation reactions of macromolecules.

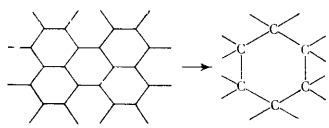
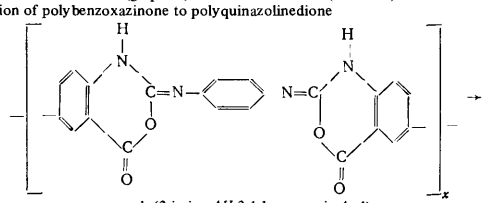
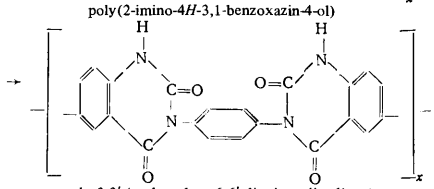
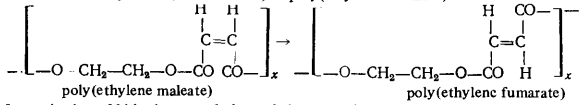
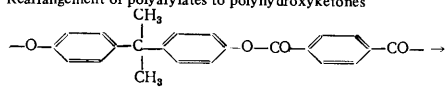
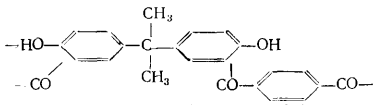
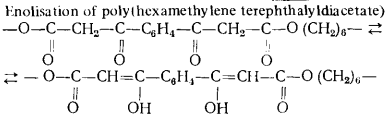
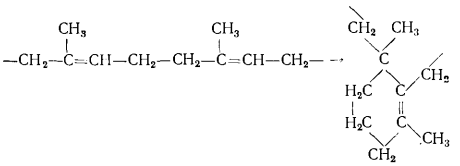
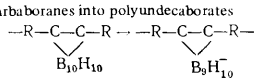
Name and equation of macromolecule isomerisation reaction	References
Isomerisation of α-carbyne to β-carbyne $-[-C\equiv C-C\equiv C-]_x \rightarrow =[=C=C=C=C=]_x=$ (α-carbyne) (β-carbyne)	55
Isomerisation of graphite to diamond  (graphite) (diamond)	116
Isomerisation of polybenzoxazinone to polyquinazolinedione  poly(2-imino-4*H*-3,1-benzoxazin-4-ol)  poly-3,3′-(*p*-phenylene-6,6′-diquinazolinedione)	117
Isomerisation of poly(alkylene maleate) to poly(alkylene fumarate)  poly(ethylene maleate) poly(ethylene fumarate)	118
Isomerisation of bishydroxymethyl-*o*-carbaborane polyesters to bishydroxymethyl-*m*-carbaborane polyesters $-OCRCO-OCH_2C(B_{10}H_{10})CCH_2- \longrightarrow -OCRCO-OCH_2CB_{10}H_{10}CCH_2O-$	119
Rearrangement of polyarylates to polyhydroxyketones 	120

Table 7 (cont'd).

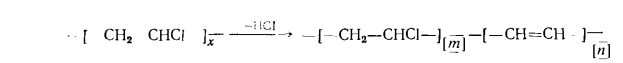
Name and equation of macromolecule isomerisation reaction	Refs.
 Enolisation of poly(hexamethylene terephthalyldiacetate) 	121
Cyclisation of rubber under the influence of acids 	122
Conversion of polycarbaboranes into polyundecaborates 	74

5. Polymer Modification Reactions Involving Elimination

The elimination of low-molecular-weight substances such as water, alcohols, hydrogen halides, etc. is one of the important polymer modification methods. As a result of the elimination of low-molecular-weight substances, a double or triple bond or even a heterocycle is formed in the macromolecule of the initial polymer.

All these reactions involving the elimination of low-molecular-weight substances are used to modify polymers, as shown in Table 6. According to the data in Table 6, the elimination of such low-molecular-weight substances results in the appearance of multiple bonds in the polymer chain or rings are produced.

As an example of a reaction leading to the formation of a heterounit polymer in such processes, we may quote the dehydrochlorination of poly(vinyl chloride):

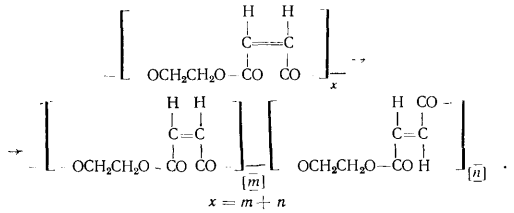


$x = m + n$

6. Polymer Modification Reactions Involving Isomerisation

In all the polymer modification reactions considered above, the composition of the resulting product differed from that of the initial polymer. The next group of polymer modification reactions involves isomerisation reactions which, in contrast to the previous ones, proceed without a change in the elemental composition of the polymer and consist in the rearrangement of the basic skeleton of the macromolecule. Isomerisation requires a vigorous treatment, such as heating, sometimes combined with a high pressure. Table 7 presents examples of polymer isomerisation reactions.

As an example of the formation of a heterounit polymer in isomerisation reactions, we shall consider a more detailed scheme for the transformation of poly(alkylene maleate) into poly(alkylene fumarate):

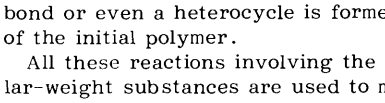
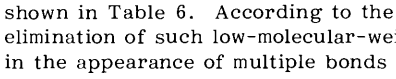
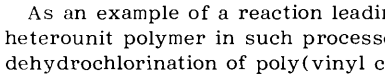
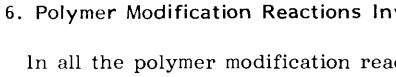
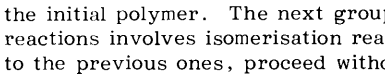


$x = m + n$

7. Polymer Modification Reactions Involving Exchange

All the modification methods examined previously led to the formation of polymers in which the structure of the initial polymer chain remained unaltered in most cases. In contrast to this, the next modification method, based on the use of exchange reactions between macromolecules, leads to the formation of a polymer containing the units of both initial polymers in the chain. The macromolecules of this polymer therefore constitute in essence a copolymer whose composition corresponds to that of the initial mixture of polymers. Consequently, this modification method also constitutes simultaneously an unusual copolymerisation method.

Table 8. Examples of the modification of polymers by exchange reactions between heterochain polymers.

Name and equation of exchange reaction	Refs.
Exchange reaction between heterochain polyesters 	56
Exchange reaction between heterochain polyamides 	124
Exchange reaction between heterochain polyesters and polyamides 	125
Exchange reaction between polysulphides	126
Synthesis of block copolymers by exchange reaction between heterochain polyamides	127
Formation of block copolymers by the polydisproportionation reaction (metathesis) 	128,129
Synthesis of deuterated polyesters by treating poly(ethylene sebacate) with diethyl 2,3-deuterosuccinate 	130

An important feature of this method is that heterochain polymers with fairly polar bonds between the units can be used as the starting materials for the reaction. On the other

hand, if heteroatoms are incorporated in the composition of the aromatic heterocycles, then polymers of this kind do no undergo exchange reactions[123]. It was believed previously that carbochain polymers are also unsuitable for these reactions, but it has now been established that the metathetical reaction makes it possible to carry out exchange reactions also between carbochain polymers[128,129]. Table 8 presents examples of the modification of polymers by exchange reactions between different polymers.

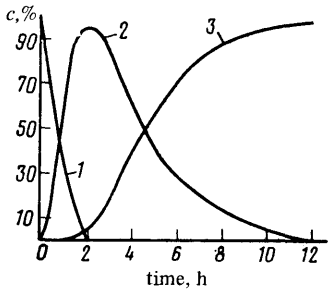


Figure 9. An exchange reaction between two polyamides. Variation of the contents (*c*) of homopolymers (curve *1*), block copolymers (curve *2*), and statistical copolymers (curve *3*).

An interesting feature of the exchange reactions is that after a time they lead to the formation of different products depending on the duration of the reaction.

Fig.9 shows which intermediates are formed in an exchange reaction between two polymers[127]. Evidently in the initial stage of the process there is a mixture of the two initial polyamides with an increasing admixture of a block copolymer. After 2 h, the final product is the block copolymer and then its content decreases and, when 12 h have elapsed, the only product becomes a statistical copolymer of the two initial diamine salts. Thus, by interrupting the process for any period at any stage, it is possible to obtain a large set of polymers of different structure and with different properties.

---o0o---

In conclusion we must consider the problem of the prospects for the development of polymer modification processes. We may note in the first place that the number of reactions used to modify polymers is increasing and that the relevant research is being presented on a rapidly widening front. Our knowledge of this field has now become much deeper and fairly clear ideas have been developed concerning the characteristics of the polymer modification processes and their specific features, due to the polymeric nature of the starting materials, have been established. The fundamental characteristics of these reactions, which determine the results of the substitution reaction, have been discovered. It has been established that the polymers obtained in modification reactions contain in their macromolecules anomalous units and are therefore of the heterounit type. A definite relation between the properties of heterounit polymers obtained by modification methods and their structure has been demonstrated.

REFERENCES

1. H.Braconnot, Ann.Pharm., **7**, 245 (1833); Ann.Chim. Phys., **52**, 290 (1833).
2. V.V.Korshak and N.M.Kozyreva, Uspekhi Khim., **48**, 5 (1979) [Russ.Chem.Rev., No.1 (1979)].
3. V.V.Korshak, "Raznozvennost' Polimerov" (The Heterounit Structure of Polymers), Izd.Nauka, Moscow, 1977, p.186.
4. N.A.Plate and A.D.Litmanovich, Vysokomol.Soed., **14A**, 2503 (1972).
5. N.A.Plate, A.D.Litmanovich, and O.V.Noa, "Makromolekulyarnye Reaktsii" (Macromolecular Reactions), Izd.Khimiya, Moscow, 1977, p.18.
6. A.B.Robertson and H.J.Harwood, Amer.Chem.Soc., Polymer Preprints, **12**, 620 (1971).
7. M.L.Bender and N.S.Neveu, J.Amer.Chem.Soc., **80**, 5388 (1958).
8. O.V.Noa and A.Ya.Temkin, Vysokomol.Soed., **11A**, 1689 (1969).
9. N.A.Plate, A.D.Litmanovich, O.V.Noa, and V.I.Golyakov, Vysokomol.Soed., **11A**, 2204 (1969).
10. N.A.Plate, A.D.Litmanovich, and O.V.Noa, "Makromolekulyarnye Reaktsii" (Macromolecular Reactions), Izd.Khimiya, Moscow, 1977, p.23.
11. H.Morawetz, in "Chemical Reactions of Polymers" (Edited by E.Fettes) (Translated into Russian), Izd. Mir, Moscow, 1968, Vol.1, pp.16, 46.
12. M.M.Van Beylen, in "The Stereochemistry of Macro-Molecules" (Edited by A.D.Ketley), M.Dekker, New York, 1967, Vol.3, p.333.
13. I.Sakurada, J.Sakaguchi, and Z.Shiiki, Chem.High Polymers (Japan), **21**, 241 (1964); Makromol.Chem., **78**, 239 (1964).
14. P.Flory, J.Amer.Chem.Soc., **61**, 1518 (1939).
15. A.Wielopolski, J.Krajewski, and J.Swierkot, Plaste und Kautschuk, **10**, 467 (1963).
16. L.B.Krentsel', A.D.Litmanovich, I.V.Pastukhova, and V.A.Agasandyan, Vysokomol.Soed., **A13**, 2489 (1971).
17. C.L.Arcus, J.Chem.Soc., 2732 (1949).
18. S.H.Pinner, J.Polymer Sci., **10**, 379 (1953).
19. N.A.Plate, A.D.Litmanovich, and O.V.Noa, "Makromolekulyarnye Reaktsii" (Macromolecular Reactions), Izd.Khimiya, Moscow, 1977, pp.26, 168.
20. A.I.Marei, Kauchuk i Rezina, No.7, 1 (1965).
21. N.A.Plate, A.D.Litmanovich, and O.V.Noa, "Makromolekulyarnye Reaktsii" (Macromolecular Reactions), Izd.Khimiya, Moscow, 1977, p.12.
22. A.Renfrew and P.Morgan, Polythene, Illiffe and Sons, London, 1957, p.567.
23. K.Matsuzaki, T.Uryu, and M.Okada, Makromol.Chem., **140**, 295 (1970).
24. J.Semen and J.B.Lando, Macromolecules, **2**, 570 (1969).
25. B.Philipp, Faserforsch.Textiltechn., **24**, 437 (1973).
26. V.Ya.Bytenskii, E.P.Kuznetsova, and N.I.Klenkova, Zhur.Prikl.Khim., **39**, 185 (1966).
27. N.G.Gaylord, J.Polymer Sci., **C**, No.24, 1 (1968).
28. D.A.Ravens, Polymers, **1**, 375 (1960).
29. R.V.Dzhagatspanyan, V.I.Kolbasov, S.B.Bardenshtein, V.M.Korolev, I.A.Romanskii, and V.I.Zetkin, Vysokomol.Soed., **7**, 1959 (1965).
30. F.H.Winslow and W.Matreyek, Amer.Chem.Soc.Polymer Preprints, **3**, 229 (1962).
31. V.V.Korshak, K.K.Mozgova, and M.A.Shkolina, Vysokomol.Soed., **1**, 1573 (1959).
32. V.V.Korshak, G.L.Berestneva, S.A.Astaf'ev, A.Zh.Taova, and E.P.Churkova, Dokl.Akad.Nauk SSSR, **245**, 1118 (1979).

33. K.Konishi, K.Yamaguchi, and M.Takehisa, J.Appl. Polymer Science, **15**, 257 (1972).
34. Z.A.Rogovin, "Khimiya Tsellyulozy" (The Chemistry of Cellulose), Izd.Khimiya, Moscow, 1972, pp.248, 379.
35. H.J.Bär, H.Dautzenberg, and B.Philipp, Faserforsch. Textiltechn., **17**, 551 (1966).
36. B.Philipp and K.-T.Liu, Faserforsch.Textiltechn., **10**, 555 (1959).
37. D.C.Bassett, Polymer (London), **5**, 457 (1964).
38. B.Helferich and H.Koester, Ber., **57**, 587 (1924).
39. V.V.Korshak, G.L.Berestneva, and I.P.Bragina, Vysokomol.Soed., **16A**, 1036 (1972).
40. V.Ya.Bytenskii, E.P.Kuznetsova, and N.I.Klenkova, Zhur.Prikl.Khim., **39**, 188 (1966).
41. K.-H.Hampe, B.Philipp, and J.Bandisch, Faserforsch. Textiltechn., **23**, 425 (1972).
42. V.V.Korshak and V.A.Zamyatina, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 106 (1946).
43. R.Gebraux, Bull.Soc.chim.Belges, **65**, 270 (1956); **66**, 382 (1957).
44. Z.A.Rogovin and N.N.Shorygina, "Khimiya Tsellyulozy i Ee Sputnikov" (The Chemistry of Cellulose and Related Substances), Goskhimizdat, Moscow–Leningrad, 1953, p.419.
45. V.V.Korshak, "Reznozvennost' Polimerov" (The Heterounit Structure of Polymers), Izd.Nauka, Moscow, 1977.
46. V.V.Korshak, Uspekhi Khim., **42**, 695 (1973) [Russ. Chem.Rev., No.4 (1973)].
47. V.V.Korshak, "Polikondensatsionnye Protsessy" (Polycondensation Processes), Sofia, 1976, p.28.
48. V.V.Korshak, "Tezisy Dokladov III Mezhdunarodnogo Mikrosimpoziuma po Polikondensatsii" (Abstracts of Reports at the IIIrd International Microsymposium on Polycondensation), Izd.Naukova Dumka, Kiev, 1971, p.18.
49. V.V.Korshak, "Ravnozvennost' Polimerov" (The Heterounit Structure of Polymers), Izd.Nauka, Moscow, 1977, p.12.
50. V.V.Korshak, Vysokomol.Soed., **19A**, 1179 (1977).
51. M.Dole, D.C.Milner, and T.F.Williams, J.Amer.Chem. Soc., **79**, 4809 (1957).
52. Yu.V.Korshak, Al.Al.Berlin, E.R.Badamshina, G.I.Timofeeva, and S.A.Pavlova, Dokl.Akad.Nauk SSSR, **248**, 372 (1979).
53. G.A.Engelhard and H.H.Day, B.P.2734 (1859).
54. Yu.P.Kudryavtseva, A.M.Sladkov, Yu.T.Aseev, Yu.N.Nedoshivin, V.I.Kasatochkin, and V.V.Korshak, Dokl.Akad.Nauk SSSR, **158**, 389 (1964).
55. V.V.Korshak, A.M.Sladkov, Yu.P.Kudryavtseva, and V.I.Kasatochkin, Vestnik Akad.Nauk SSSR, No.9, 89 (1968).
56. P.J.Flory, J.Amer.Chem.Soc., **64**, 2205 (1942).
57. M.P.Schützenberger, Compt.rend., **261**, 2419 (1965).
58. V.V.Korshak and V.A.Zamyatina, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 111 (1946).
59. A.Weihe, Kunststoffe, **31**, 52 (1941).
60. G.Frank and H.-E.Krüger, German P.537 303 (1929).
61. French P.755 048 (1933); Chem.Zbl., **105**, I, 2204 (1934).
62. M.A.Smook, E.T.Pieski, and C.F.Hammer, Ind.Eng. Chem., **45**, 2731 (1953).
63. G.B.Bachmann, H.Hellman, K.R.Robinson, R.W.Tinholt, E.I.Kahler, L.I.Filar, L.V.Heisey, L.L.Lewis, and D.D.Micucci, J.Org.Chem., **12**, 108 (1947).
64. R.C.Fuson and C.H.McKeever, Org.Reactions, 1, 63 (1942).
65. A.McAlevy, US P.240 597 (1946); Chem.Abs., **40**, 7702 (1946).
66. R.C.Houtz and H.Adkins, J.Amer.Chem.Soc., **55**, 1609 (1933).
67. V.V.Korshak, K.K.Mozgova, and Yu.V.Egorova, Vysokomol.Soed., **6**, 571 (1964).
68. S.R.Rafikov, G.N.Chelnokova, and P.N.Gribkova, Vysokomol.Soed., **1**, 378 (1959).
69. H.Staudinger and E.Frommsdorff, Ann., **502**, 201 (1933).
70. W.O.Herrmann and W.Haehnel, Ber., **60**, 1658 (1927).
71. G.W.Miles, US P.733 729 (1903).
72. L.G.Grigor'eva, V.A.Sergeev, V.K.Shitikov, and V.V.Korshak, Izv.Akad.Nauk SSSR, Ser.Khim., 1488 (1973).
73. G.D.Jones, Ind.Eng.Chem., **44**, 2686 (1952).
74. V.V.Korshak, V.G.Danilov, L.G.Komarova, N.I.Bekasova, and L.A.Leites, Vysokomol.Soed., **13A**, 1517 (1971).
75. K.A.Andrianov, Dokl.Akad.Nauk SSSR, **140**, 1310 (1961).
76. I.W.Fischer, E.W.Wheatly, and H.Batles, J.Appl. Chem., **4**, 212 (1954).
77. A.V.D'yachenko, V.V.Korshak, and E.S.Krongauz, Vysokomol.Soed., **9**, 2231 (1967).
78. V.Frillet, J.Hanley, and H.Mark, J.Amer.Chem.Soc., **70**, 1107 (1948).
79. S.S.Ivanchev, T.A.Tolpygina, A.I.Prisashnyuk, and V.I.Galibei, Vysokomol.Soed., **70**, 1107 (1948).
80. B.A.Dogadkin, "Khimiya i Fizika Kauchuka" (The Chemistry and Physics of Raw Rubber), Goskhimizdat, Moscow–Leningrad, 1947, p.13.
81. I.I.Ostromyslenskii, Zhur.Russ.Fiz.Khim.Obshch., **47**, 1467 (1915); Indian Rubber J., **52**, 470 (1916).
82. A.Charlesby, Proc.Roy.Soc.London, Ser.A, **215**, 187 (1952).
83. V.V.Korshak, "Khimicheskoe Stroenie i Temperaturnye Kharakteristiki Polimerov" (The Chemical Structure and Temperature Characteristics of Polymers), Izd.Nauka, Moscow, 1970, p.165.
84. V.V.Korshak, "Khimicheskoe Stroenie i Temperaturnye Kharakteristiki Polimerov" (The Chemical Structure and Temperature Characteristics of Polymers), Izd.Nauka, Moscow, 1970, pp.167, 168.
85. P.P.Shorygin and Yu.A.Rymashevskaya, Zhur.Obshch. Khim., 7, 2428 (1937).
86. I.Sakurada, Kobunshi-Tenbo, **6**, 59 (1952).
87. B.T.Hayes, W.J.Read, and L.H.Vaughan, Chem.Ind. (London), 1162 (1957).
88. R.H.Kienle, P.A.Van der Meulen, and F.E.Perke, J.Amer.Chem.Soc., **61**, 2258 (1939).
89. A.H.Frazer, W.Sweeny, and F.T.Wallenberger, J.Polymer Sci., **A2**, 1157 (1964).
90. V.V.Korshak, Vysokomol.Soed., **A16**, 926 (1974).
91. V.A.Zakrevskii and V.E.Korsukov, Vysokomol.Soed., **14A**, 955 (1972).
92. D.B.Porrit, Trans.Faraday Soc., **16**, 81 (1921).
93. Z.A.Rogovin, "Khimiya Tsellyulozy" (The Chemistry of Cellulose), Izd.Khimiya, Moscow, 1972, p.157.
94. V.V.Korshak and S.V.Vinogradova, "Geterotsepnye Poliefiry" (Heterochain Polyesters), Izd.Akad.Nauk SSSR, Moscow, 1958, p.212.
95. V.V.Korshak and T.M.Frunze, "Sinteticheskie Geterotsepnye Poliamidy" (Synthetic Heterochain Polyamides), Izd.Akad.Nauk SSSR, Moscow, 1962, p.260.
96. K.Tada, T.Saegusa, and J.Furukawa, J.Makromol. Chem., **71**, 71 (1964).

97. L.I.Komarova, S.N.Salazkin, V.V.Korshak, S.V.Vinogradova, V.I.Nokolaichik, E.E.Zaborovskaya, and I.A.Bulgakova, Vysokomol.Soed., **16B**, 718 (1974).
98. L.M.Vardanyan, Candidate's Thesis, INKhS, USSR Academy of Sciences, Moscow, 1973.
99. N.Grassie, "Chemistry of High Polymer Degradation Processes", Butterworths, New York, 1958.
100. V.V.Korshak and G.S.Kolesnikov, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 1090 (1955).
101. O.Bayer, Angew.Chem., **A59**, 257 (1947).
102. C.F.Gross, E.J.Bevan, and C.Beadle, B.P.8700 (1892); Chem.Ber., **26**, 1090 (1893).
103. Z.A.Rogovin, "Khimiya Tsellyulozy" (The Chemistry of Cellulose), Izd.Khimiya, Moscow, 1972, p.145.
104. B.D.Coleman and R.M.Fuoss, J.Amer.Chem.Soc., **77**, 5472 (1955).
105. I.A.Tutorskii, I.D.Khodzhaeva, and B.A.Dogadkin, Vysokomol.Soed., **16A**, 157 (1974).
106. A.H.Frazer and F.T.Wallenberger, J.Polymer Sci., **A2**, 1137 (1964).
107. W.M.Edwards and A.L.Endrey, B.P.903 271 (1960); Chem.Abs., **58**, 3520 (1963).
108. V.V.Korshak, G.M.Tseitlin, and A.A.Izyneev, USSR P.170 659 (1964); Byul.Izobret., No.9, 76 (1965).
109. A.H.Frazer and E.T.Wallenberger, J.Polymer Sci., **A2**, 1137 (1964).
110. C.S.Marvel and G.E.Hartzell, J.Amer.Chem.Soc., **81**, 448 (1959).
111. S.E.Bresler, M.M.Koton, A.T.Os'minskaya, A.T.Popov, and M.I.Savitskaya, Vysokomol.Soed., **1**, 1070 (1959).
112. N.W.Johnston and H.J.Harwood, J.Polymer Sci., C, 591 (1969).
113. R.C.Houtz, Text.Res.J., **20**, 786 (1950).
114. J.Electroch.Soc., **106**, 147C (1959); Industrial Heating, 2111 (1959).
115. S.Iamoda and H.Sato, Nature, **193**, 261 (1962).
116. R.Berman and J.Thewlis, Nature, **176**, 834 (1955).
117. N.Joda, M.Kurihara, S.Tohyama, and N.Nakanichi, J.Polymer Sci., **B4**, 551 (1966).
118. H.Batzer and B.Mohr, Makromol.Chem., **8**, 217 (1952).
119. V.A.Zamyatina, Doctoral Thesis, Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow, 1970.
120. V.V.Korshak, S.V.Vinogradova, and S.A.Siling, Vysokomol.Soed., **8**, 1608 (1966).
121. N.A.Plate, V.A.Barbanova, and S.L.Davydova, Vysokomol.Soed., **10A**, 1004 (1968).
122. Leonhardi, "Chemisches Warterbuch oder allgemeine Beigruppe der Chemie", Leipzig, 1781, p.27.
123. V.V.Korshak, G.N.Chelnokova, and M.A.Shkolina, Vysokomol.Soed., **1**, 1772 (1959).
124. V.V.Korshak and T.M.Frunze, Dokl.Akad.Nauk SSSR, **97**, 675 (1954).
125. V.V.Korshak, S.V.Vinogradova, M.M.Teplyakov, and Yu.A.Chernomordik, Dokl.Akad.Nauk SSSR, **147**, 1365 (1962).
126. E.R.Bertozzi, F.O.Davis, and E.M.Fettes, J.Polymer Sci., **19**, 17 (1956).
127. V.V.Korshak, T.M.Frunze, and I-Nan Lu, Vysokomol. Soed., **2**, 984 (1960).
128. Yu.V.Korshak, G.N.Bondarenko, V.M.Kuteinikov, and B.A.Dolgoplosk, Dokl.Akad.Nauk SSSR, **227**, 1383 (1976).
129. A.M.Vardanyan, Yu.V.Korshak, and B.A.Dolgoplosk, Vysokomol.Soed., **15B**, 268 (1973).
130. D.N.Kursanov, V.V.Korshak, and S.V.Vinogradova, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 217 (1958).

Institute of Organoelemental Compounds,
USSR Academy of Sciences, Moscow

Translated from *Uspekhi Khimii*, 49, 2314-2343 (1980) U.D.C. 678.84.765:54.07.09(047)

Advances in the Chemistry of Compounds with the Cyclodisilazane Structure

D.Ya.Zhinkin (deceased), Yu.M.Varezhkin, and M.M.Morgunova

Data on the monomeric four-membered cyclic silazane systems are surveyed and arranged systematically. The available methods for the synthesis of these compounds are examined in detail, the results of studies on the mechanism of the formation of organocyclodisilazanes are described, and the mechanisms of individual stages of this process are considered. The review includes an exhaustive bibliography on monomeric organocyclodisilazane compounds up to 1978, comprising 116 references.

CONTENTS

I. Introduction 1149
II. Fundamentals of the nomenclature and certain characteristics of organocyclodisilazane compounds 1149
III. Synthesis of organocyclodisilazanes 1150

I. INTRODUCTION

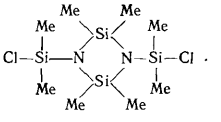
Studies in the field of organosilicon compounds containing a silicon–nitrogen bond have developed particularly vigorously in the last two decades. During this period, it has been shown that such compounds are of great theoretical interest and can be of practical importance as valuable heat-resistant materials capable of being used at high temperatures and exhibiting high thermal and chemical stabilities, great mechanical strength, and effective electrical insulating, semiconducting, and other valuable properties; in addition, they can be hardened at room temperature and exhibit an effective adhesion to various materials.

The principal trend in the development of the chemistry of compounds containing the ≡Si—Ni= bond has been until recently the synthesis of open-chain silazanes and silylamines and the study of their properties. However, nowadays cyclic compounds with the silazane structure, particularly four-membered cyclic silazane systems—cyclodisilazanes and polymers with alternating units comprising such systems—have attracted increasing attention. Studies in recent years on the properties and practical applications of four-membered cyclic silazane systems have shown that such compounds have a striking thermal stability.

Until now, there have been no reviews on monomeric four-membered cyclodisilazane systems. Isolated information about the methods of synthesis and chemical properties of these compounds can be found in a few publications[1-4]. This review surveys the published literature data on the synthesis of monomeric four-membered cyclic silazane systems.

II. FUNDAMENTALS OF THE NOMENCLATURE AND CERTAIN CHARACTERISTICS OF ORGANOCYCLODISILAZANE COMPOUNDS

In the literature there is no clear-cut system of nomenclature for four-membered cyclic silazane systems, but the majority of authors adhere to the following methods for the naming of such substances, which can be illustrated in relation to the compound.



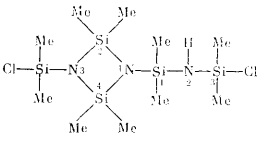
(1) *N,N'*-bis(chlorodimethylsilyl)tetramethylcyclodisilazane;

(2) 1,3-bis(dimethylchlorosilyl)-2,2,4,4-tetramethylcyclodisilazane;

(3) 1,3-bis(dimethylchlorosilyl)-2,2,4,4-tetramethyl-1,3,2,4-diazadisiletidine;

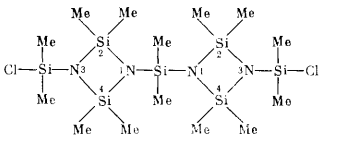
(4) 1,3-bisdimethylchlorosilyl-1,3-diaza-2,2,4,4-tetramethylcyclodisilazane.

Nomenclatures (1) and (2) are most widely used. From our point of view, the second system is most convenient as regards simplicity and yields the maximum information about the structure of the compound and will in fact be used in this review. An advantage of this system is its universality and rationality. The names of compounds containing a single cyclodisilazane ring are derived from the name of this ring; for example,



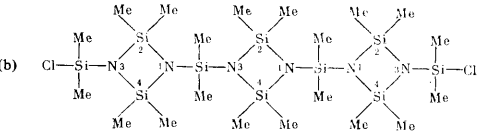
is 1-(1,1,3,3-tetramethyl-3-chlorodisilazanyl)-2,2,4,4-tetramethyl-3-dimethylchlorosilylcyclodisilazane.

The names of cyclodisilazane oligomers containing repeating cyclodisilazane fragments are constructed on the basis of the "central symmetry" rule; for example, in case (a) the dimethylsilyl unit is central and two similar cyclodisilazane fragments are located symmetrically relative to it, so that this unit is adopted as the basis for the name:

(a) 

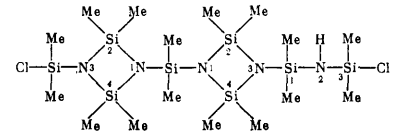
is dimethylbis(2,2,4,4-tetramethyl-3-dimethylchlorosilyl-1-cyclodisilazanyl)silane.

In case (b) the name is based on the cyclodisilazane ring, which is the centre of the oligomer molecule:

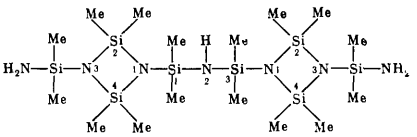
(b) 

is 1,3-bis[dimethyl(2,2,4,4-tetramethyl-3-dimethylchlorosilylcyclodisilazanyl)silyl]-2,2,4,4-tetramethylcyclodisilazane.

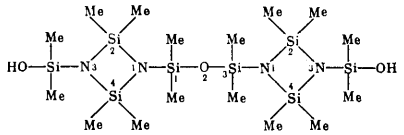
In all the remaining cases the molecular fragment most convenient for the construction of the name is adopted as central—the dimethylsilyl unit for (c), the disilazane unit for (d), and the disiloxane unit for (e):

(c) 

is dimethyl(2,2,4,4-tetramethyl-3-dimethylchlorosilyl-1-cyclodisilazanyl)-[2,2,4,4-tetramethyl-3-(1,1,3,3-tetramethyl-3-chlorodisilazanyl)-1-cyclodisilazanyl]silane.

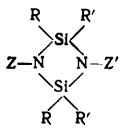
(d) 

is 1,1,3,3-tetramethyl-1,3-bis(2,2,4,4-tetramethyl-3-aminodimethylsilyl-1-cyclodisilazanyl)disilazane.

(e) 

is 1,1,3,3-tetramethyl-1,3-bis(2,2,4,4-tetramethyl-3-hydroxydimethylsilyl-1-cyclodisilazanyl)disiloxane.

All the known monomeric four-membered cyclic silazane systems can be divided into three groups:

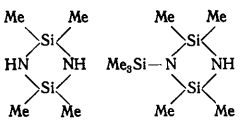


(1) Symmetrical or asymmetric 1,3-bis(organo)-substituted cyclodisilazanes (Z and Z′ are organic groups of H);

(2) symmetrical or asymmetric 1,3-bis(silyl)-substituted cyclodisilazanes (Z and Z′ $=SiR''_3$ or SiR''_nHal_{3-n}, where R″ is an organic group or H and Hal is a halogen atom);

(3) asymmetric 1,3-substituted cyclodisilazanes (one of the substituents is an organic group and the other is a triorganosilyl, diorganohalogenosilyl, organodihalogenosilyl, or trihalogenosilyl group).

2,2,4,4-Tetramethylcyclodisilazane[5] and 1-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane[6] can be quoted as the simplest representatives of the series of organocyclodisilazanes containing hydrogen atoms at the endocyclic nitrogen atoms and methyl groups at the silicon atoms:



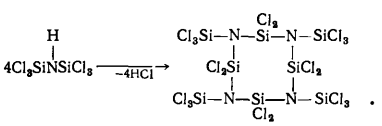
1,3-Bis(silyl)-substituted organocyclodisilazanes are thermally and hydrolytically stable; these compounds are fairly reactive via their functional groups, which makes it possible to obtain oligomeric and polymeric products based on them.

The high thermal and hydrolytic stability of 1,3-bis(silyl)-substituted organocyclodisilazanes can be accounted for by a number of factors. An increase of the electronegativity of the substituents at the nitrogen or silicon atoms (H, Me, $SiMe_3$, Ph) causes a corresponding decrease of electron density at this atom and an increase of the hydrolytic stability of the endocyclic silicon–nitrogen bond[1,7]. The p_π–d_π interaction of the exocyclic organosilyl groups with an endocyclic nitrogen atom reduces the electron density at the nitrogen atom with a simultaneous increase of electron density at the exocyclic silicon atoms, which leads to an increase of the thermal and hydrolytic stability of 1,3-bis(silyl)-substituted organocyclodisilazanes[8,9].

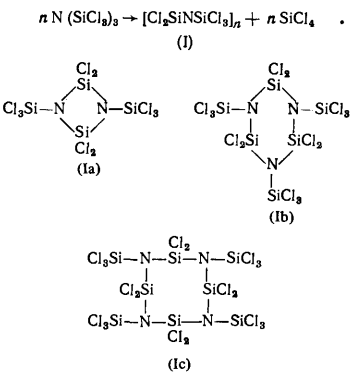
The high degree of hyperconjugation in the ring, which is characteristic of four-membered cyclic silazane systems and leads to a change in bond lengths, a deformation of angles[1,10], and a decrease of the basicity of the endocyclic nitrogen[6], determines to a significant extent the reactivity and physical properties of organocyclodisilazanes[11]. Thus, the high degree of conjugation in the 1-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane ring leads to an increase of the acidity of the protons at the nitrogen atoms and to a corresponding increase of the reactivity of this compound[6]. On the other hand, the electronic nature of the substituents at the nitrogen atom also affects the properties of the compounds. Thus the temperature range of the decomposition is 450–500 °C for cyclodisilazanes with organosilyl groups at a nitrogen atom, 400–450 °C for cyclodisilazanes with organic substituents, and 320–360 °C for hexaorganocyclotrisilazanes[11,12].

III. SYNTHESIS OF ORGANOCYCLODISILAZANES

For a long time the existence of four-membered cyclic silazane compounds with alternating silicon–nitrogen bonds gave rise to doubts. Thus in 1953 a new compound was obtained by the condensation of hexachlorodisilazane, for which the authors suggested the cyclotetrasilazane structure[13]:



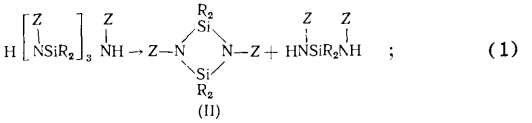
Somewhat later an analogous cyclic perchlorosilazane was obtained by a different procedure[14]—the condensation of tris(trichlorosilyl)amine (isolated from the product of the pyrolysis of the $SiCl_4/N_2$ mixture), for which the authors proposed structures (Ia), (Ib), and (Ic):



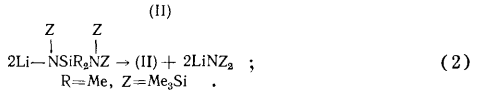
But the authors[14] gave preference to the cyclotetrasilazane structure (Ic) for their compound, having excluded the four-membered system (Ia) in view of the expected high ring strain. However, in 1958 it was demonstrated for the first time that the compound had in fact the cyclodisilazane structure[15].

1. N-Alkyl-, N-Trialkylsilyl, and N-Aryl-substituted Organocyclodisilazanes

1,3-Bis(trimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (II) was obtained by the thermolysis of long-chain or metallated silazanes[16,17] via reactions (1) and (2):



(1)

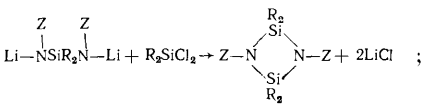


(2)

Compound (II) can also be obtained by the thermolysis of *N*-trimethylsilylated cyclotri- and cyclotetra-silazanes; compound (III, R = Z = Me), having an analogous structure, is obtained by the thermolysis of permethylated cyclosilazanes[18,19].

The structure of four-membered silazane systems was established by X-ray diffraction[10] and by specific synthesis[1].

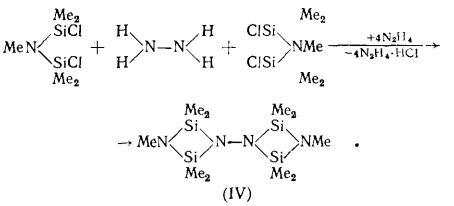
1,3-Bis(trimethylsilylated) organocyclodisilazanes can be obtained in high yields by the reaction of doubly metallated octamethyltrisilazane with organodichloro- and organotrichloro-silanes or with silicon tetrachloride[16,18]. Cyclodisilazanes (II) and (III) with methyl substituents at a nitrogen atom were obtained similarly from the doubly metallated bis(methylamino)dimethylsilane[20,21]:



(II): R = Me, Z = Me_3Si;

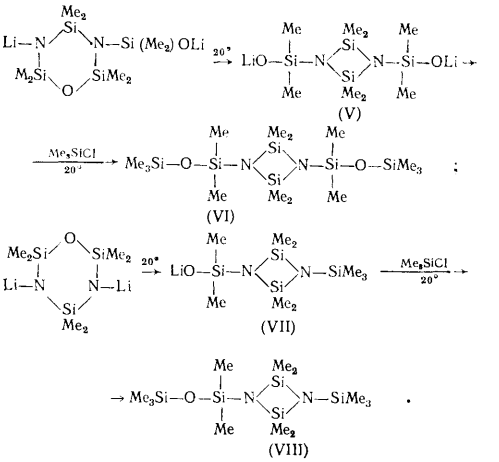
(III): R = Z = Me .

The interesting *N*-methyl-substituted biscyclodisilazane (IV) was obtained by the reaction of 1,3-dichloropentamethyldisilazane with hydrazine[22]:



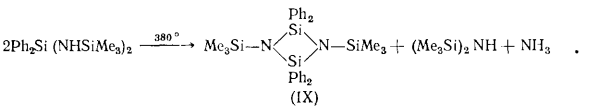
(IV)

Symmetrical and asymmetric *O*-lithiocyclodisilazanes (V) and (VII) have been isolated after condensing six-membered *N*-lithio-organocyclosiloxazanes at room temperature and their subsequent treatment with trimethylchlorosilane yielded *N*-substituted organocyclodisilazanes (VI) and (VIII):[23,24]



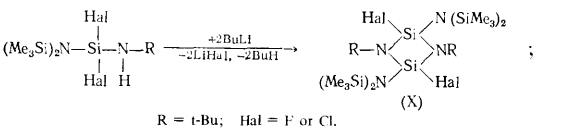
(V), (VI), (VII), (VIII)

Organoaminosilanes containing phenyl groups linked to the silicon atom cyclise on thermal condensation to form 1,3-bis-(trimethylsilyl)phenylcyclodisilazanes. Thermal condensation of *N,N'*-bis(trimethylsilylamino)diphenylsilane leads to the formation of 1,3-bis(trimethylsilyl)-2,2,4,4-tetraphenylcyclodisilazane (IX):[25,26]



(IX)

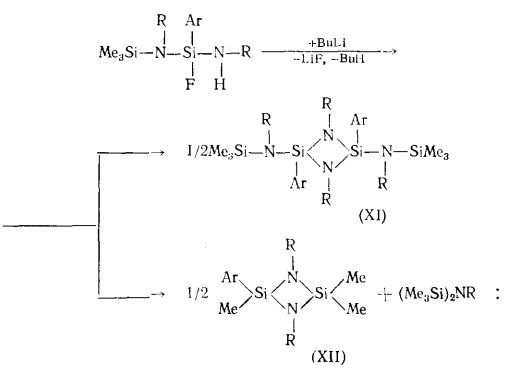
Symmetrical organocyclodisilazanes containing fluorine or chlorine atoms or amino-groups attached to a silicon atom have been obtained[27,28]:



(X)

R = t-Bu; Hal = F or Cl.

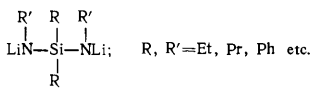
This reaction proceeds fairly smoothly when alkylaminobis(trimethylsilyl)aminodifluorosilane is used but, when one fluorine atom at a silicon atom is replaced by an aryl residue and the trimethylsilyl group is replaced by the t-butyl group, the symmetric cyclodisilazane (XII) is formed instead of the symmetrical compound (XI);[27] as a result of steric hindrance, a 1,3-rearrangement of the Me anions at the silicon atoms with subsequent cyclisation takes place instead of the expected cyclodimerisation:



(XI), (XII)

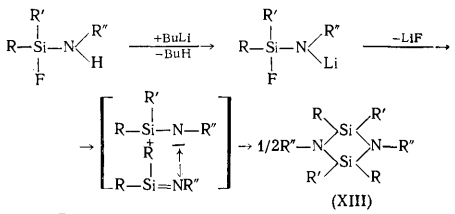
R = t-Bu .

Other *N*-alkylated and *N*-arylated cyclodisilazanes (see Table 1 below) have been obtained analogously from dilithio-derivatives of the corresponding silylamines[29–34]:



R, R′=Et, Pr, Ph etc.

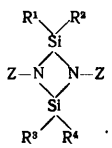
or by the reaction of aminofluorosilanes with butyl-lithium[35]:



(XIII)

R = Me or Ph; R′=Me, *s*-Bu, or Ph; R″ = iso-Pr, t-Bu, -Bu, 2, 4, 6-$Me_3C_6H_2$

Table 1. Symmetrical *N*-substituted organocyclodisilazanes



Z	R^1	R^2	R^3	R^4	B.p., °C/mmHg	M.p., °C	n_D^{20}	d_4^{20}	References*
Cl_3Si	Cl	Cl	Cl	Cl	83–85/0.01	66	—	—	14,15,106,108
Me_3Si	Me	Me	Me	Me	85/7	39	1.4237 (45°)	0.998	16,18,19,66,76
Me_3Si	Et	Me	Et	Me	74/0.9	—	1.4502	—	16
Me_3Si	Et	Et	Et	Et	80—82/0.9	—		—	16
Me_3Si	Me	Me	Ph	H	147/5	—	1.4794	—	116
Me_3Si	Me	Me	Ph	Ph	120/0.03	52	—	—	51
Me_3Si	Ph	Ph	Ph	Ph	—	256—257	—	—	25
Me_3Si	Me	Me	Cl	Cl	118/21	28	1.4360 (45°)	—	16
Me_3Si	Me	Me	EtO	EtO	79.5/1.5	—	1.4312	—	16
$n\text{-}Bu_3Si$	Ph	Ph	Ph	Ph	240—242/0.04	111	—	—	51
$ClMe_2Si$	Me	Me	Me	Me	64/0.08	68—69	—	—	21,76,77,79,80, 82,84,99,111,112
$ClMe_2Si$	Me	Me	Ph	Cl	170/12	—	1.5046	—	26
Cl_2PhSi	Me	Me	Me	Me	225/12	102	—	—	26
$EtOMe_2Si$	Me	Me	Me	Me	115—116/18	—	1.4332	—	76
$(MeO)_3Si$	MeO	MeO	MeO	MeO	127—129/2	—41	1.4187	1.1721	108
$(EtO)_3Si$	EtO	EtO	EtO	EtO	142/2	21	1.4180	1.0388	108
$(MeNH)_3Si$	MeNH	MeNH	MeNH	MeNH	70/0.01 (subl.)	83	—	—	108
$(Me_2N)_3Si$	Me_2N	Me_2N	Me_2N	Cl	185—195/0.1	103—106	—	—	108
$Cl(Et_2N)_2Si$	Et_2N	Cl	Et_2N	Cl	215—220/0.1		1.4961	1.1263	108
$Me_3SiO(Me_2)Si$	Me	Me	Me	Me	80/0.25	—	—	—	23
H	Me	Ph	Ph	Ph	—	65	—	—	72,73
H	Ph	Ph	Ph	Ph	—	206	—	—	72,73
H	Me_3SiO	Me_3SiO	Me_3SiO	Me_3SiO	180—183/4	103—104	—	—	74,75
H	Et_3SiO	Et_3SiO	Et_3SiO	Et_3SiO	—	186	—	—	75
H	Me_3SiNH	Me_3SiNH	Me_3SiNH	n-BuNH	153—155/1.5	—	—	—	25
Me	Me	Me	Me	Me	52/51	17	1.4210	0.8403 (23°)	20,21
Me	Me	Me	Me	Ph	69—71/3	—	1.4932	—	20,21
Me	Me	Me	Ph	Ph	144/4	—	1.5460	1.0234 (24°)	20,21
Me	Et	Et	Et	Et	115—120/0.01	95	—	—	31
Me	Ph	Ph	Ph	Ph	262	95	—	—	44
Et	Me	Me	Me	Me	98—98.5/82	—	1.4250	—	29
Et	Ph	Ph	Ph	Ph	—	195—196	—	—	29
Et	CH_2=CH	Et	CH_2=CH	Et	54/0.05	—	1.4638	—	51
Et	CH_2=$CHCH_2$	CH_2=$CHCH_2$	CH_2=$CHCH_2$	CH_2=$CHCH_2$	90/0.02	—	1.4877	—	51
Et	CH_2=CH	CH_2=CH	CH_2=CH	CH_2=CH	100/12	—	1.4745	—	44
iso-Pr	Me	Ph	Me	Ph	—	23—25	—	—	35
iso-Pr	Ph	Ph	Ph	Ph	—	181—184	—	—	35
n-Bu	Me	Me	Me	Me	89/6	—	1.4367	—	51
n-Bu	Me	Ph	Me	Ph	220—225/2	—	1.5460	1.0280	57
n-Bu	n-BuNH	n-BuNH	n-BuNH	n-BuNH	190/1	—	1.4640	—	48
t-Bu	Me	Me	Me	Me	100/12	35	1.4450	—	51
t-Bu	Me	s-Bu	Me	s-Bu	91/0.01	—	—	—	35
t-Bu	Me	Ph	Me	Me	—	57	—	—	27
t-Bu	F	$(Me_2Si)_2N$	F	$(Me_3Si)_2N$	—	204	—	—	27
t-Bu	Cl	Me	Cl	Me	—	68	—	—	28
CH_2=$CHCH_2$	Me	Me	Me	Me	74/11	—	—	—	51
CH_2=$CHCH_2$	Ph	Ph	Ph	Ph	—	167	—	—	51
n-C_7H_{15}	Me	Me	Me	Me	123/0.01	105	—	—	29
n-$C_{12}H_{25}$	Ph	Ph	Ph	Ph	300/0.05	—	—	—	51
Ph	Me	Me	Cl	Cl	210/720 (subl.)	210—215	—	—	29
Ph	Me	Me	Me	Cl	—	243—245	—	—	29,30
Ph	Me	H	Me	H	193/0.05	91	—	—	1
Ph	Me	Me	Me	Me	—	252.5	—	—	29
Ph	Me	Me	Ph	Ph	—	180—181	—	—	29,30
Ph	Me	Ph	Ph	Me	—	251—252	—	—	37
Ph	Ph	Ph	Ph	Ph	—	355.5	—	—	29
Ph	Me	PhNH	Me	PhNH	—	229—230	—	—	49
Ph	Me	PhNH	Me	$(PhNH)_2Si(Me)N(Ph)$	—	186—187	—	—	49
Ph	Ph	PhNH	Ph	PhNH	—	285—286	—	—	49
Ph	PhNH	PhNH	PhNH	PhNH	—	204—207	—	—	48
Ph	Ph_2SiO	Me	Ph_2SiO	Me	—	259—261	—	—	49
Ph	Ph_2SiO	Ph	Ph_2SiO	Ph	—	288	—	—	49
Ph	4-$PhOC_6H_4$	4-$PhOC_6H_4$	4-$PhOC_6H_4$	4-$PhOC_6H_4$	—	322	—	—	44
Ph	$-(CH_2)_4-$ $Si_2O_2Ph_4$		$-(CH_2)_4-$ $Si_2O_2Ph_4$		—	227	—	—	44
Ph					—	261	—	—	47
α-Naphthyl	Me	Me	Me	Me	—	252—253	—	—	29

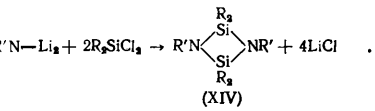
Table 1 (contd.)

Z	R^1	R^2	R^3	R^4	B.p., °C/mmHg	M.p., °C	n_D^{20}	d_4^{20}	References*
β-Naphthyl	Me	Me	Me	Me	—	237	—	—	29
β-Naphthyl	Ph	Ph	Ph	Ph	—	319,5	—	—	29
$3\text{-}FC_6H_4$	Ph	Ph	Ph	Ph	—	311—312	—	—	29
$4\text{-}FC_6H_4$	Ph	Ph	Ph	Ph	—	322—323	—	—	29
$2.5\text{-}F_2C_6H_3$	Ph	Ph	Ph	Ph	—	326	—	—	44
$2.4\text{-}F_2C_6H_3$	Ph	Ph	Ph	Ph	—	338	—	—	44
$3\text{-}CF_3C_6H_4$	Me	Me	Me	Me	—	153—154	—	—	29,44,45
$3\text{-}CF_3C_6H_4$	Ph	Ph	Ph	Ph	—	183—185	—	—	29
$3.5\text{-}(CF_3)_2C_6H_3$	Ph	Ph	Ph	Ph	—	364	—	—	44
$3\text{-}ClC_6H_4$	Ph	Ph	Ph	Ph	—	261—262	—	—	29
$3\text{-}BrC_6H_4$	Ph	Ph	Ph	P t	—	272	—	—	44
$3\text{-}MeOC_6H_4$	Me	Me	Me	Me	—	171	—	—	44
$4\text{-}MeC_6H_4$	Me	Me	Me	Me	—	196—197	—	—	58
$2.4,6\text{-}Me_3C_6H_2$	Me	Me	Me	Me	—	73	—	—	44
$2.4,6\text{-}Me_3C_6H_2$	Me	Ph	Me	Ph	—	228	—	—	35
$2\text{-}Me_2C_6H_3$	Me	Me	Me	Me	—	188	—	—	44
$4\text{-}Me_2C_6H_3$	Me	Me	Me	Me	—	273—276	—	—	44
$4\text{-}MeOC_6H_4CO$	Ph	Ph	Ph	Ph	—	241	—	—	44
Me_3SiCH_2	Me	Me	Me	Me	—	63—64	—	—	44
$3\text{-}PhOC_6H_4$	Ph	Ph	Ph	Ph	470/728	169—172	—	—	44
$4\text{-}PhOC_6H_4$	$3\text{-}PhOC_6H_4$	$3\text{-}PhOC_6H_4$	$3\text{-}PhOC_6H_4$	$3\text{-}PhOC_6H_4$	425—435/721	—	—	—	44
$2.6\text{-}(PhO)_2C_6H_3$	Me	Me	Me	Me	315—319/728	—	—	—	44
$3'\text{-}PhO\text{-}3\text{-}C_6H_4OC_6H_4$	Me	Me	Me	Me	—	212	—	—	44
C_6F_5	Me	Me	Me	Me	—	305—306	—	—	38
C_6F_5	Ph	Ph	Ph	Ph	—	296	—	—	38
$3,5\text{-}Me_2C_6H_3CH_2$	Me	Me	Me	Me	—	248—250	—	—	45
$4\text{-}Me_2NC_6H_4$	Me	Me	Me	Me	—	233—236	—	—	44
$3\text{-}MeOC_6H_4$	Me	Me	Me	Me	—	169—171	—	—	44,45
Me_2NSO_2	Me	Me	Me	Me	—	185—187 (decomp.)	—	—	62
Me_2NSO_2	Ph	Ph	Ph	Ph	—	231—233	—	—	62
$O(CH_2CH_2)_2NSO_2$	Me	Me	Me	Me	—	185 (decomp.)	—	—	62

*Only the references to the main literature are given.

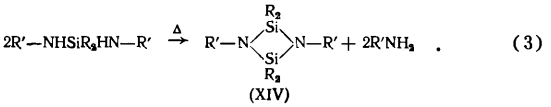
The mechanism of the latter reaction was demonstrated by mass spectrometry and NMR.[35]

The direct reaction of dilithio-derivatives of primary, preferentially aromatic, amines [or compounds described by the formula $R''R_2SiNSi(R_2)NSiR_2R''$] with diorganodichlorosilanes can also be used to synthesise the corresponding organocyclodisilazanes (XIV):[29,30,33,36–38]



(XIV)

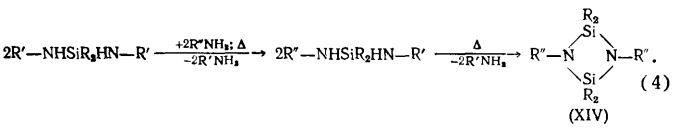
The pyrolysis of diaminodiorganosilanes at 200–450 °C is used particularly widely for the synthesis of *N*-alkylated and *N*-arylated cyclodisilazanes[29–31,39]:



(XIV) (3)

It has been suggested[40–43] that cyclodisilazanes of type (XIV) be synthesised by heating the diaminosilanes $R'-NHSiR_2HN-R'$ (R = substituted alkyl, alkenyl, cycloalkyl, aryl, arylalkyl, or alkoxy-group; R′ = organic group) or the asymmetric disilylamines $XR_2Si-NR'-SiR_2R''$ (R, R′, R″ = organic groups; X = halogen).

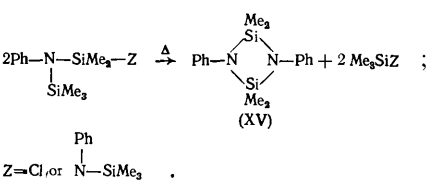
Reaction (3) (particularly for R′ = aryl) is as a rule used only for compounds whose decomposition temperature is much above the boiling point. If the removal of the high-boiling amine formed as a result of the reaction is difficult, the initial diaminosilane is sometimes subjected to a preliminary transamination with subsequent formation of cyclodisilazanes[29,31,32,44,45]:



(XIV) (4)

Reaction (4) takes place only when the boiling point of $R''NH_2$ is higher than that of $R'NH_2$.

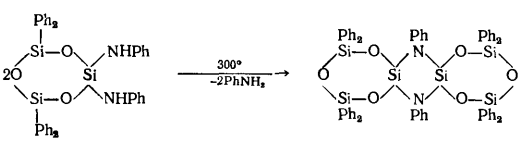
The synthesis of *N*-phenylated tetramethylcyclodisilazanes (XV) is based on the pyrolysis of *N*-phenyl-substituted di- and tri-silazanes[29] in accordance with the mechanism



(XV)

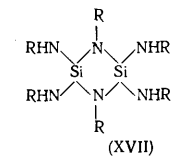
Cyclodisilazanes (XV) are also formed[46] on thermal condensation of tetra-aminosilane with dimethyldianilinosilane at 360–400 °C.

Thermal condensation of 2,2-dianilinotetraphenylcyclotrisiloxane, which takes place with the liberation of aniline only above 300 °C, led to the isolation of an *N*-phenylated four-membered silazane ring having the complex structure (XVI):[47]



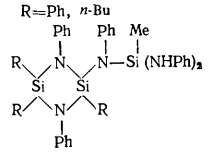
(XVI)

At low degrees of conversion the polycondensation of tetra(arylamino)- and tetra(alkylamino)-silanes proceeds with formation of the corresponding *N*-substituted cyclodisilazanes (XVII).[48] Asymmetric *N*-phenylated cyclodisilazanes (XVIII) have been obtained by the pyrolysis of methyltris(anilino)silane at 400 °C:[49]



(XVII)

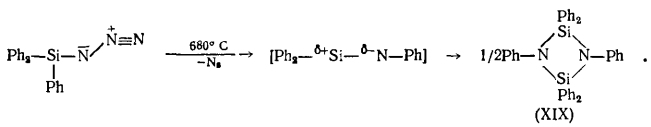
R=Ph, *n*-Bu



(XVIII)

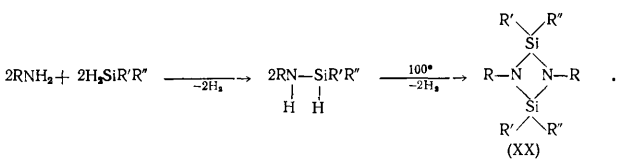
R = Me or NHPh

Hexaphenylcyclodisilazane (XIX) is formed in the pyrolysis of triphenylsilyl azide at 680 °C:[50]



(XIX)

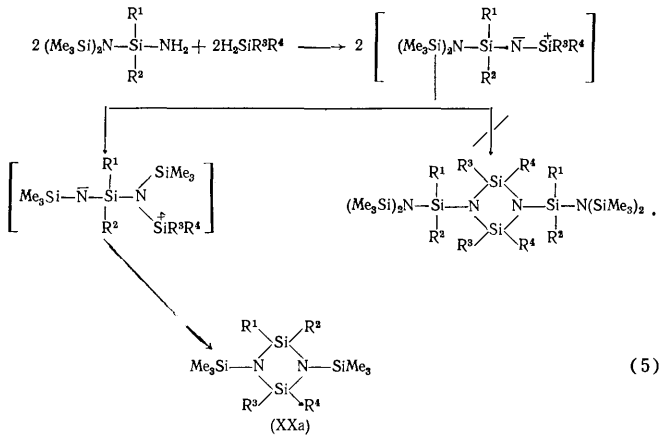
Organocyclodisilazanes can be synthesised by silylating primary aliphatic and aromatic amines or organosilylamines by diorganosilanes in the presence of alkali metals or their hydrides[51–58]:



(XX)

This results in the formation of the cyclodisilazanes (XX), where R′ and R″ are unsubstituted or substituted alkyl, alkenyl, cycloalkyl, arylalkyl, aryl, or polymethylene chains, while R is a lower alkyl, phenyl, benzyl, tolyl, xylyl, quinolinyl, etc. This reaction, which proceeds at a higher rate and with a quantitative field of organocyclodisilazanes, can be carried out in both polar (tetrahydrofuran, 1,2-dimethoxyethane, diethyl ether) and non-polar (benzene and hexane) solvents or altogether without a solvent.

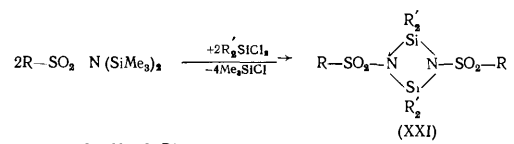
Compound (XXa) with different organic groups at the silicon atom in the ring and with trimethylsilyl groups at the nitrogen atoms can be obtained by reaction (5) via an unstable intermediate. It has been shown[51] that the intermediate does not dimerise but rearranges with migration of the trimethylsilyl group and subsequent formation of the cyclodisilazane:



(XXa) (5)

Organocyclodisilazanes containing halogen atoms or amino-groups in the substituent linked to a nitrogen atom can be obtained by heating the organodisilazanes $X_{3-n}R_nSi-NZ-SiR_nX_{3-n}$ (R is an organic substituent, X a halogen, $n = 0–3$, and Z is a halogenoaryl, halogenoalkylaryl, alkylaminoaryl, cyclohexylamino-, or phenylamino-group) in the absence of oxygen[59–61].

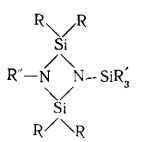
Disilylated sulphamide reacts with the dimethyl- or diphenyl-dichlorosilane to form the corresponding cyclodisilazanes (XXI):[62]



(XXI)

R=OC_4H_8N or Me_2N; R′= Me or Ph.

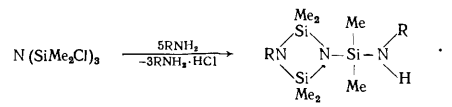
Asymmetric organocyclodisilazanes (XXII) with one triorganosilyl group (R and R′ are different or identical alkyl substituents containing between one and five carbon atoms or aryl, vinyl, and allyl groups; R″ = H, Me, Et, or Pr) have been obtained by the reaction of ammonia or amines R″ – NH_2 with tris(organosilyl)amines $(XR_2Si)_2NSiR'_3$, where X = H, Cl, Br, or I, in an inert solvent at 18–20 °C:[63–65]



(XXII)

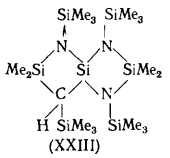
Analogous *N*-alkyl-, *N*-aryl-, or *N′*-triorganosilyl-cyclodisilazanes have been synthesised by the reaction of an asymmetric trisilylamine, for example, bis(chlorodimethylsilyl)(trimethylsilyl)amine or bis(chlorodimethylsilyl)(dimethylphenylsilyl)-amine with primary amines at low temperatures (between –20° and –60 °C).[66–67] The reaction of tris(dimethylchlorosilyl)-amine with primary amines at room temperature yielded asymmetric organocyclodisilazanes containing an amino-group in one of the substituents linked to an endocyclic nitrogen

atom[68]:



R = Me, Ef, or *iso*-Pr

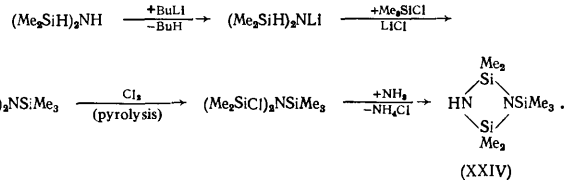
The cyclodisilazane (XXIII), asymmetric relative to the endocyclic silicon atoms and containing a cyclic system as a substituent at one of them, has been obtained by the interaction of $SiCl_4$ with $NaN(SiMe_3)_2$ at 200 °C:[69]



(XXIII)

Its structure was established by ^{1}H NMR [69] and X-ray diffraction[70].

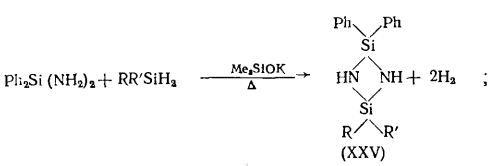
As already mentioned above, *N*-substituted (particularly *N*-triorganosilylsubstituted) organocyclodisilazanes are stable. However, since the cyclodisilazane ring is a highly strained system, the replacement of one of the substituents at a nitrogen atom by hydrogen leads to chemically fairly reactive compounds[6,71], for example, the cyclodisilazane (XXIV):



(XXIV)

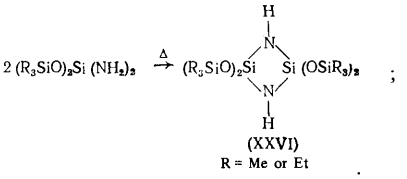
In the spectra of these compounds there is an anomalous distribution of the absorption bands associated with stretching vibrations. Thus in the spectrum of compound (XXIV) the "upper" band due to the NH bond is displaced to 3510 cm^{-1}, which indicates an increased acidity of the proton at the nitrogen atom, and the corresponding shift of the "lower" band to 1000 cm^{-1}. The absorption band of the $\equiv Si-N-Si\equiv$ group, corresponding to anti-symmetric stretching vibrations, which probably also characterises the cyclodisilazane ring[21], is located[6] in the region of 870 cm^{-1}.

Andrianov and coworkers obtained organocyclodisilazanes containing hydrogen at both endocyclic nitrogen atoms by heating diphenyldiaminosilane with diphenylsilane or methylphenylsilane in molar proportions of 1 : 1 in the presence of potassium trimethylsilanoxide[72,73] or by prolonged heating of bis(triorganosiloxy)diaminosilanes[74,75] (at 212–304 °C for R = Me and 280–340 °C for R = Et):



(XXV)

R=R′=Ph; R=Me, R¹=Ph .

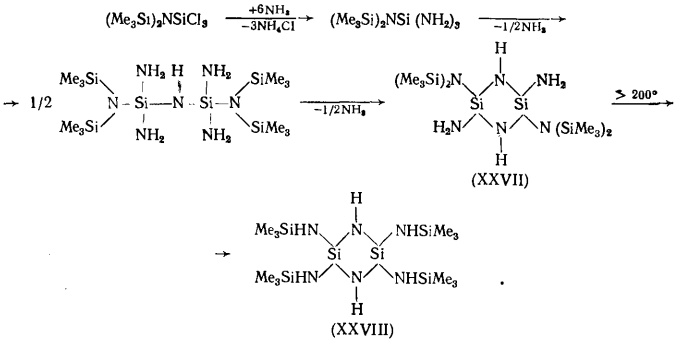


(XXVI)

R = Me or Et

Compounds (XXVI) having an analogous structure were isolated in the ammonolysis of the corresponding bis(triorganosiloxy)dichlorosilanes at elevated temperatures (55 °C for R = Me and 75 °C for R = Et).[75]

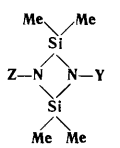
The ammonolysis of hexamethyldisilylaminotrichlorosilane with gaseous ammonia in benzene leads to the formation of products with the cyclodisilazane structure, which contain hydrogen at the endocyclic nitrogen atoms and amino-groups at the silicon atoms[25]:



(XXVII)

(XXVIII)

Table 2. Asymmetric *N*-substituted organocyclodisilazanes.

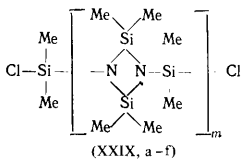


Z	Y	B.p., °C/mmHg	M.p., °C	n_D^{20}	References
H	$SiMe_3$	—	—	—	6
Me	$SiMe_3$	52—53/7	—	1.4273	66
Me	$SiMe_2Ph$	86—87/0.65		1.4863	66
Me	$Si(Me_2)NHMe$	72/10	—	1.4387	68
Et	$SiMe_3$	61—62/7	—	1.4301	66
Et	$Si(Me_2)NHEt$	91.5/8	—	1.4390	68
iso-Pr	$Si(Me_2)NHPr$-iso	98.5/5	—	1.4407	68
Ph	$SiMe_3$	—	95	—	66
Me_3Si	$SiMe_2Cl$	103/12	52	—	79,80,111,113
Me_3Si	$SiMe_2(OH)$	—	56	—	75,111
Me_3Si	$SiMe_2(NH_2)$	—	36	—	114,115
Me_3Si	$Si(Me_2)OSiMe_3$	—	—	—	23
Me_3Si	$SiMePh_2$	124/0.005	—	1.5210	26,67
$PhMe_2Si$	$SiMe_2Cl$	104/0.05	—	1.4892	79,80
$PhMe_2Si$	$SiMe_2(NH_2)$	87/0.005	—	1.4880	79
Cl_2PhSi	$SiMe_2Cl$	132/0.005	—	1.5485	26
$ClMe_2Si$	$SiMe_2(C_6H_4C_6H_5$-4)	49	—	—	79,80

The properties of symmetrical organocyclodisilazanes are listed in Table 1 and those of the asymmetric compounds are in Table 2.

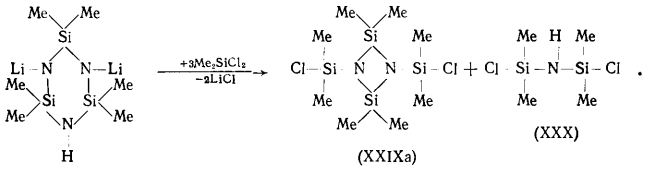
2. α,ω-Bis(diorganohalogenosilyl)-Substituted Cyclodisilazanes

Reports[2,76–93] of the synthesis of α,ω-bis(dimethylchlorosilyl)-substituted monomeric and oligomeric cyclodisilazane (XXIX, a–f) with chlorodimethylsilyl groups at a nitrogen atom, which can be used for the synthesis of linear polymers with cyclodisilazane chain units, are appearing at an increasing frequency at the present time; in compounds (XXIX, a–f) *m* varies from 1 to 6 respectively.



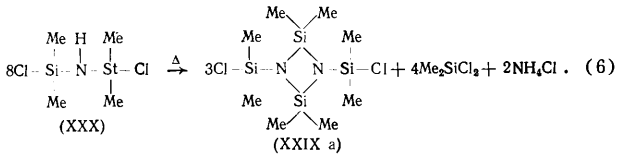
(XXIX, a–f)

When doubly or triply metallated hexamethylcyclotrisilazane (or octamethylcyclotetrasilazane) is treated with an excess of dimethyldichlorosilane, the corresponding dimethyldichlorosilyl derivative is not formed; the reaction yielded 1,3-dichlorotetramethyldisilazane (XXX) and 1,3-bis(dimethylchlorosilyl)-2,2,4,4-tetramethylcyclodisilazane (XXIXa).[77,79] The readily crystallisable compound (XXIXa) can be isolated in a yield of 75% or higher:



(XXIXa) (XXX)

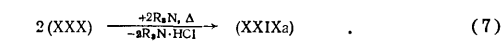
1,3-Dichlorotetramethyldisilazane (XXX) can also be converted into compound (XXIXa) by prolonged refluxing. The temperature of the reaction mass then increases from 143 °C [the boiling point of compound (XXX)] to 235 °C [the boiling point of compound (XXIXa)]. According to the authors' hypothesis[79], the reaction proceeds via the formation of 1,5-dichlorohexamethyltrisilazane. The yield of the cyclodisilazane (XXIXa) is 70–75% of theoretical:



(XXX) (XXIX a)

(6)

In the presence of a tertiary amine, for example, triethylamine, compound (XXX) is also converted into compound (XXIXa):[79]



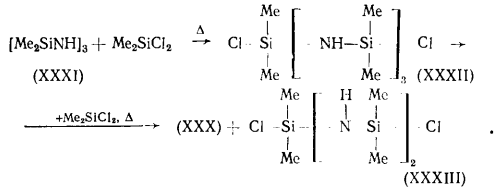
(7)

The optimum yield of compound (XXIXa) is obtained when the reaction is carried out under a low pressure at a temperature somewhat above 150 °C. Partly and fully phenylated substituted 1,3-dichlorotetraorganodisilazanes can be converted into the corresponding organocyclodisilazanes[79]. 1-Chloropentaorganodisilazane can be converted into 1,3-bis(triorganosilyl)-substituted cyclodisilazanes[79].

Hexamethylcyclotri- and octamethylcyclotetra-silazanes are cleaved by dimethyldichlorosilane with formation of compound (XXX) in 70–80% yield[2,78,86,94–97]:



The cleavage of hexamethylcyclotrisilazane (XXXI) by dimethyldichlorosilane has been investigated by quantitative gas chromatography[84,98]. It was established that hexamethylcyclotrisilazane (XXXI) is initially cleaved by dimethyldichlorosilane at a temperature below 100 °C with formation of 1,7-dichloro-octamethyltetrasilazane (XXXII); the latter reacts further with dimethyldichlorosilane to form 1,3-dichlorotetramethyldisilazane (XXX) and 1,5-dichlorohexamethyltrisilazane (XXXIII):



(XXXI) (XXXII) (XXXIII)

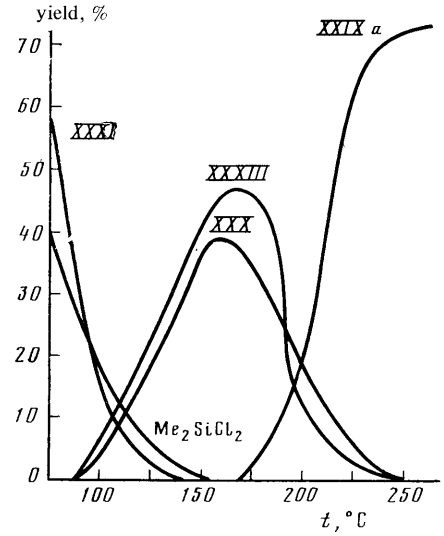


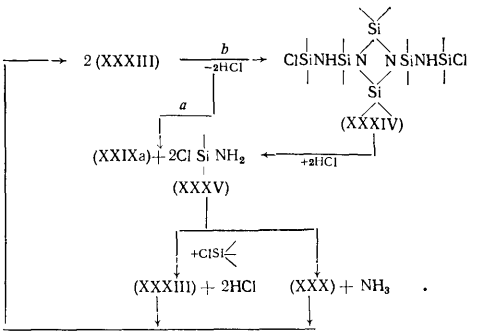
Figure 1. The interaction of hexamethylcyclotrisilazane with dimethyldichlorosilane (in proportions of 1 : 2); the yield with respect to silicon is indicated.

The content of compounds (XXX) and (XXXIII) in the mixture increases up to 160–170 °C, while at a higher temperature it falls and the formation of compound (XXIXa) begins at the same time (Fig.1).[79]

In a study of the pyrolysis of compound (XXX) it was found that dimethyldichlorosilane is evolved in the range 150–170 °C and compound (XXXIII) is formed (Fig.2). Compound (XXIXa) is not formed under these conditions, but even at 170–180 °C the content of compound (XXXIII) in the mixture diminishes and compound (XXIXa) appears[79].

Compound (XXIXa) can be formed from compound (XXXIII) via two pathways: (*a*) via intermolecular migration of hydrogen; (*b*) via the elimination of hydrogen chloride with formation of the intermediate (XXXIV), which subsequently

interacts with hydrogen chloride:



(8)

In both cases the same desired product is obtained. The unstable compound (XXXV), formed via both reaction *a* and *b*, can evolve ammonia to form compound (XXX) or can react with dimethyldichlorosilane to form compound (XXXIII) and then compound (XXIXa).[79]

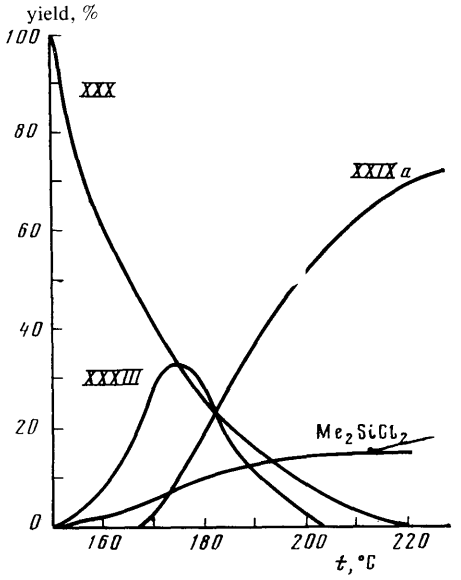
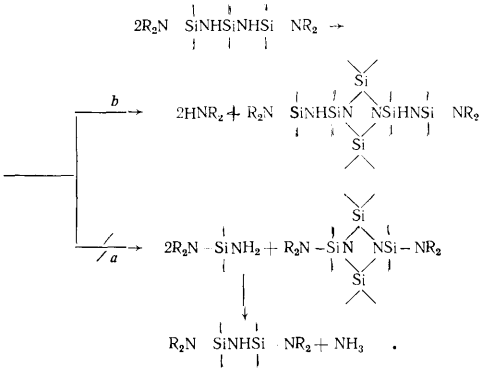


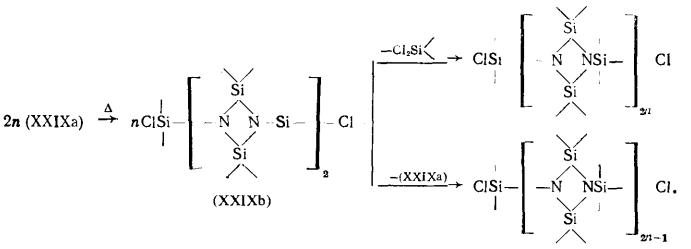
Figure 2. The pyrolysis of 1,3-dichlorotetramethyldisilazane; the yield with respect to silicon is indicated.

The probability of mechanism *b* is confirmed by the results of the pyrolysis of 1,5-bis(diethylamino)hexamethyltrisilazane [Eqn.(9)]. Diethylamine is then formed in amounts corresponding to the formation of hydrogen chloride by reaction (8) (mechanism *b*); ammonia, which can be formed via mechanism *a*, is not evolved[79]:



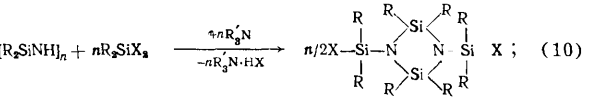
(9)

The final stage of the interaction of hexamethylcyclotrisilazane (XXXI) with dimethyldichlorosilane is the condensation of compound (XXIXa) to (XXIXb) [at the boiling point of compound (XXIXa)] and the subsequent formation of the oligomers (XXIXc)–(XXIXf) takes place fairly slowly at temperatures of the order of 300 °C with evolution of dimethyldichlorosilane and the possible elimination of compound (XXIXa):[79]



The author[79] notes that the mechanism of the formation of compound (XXIXa) and oligomers with a small number of cyclodisilazane units [compounds (XXIXb)–(XXIXf)] is not yet entirely clear.

Since compound (XXX) reacts subsequently with formation of compound (XXIXa), the simplest and most rational method for the synthesis of the cyclodisilazane (XXIXa) is direct interaction of six- and eight-membered methylcyclosilane respectively[2,76,78,79,86,87,93,97,99–101]. This reaction can be carried out between cyclic silazanes having substituents at a nitrogen atom and dimethyldichlorosilane[79,84,98], between cyclic silazanes $(R_2SiNH)_n$ and dihalogenodiorganosilanes R_2SiX_2, where R = hydrogen, fluorine, or a substituted or unsubstituted hydrocarbon, heterocyclic, or triorganosilyl group, while X = chlorine, bromine, or iodine[81,83,86], and also in the presence of the corresponding amount of a tertiary amine under an excess pressure[82], whereupon there is a sharp reduction of the reaction time, an increase of the yield of the desired product, and some decrease of the reaction temperature:



(10)

n = 3 or 4.

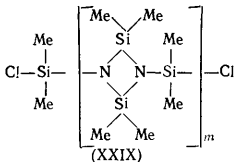
A study of the reaction of 1,3-dichlorotetramethyldisilazane (XXX) with a tertiary amine [Eqn.(7)] or of the interaction

of hexamethylcyclotrisilazane (XXXI) with dimethyldichlorosilane in an excess of a tertiary amine [Eqn.(10)] showed that even at elevated temperatures they are not fully converted into compound (XXIXa).[79] It was established that the optimum yields (89%) are reached when the reaction is carried out in the temperature range 170–190 °C.[79] At higher temperatures the yield of compound (XXIXa) decreases appreciably, since the rate of the reverse reaction increases and the equilibrium shifts towards the initial compound. On the other hand, when the reaction is carried out under an excess pressure (23–28 atm), the yield of compound (XXIXa) increases to 93–97%.[83]

If the reaction between hexamethylcyclotrisilazane (XXXI) and dimethyldichlorosilane is carried out in the absence of a tertiary amine, the maximum yield of compound (XXIXa) is reached for the ratio (XXXI) : dimethyldichlorosilane = 1 : 3 and the amount of oligomers formed is minimal.

On decrease of the amount of dimethyldichlorosilane by 1–2 moles, the yield of compound (XXIXa) falls and increasing amounts of α,ω-bis(dimethylchlorosilyl)-substituted cyclodisilazane oligomers are formed. For example, when compound (XXXI) is heated with dimethyldichlorosilane in proportions of 1 : 3 at 175 °C for 48–77 h, compound (XXIXa) is formed in 60–85% yield[76,85,87]; when the proportions are 1 : 2 (the reaction temperature increases), the yield of compound (XXIXa) falls somewhat and compound (XXIXb) [2,76–79,81–87]—the first member of the series of α,ω-bis(dimethylchlorosilyl)-substituted oligomeric cyclodisilazanes—is isolated on repeated fractionation from the oily material remaining after the removal of ammonium chloride and compound (XXIXa) (Table 3).

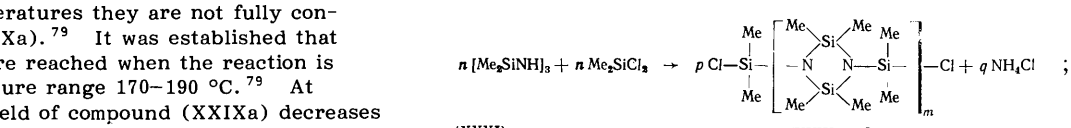
Table 3. The properties of α,ω-bis(dimethylchlorosilyl)-substituted cyclodisilazanes (XXIX) [79]



(XXIX)

Compound	*m*	B.p., °C/mmHg	M.p., °C
(XXIXa)	1	64/0.08	68–69
(XXIXb)	2	118/0.05	43.5
(XXIXc)	3	186/0.01	109–110
(XXIXd)	4	248/0.01	93
(XXIXe)	5	287/0.005	149–152
(XXIXf)	6	315/0.005	147

When a mixture of hexamethylcyclotrisilazane (XXXI) and dimethyldichlorosilane in proportions of 1 : 1 is heated, its temperature rapidly reaches 280 °C and then increases slowly to 330–340 °C. The resulting reaction mixture contains only 10–15% of compound (XXIXa) and 75–85% of oligomeric cyclodisilazanes in terms of the silicon introduced into the reaction; the oligomers (XXIXb)–(XXIXf) can be isolated in a pure form from this mixture[79]. It is of interest that the melting points or softening temperatures of the oligomers with an odd number of cyclodisilazane units in the chain are significantly higher than the corresponding temperatures of the compounds with an even number of units (Table 3):



(XXXI) $m = 1–6$.

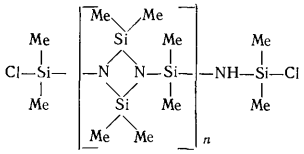
(XXIX, a–f)

The yield of oligomers (XXIX, b–f) depends on the reaction time and temperature (Table 4).[79] The isolation of individual compounds from the mixture by repeated fractionation is difficult.

Table 4. Dependence of the yield of oligomeric α,ω-bis-(dimethylchlorosilyl)-substituted cyclodisilazanes on temperature[79] .

Reaction time, h	Final temp., °C	Amount of NH_4Cl, g	Yield, %					
			(XXIXa)	(XXIXb)	(XXIXc)	(XXIXd)	(XXIXe)	(XXIXf)
6	285	32.8	32.5	35.3	10.8	12.6	5.7	1.5
11	292	36.9	29.0	34.5	12.7	12.4	7.3	2.1
18	314	39.3	16.2	29.4	17.0	14.3	12.7	6.5
45	334	42.5	10.9	18.3	17.8	16.1	13.3	8.5

Table 5. The properties of the cyclodisilazanes (XXXVI) [79]

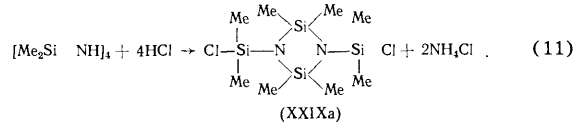


(XXXVI)

Compound	*n*	B.p., °C/mmHg	M.p., °C	n_D^{20}
(XXXVIa)	1	93/0.04	–	1.4598
(XXXVIb)	2	144/0.01	46	–
(XXXVIc)	3	209/0.005	–	–

Apart from compounds (XXIX, a–f), the oligomers (XXVI), containing NH groups in the side chain, are formed as side (or intermediate) products whatever the ratio of the initial reactants. The content of compounds of type (XXXVI) in the reaction mixture depends on the ratio of the initial reactants and on the reaction temperature; although these compounds are in most cases present only in insignificant amounts, they hinder to a large extent the isolation and purification of individual compounds of type (XXIX, a–f). If the reaction terminates at 200–240 °C, the main products are compounds of type (XXIXa) and (XXXVI).[79] Compound (XXXVIa) is formed in an amount of ~12% at a reaction temperature below 170 °C. The oligomers (XXXVI, a–c) are colourless compounds, which are very sensitive to moisture. The physical constants of compounds (XXXVI) are listed in Table 5.

One of the ways of obtaining compound (XXIXa) involves the interaction of hexamethylcyclotrisilazane or octamethylcyclotetrasilazane with hydrogen chloride[2,86,95,96,99,102]:

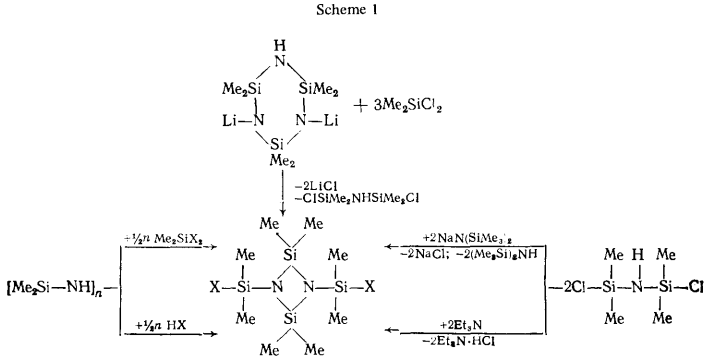


(XXIXa)

Compound (XXIXa) is also obtained in a high yield (70%) by the interaction of compound (XXX) with sodium bis(trimethylsilyl)amide in petroleum ether[78].

Other *N,N'*bis(dimethylhalogenosilyl)-substituted cyclodisilazanes—1,3-bis(dimethylbromosilyl)-2,2,4,4-tetramethylcyclodisilazane (XXXVII) and 1,3-bis(dimethyliodosilyl)-2,2,4,4-tetramethylcyclodisilazane (XXXVIII)—are obtained analogously by reactions of types (6) and (11).[86,96,102]
The methods for the synthesis of 1,3-bis(dimethylhalogenosilyl)-2,2,4,4-tetramethylcyclodisilazanes can be represented by Scheme 1 below:

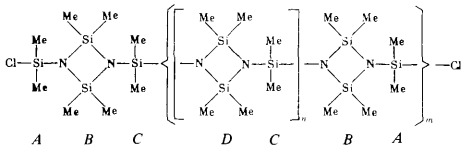
Scheme 1



n=3 or 4; X=Cl, Br, or I.

Tables 6 and 7. For compounds (XXXVII) and (XXXVIII), the spectra were recorded in 5% solution in cyclohexane[86]. For compound (XXXVII), the chemical shifts of the signals due to the protons in the exocyclic fragment XMe_2SiN and the cyclic fragment Me_2SiN_2 are respectively 9.41 and 9.57 p.p.m.; for compound (XXXVIII), $\tau = 9.32$ and 9.57 p.p.m. respectively. The study of the infrared spectra of α,ω-bis(dimethylhalogenosilyl)-substituted cyclodisilazanes showed that the absorption bands characteristic of the stretching vibrations of the cyclodisilazane fragment are in the ranges 880–890 and 1010–1040 cm^{-1}.[76,86,87,103,104] Table 8 presents the ν_1–ν_6 stretching vibrations characteristic of the Si_4N_2 fragment[86].

Table 6. The chemical shifts (τ, p.p.m.) in the ^1H NMR spectra of the cyclodisilazanes (XXIX) [79]

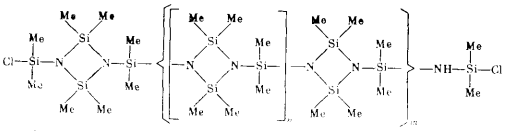


A B C D C B A

Compound	*m*	*n*	*A*	*B*	*C*	*D*
(XXIXa)	0	0	9.72	9.67	9.67	—
(XXIXb)	1	0	9.66	9.64	9.94	9.64
(XXIXc)	1	1	9.64	9.60	9.90	9.63
(XXIXd)	1	2	9.64	9.59	9.87	9.59
(XXIXe)	1	3	9.64	5.59	9.88	9.58
(XXIXf)	1	4	9.64	9.59	9.88	9.59

In order to confirm the structure of compounds (XXIX, a–f) and (XXXVI, a–c), ^1H NMR spectra, recorded in benzene as the solvent (only minimal differences between the chemical shifts τ for different types of protons are observed in CCl_4 or $CDCl_3$), were mainly used with tetramethylsilane as the internal standard[79]. The ^1H NMR spectra are presented in

Table 7. The chemical shifts (τ, p.p.m.) in the ^1H NMR spectra of the cyclodisilazanes (XXXVI) [79]



A B C D E B C A

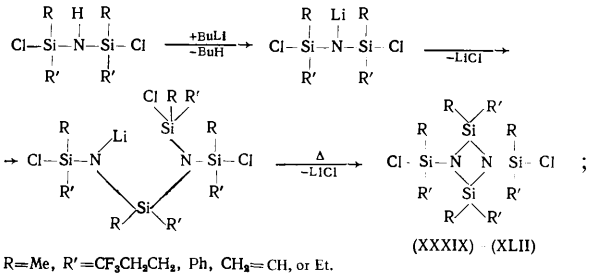
Compound	*m*	*n*	*A*	*B*	*C*	*D*	*E*
(XXXVIa)	0	0	9.69 9.68	9.67	9.86	—	
(XXXVIb)	1	0	9.65	9.63	9.85	—	
(XXXVIc)	1	1	9.65	9.62	9.83	9.61	9.89

Table 8. Vibrations (cm^{-1}) characteristic of the Si_4N_2 fragment in the cyclodisilazanes (XXIXa), (XXXVIa), (XXXVII), and (XXXVIII).

Vibration	(XXIXa)	(XXXVIa)	(XXXVII)	(XXXVIII)
ν_1	1045	1038	1037	1028
ν_2	884	883	882	887
ν_3	780	778		
ν'_4	720	722	695	695
ν_4	525	513	505	497
ν_5	440	440		
ν_6	423		428	421

The characteristics of the mass-spectrometric fragmentation of cyclodisilazanes have been found[105] and used to determine the structure of the hydrolysis products—derivatives of compound (XXIXa).

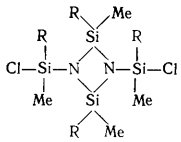
Organocyclodisilazanes (XXXIX)–(XLII) (Table 9) with different organic groups can be obtained either by reactions (6) and (11) or by the reaction of 1,3-dichloro-1,1,3,3-tetraorganodisilazane with butyl-lithium:



R=Me, R′=$CF_3CH_2CH_2$, Ph, CH_2=CH, or Et.

Cooling is used in the treatment with butyl-lithium, while the condensation stage is carried out at elevated temperatures[100]. The principal conditions of the synthesis and the yields of organocyclodisilazanes (XXXIX)–(XLII) are presented in Table 10.

Table 9. The structure, properties, and infrared and ^1H NMR spectroscopic data for the organocyclodisilazanes (XXXIX)–(XLII) [100]



Compound	R	B.p., °C/mmHg	M.p., °C	τ for Me protons, p.p.m.	ν, cm^{-1}	
					Si_2N	Si_4N_2
(XXXIX)	$CF_3CH_2CH_2$	130–132/0.2	60–73	9.56 and 9.59	868	1022
(XL)	Ph	220–221/0.2	—	9.27–9.54 and 9.65–9.73*	850	1019
(XLI)	CH_2=CH	120/2	—	9.56 and 9.59	860	1038
(XLII)	Et	114/0.2	—	9.68	855	1032

* Multiplets.

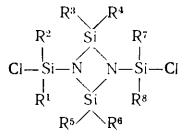
Table 10. The principal conditions of the synthesis and yields of the organocyclodisilazanes (XXXIX)–(XLII).[100]

Compound	Reaction (6)			Reaction (11)		
	t, °C	time, h	yield, %	t, °C	time, h	yield, %
(XXXIX)	230	6	56	270–300	1.5	81
(XXXIX)	290	3	56			
(XL)	295	4	45	285	1	72
(XLI)	175	48	42	—	—	—
(XLII)	140	16	34	175	1	41
(XLII)	180	10	34			

Treatment of 1,3-bis(dimethylchlorosilyl)-2,2,4,4-tetramethylcyclodisilazane (XXIXa) with diphenyldichlorosilane using different proportions of the initial reactants makes it possible to replace one, two, three, or all the dimethylsilyl groups, whereupon the dimethylchlorosilyl (exocyclic) and dimethylsilyl (endocyclic) groups are substituted almost equally readily by the diphenylchlorosilyl and diphenylsilyl groups respectively. It is noteworthy that the complete substitution of the dimethylsilyl groups requires comparatively high temperatures (~400 °C).[26] The compounds isolated as a result of these reactions are listed in Table 11.

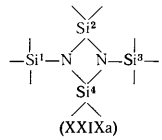
Trans-silylation of compound (XXIXa) with diphenyldichlorosilane (1 : 1 ratio) yields two isomers (XLIIIa) and (XLIIIb) (with endocyclic and exocyclic diphenylsilyl groups) in proportions of 1 : 1 and with an overall yield of 80%.

Table 11. Organocyclodisilazanes obtained by the trans-silylation of 1,3-bis(dimethylchlorosilyl)-2,2,4,4-tetramethylcyclodisilazane (XXIXa) with diphenyldichlorosilane or phenyltrichlorosilane[26]



Compound	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	B.p., °C/mmHg	M.p., °C	n_D^{20}
(XLIIIa)	Me	Me	Ph	Ph	Me	Me	Me	Me	134/0.005	73	—
(XLIIIb)	Ph	Ph	Me	Me	Me	Me	Me	Me	144/0.005	41	—
(XLIVa)	Ph	Ph	Ph	Ph	Me	Me	Me	Me	218/0.05	—	1.5863
(XLIVb)	Ph	Ph	Me	Me	Me	Me	Ph	Ph	218/0.05	139	—
(XLVa)	Ph	Ph	Ph	Ph	Me	Me	Ph	Ph	282/0.05	106	—
(XLVb)	Ph	Ph	Ph	Ph	Ph	Ph	Me	Me	282/0.05	283	—
(XLVI)	Ph	Ph	Ph	Ph	Ph	Ph	Ph	Ph	—	260	—
(XLVII)	Me	Me	Ph	Cl	Me	Me	Me	Me	170/12	—	1.5046
(XLVIII)	Ph	Cl	Me	Me	Me	Me	Ph	Cl	225/12	102	—
(XLIX)	Ph	Cl	Ph	Cl	Me	Me	Me	Me	132/0.005	—	1.5485

Table 12. The chemical shifts (τ, p.p.m.) of the Me groups in the ^1H NMR spectra of the isomers obtained by the trans-silylation of the cyclodisilazane (XXIXa)



(XXIXa)

Si atom linked to Me group	(XLIIIa)	(XLIIIb)	(XLIVa)	(XLIVb)	(XLVa)	(XLVb)
Si^1	9.81	—	—	—	—	9.99
Si^2	—	9.77	—	9.92	—	—
Si^3	9.81	9.63	9.61	—	—	—
Si^4	9.45	9.77	9.83	9.92	9.78	—

When 2 moles of diphenyldichlorosilane per mole of compound (XXIXa) are used, there is a possibility of three isomeric products (XLIV)[(XLIVa) involving the substitution of one exocyclic and one endocyclic group, (XLIVb) involving the substitution of both exocyclic groups, and (XLIVc) involving the substitution of both endocyclic groups], but only two isomers, namely (XLIVa) and (XLIVb), were isolated. The high and approximately equal yields of the two isomers (86% overall) suggest that the third isomer is either not formed or is formed in a very small amount.

When the ratio of the initial components is 1 : 3, two isomers (XLV), having the same boiling point, are obtained. Isomers (XLVa) and (XLVb) are isolated by recrystallisation from petroleum ether.

Trans-silylation of compound (XXIXa) by treatment with 4 moles of diphenyldichlorosilane takes place very slowly (particularly the last stage). Compound (XLVI) is recrystallised from n-octane or from a mixture of hexane and benzene.

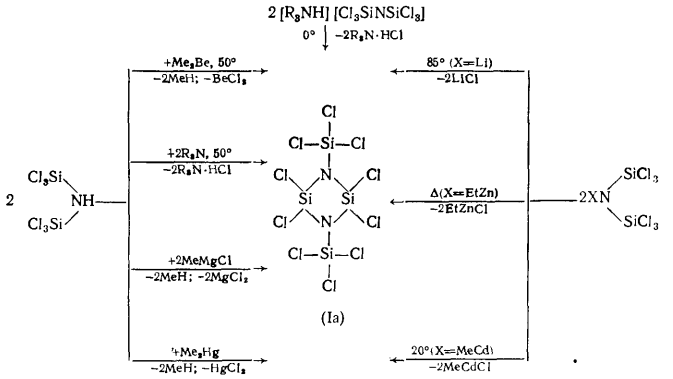
^{1}H NMR data (obtained in $CDCl_3$), confirming the structure of the isomers (XLIII)–(XLVI) obtained, are presented in Table 12.[26]

Other chlorosilanes behave similarly to diphenyldichlorosilanes; for example, phenyltrichlorosilane reacts with formation of compounds (XLVII)–(XLIX) [26] (Table 11).

As already stated, perchlorocyclodisilazanes were obtained as early as 1957 by the pyrolysis of a mixture of $SiCl_4$ and N_2,[14,15] but this synthesis was very complex and the yield of the desired product was extremely low. A new method of synthesis of 1,3-bis(trichlorosilyl)-2,2,4,4-tetrachlorocyclodisilazane (Ia) was proposed in 1967. It involves the interaction of hexachlorodisilazane with methyl-lithium in diethyl ether or with butyl-lithium in petroleum ether; the reaction takes place with cooling to −78 °C and subsequent condensation at 85 °C.[106]

A new more novel method of synthesis of compound (Ia), from lithium bis(trichlorosilyl)amide in the presence of $SiCl_4$, $SiBr_4$, $SiICl_3$, or $GeCl_4$ at 20 °C or by the condensation of tris(trichlorosilyl)amine at 50 °C, was proposed later[107].

The remaining methods of synthesis of perchlorocyclodisilazanes[107–110] are largely preparative and involve the use of organometallic derivatives. A clear idea about the syntheses of compound (Ia) is provided by the following scheme:



Numerous new studies of the formation of organocyclodisilazanes are being published nowadays, the attention of investigators being attracted to an increasing extent by the structure of these compounds, their reactivity, physical properties, and methods of analysis. The data obtained lead to the possibility of a wider practical employment of different types of organocyclodisilazanes, which can find the same applications in many branches of industry as siloxanes and it may be that they will be actually more effective.

REFERENCES

1. W.Fink, Angew.Chem., **78**, 803 (1966).
2. U.Wannagat, Pure Appl.Chem., **13**, 263 (1966).
3. U.Wannagat, Chem.Z., **97**, 105 (1973).
4. Yu.M.Varezhkin, D.Ya.Zhinkin, and M.M.Morgunova, "Sintez i Primenenie Polimerov Tsiklodisilazanovoi Struktury" (The Synthesis and Applications of Polymers with the Cyclodisilazane Structure), Izd. NIITEKhIM, Moscow, 1977.
5. B.P.1330134 (1973); Chem.Abs., **80**, 3627 (1973).
6. R.P.Bush, N.C.Lloyd, and C.A.Pearce, Chem. Communs., 1269 (1969).
7. R.P.Bush, N.C.Lloyd, and C.A.Pearce, J.Chem. Soc.A, 253 (1969).
8. Y.Vignollet and J.Maire, Chem.Communs., 1187 (1968).
9. V.E.Shklover, N.G.Bokii, Yu.T.Struchkov, K.A.Andrianov, A.B.Zachernyuk, and E.A.Zhdanova, Zhur.Strukt.Khim., **15**, 850 (1974).
10. P.J.Wheatley, J.Chem.Soc., 1721 (1962).
11. W.Fink, J.Paint Technol., **42**, No.543, 220 (1970).
12. W.Fink, Helv.Chim.Acta, **52**, 1841 (1969).
13. W.C.Schumb and L.H.Towle, J.Amer.Chem.Soc., **75**. 6085 (1953).
14. A.Pflugmacher and H.Dahmen, Z.anorg.allgem.Chem., **290**, 184 (1957).
15. H.Ernst, Dissertation, Technische Hochschule Aachen, 1958.
16. W.Fink, Chem.Ber., **96**, 1071 (1963).
17. W.Fink, Helv.Chem.Acta, **46**, 720 (1963).
18. W.Fink, Angew.Chem., **73**, 736 (1961).
19. W.Fink, Helv.Chim.Acta, **45**, 1081 (1962).
20. K.Lienhard and E.G.Rochow, Angew.Chem., **75**, 638 (1963).
21. K.Lienhard and E.G.Rochow, Z.anorg.allgem.Chem., **331**, 316 (1964).
22. U.Wannagat, E.Bogusch, and F.Rabet, Z.anorg. allgem.Chem., **385**, 261 (1971).
23. R.P.Bush, N.C.Lloyd, and C.A.Pearce, J.Chem. Soc.A, 1587 (1970).
24. B.P.1265001 (1972); Chem.Abs., **76**, 141013 (1972).
25. K.A.Andrianov, G.V.Kotrelev, V.V.Kozakova, and I.E.Rogov, Izv.Akad.Nauk SSSR, Ser.Khim., 2600 (1975).
26. W.Fink, Helv.Chim.Acta, **51**, 1743 (1968).
27. U.Klingebiel and A.Meller, Angew.Chem., **88**, 307 (1976).
28. U.Klingebiel, J.Neemann, and A.Meller, Z.anorg. Chem., **429**, 63 (1977).
29. W.Fink, Helv.Chim.Acta, **47**, 498 (1964).
30. Belg.P.630249 (1963); Chem.Abs., **60**, 15911 (1964).
31. French P.1359379 (1963) and the supplement 85867 (1965); Chem.Abs., **60**, 15911 (1964).
32. US P.3140288 (1964); Chem.Zentr., 2818 (1966).
33. K.E.Peterman and J.M.Shreeve, Inorg.Chem., **15**, 743 (1976).
34. D.W.Klein and J.W.Connolly, J.Organometal.Chem., **33**, 311 (1971).
35. U.Klingebiel, D.Bentmann, and A.Meller, J.Organometal.Chem., **144**, 381 (1978).
36. B.P.1294682 (1972); Chem.Abs., **78**, 137011 (1973).
37. I.Haiduc, Synthesis in Inorganic and Metallorganic Chemistry, **1**, 75 (1971).
38. I.Haiduc and H.Gilman, J.Organometal.Chem., **18**, P5 (1969).
39. C.M.Golino, R.D.Bush, and L.H.Sommer, J.Amer. Chem.Soc., **96**, 614 (1974).
40. B.P.1040726 (1966); Chem.Zentr., 2644 (1967).
41. B.P.1063086 (1967); Brit.Pat.Abstrs., **7**, No.16, 51 (1967).
42. BRD P.1214683 (1967); Chem.Zentr., 2745 (1967).
43. BRD P.1291338 (1969); Auszüge Patentanmeld., **15**, 885 (1969).
44. Belg.P.645148 (1964); Chem.Abs., **63**, 7043 (1965).
45. Dutch P.6507996 (1965); Chem.Abs., **64**, 19667 (1966).

46. K.A.Andrianov, G.V.Kotrelev, and E.F.Tonkikh, Dokl.Akad.Nauk SSSR, **201**, 349 (1971).
47. K.A.Andrianov and A.B.Zachernyuk, Vysokomol. Soed., **16A**, 1435 (1974).
48. K.A.Andrianov, V.N.Talanov, L.M.Khananashvili, N.P.Gashnikova, M.M.Il'in, and N.A.Sidorenko, Dokl.Akad.Nauk SSSR, **198**, 87 (1971).
49. W.Fink, Helv.Chim.Acta, **51**, 974 (1968).
50. W.T.Reichle, Inorg.Chem., 3, 402 (1964).
51. Belg.P.665774 (1965); Chem.Abs., **64**, 19677 (1966).
52. Japanese P.44-213/69 (1968); Derwent Japanese, **8**, No.1, p.5, 2 (1968).
53. Swiss Appl.No.8151/64 (1964); Industrial Property 1964.
54. Swiss Appl.No.16433/64 (1964); Industrial Property 1964.
55. BRD P.1182661 (1964); Chem.Zentr., 2909 (1966).
56. BRD Appl.1543208 (1969); Auszüge Patentanmeld., 2, 1335 (1969).
57. N.S.Nametkin, E.S.Vasil'eva, et al., Khim. Geterotsikl.Soed., 138 (1967).
58. French P.1350220 (1963); Chem.Abs., **60**, 15912 (1964).
59. Swiss Appl.No.3275/63 (1963); Industrial Property 1963.
60. BRD P.1252683 (1967); Chem.Zentr., 2745 (1967).
61. Japanese P.45-23344 (1970); Ref.Zhur.Khim., 12N803 (1970).
62. R.Appel and M.Montenarh, Z.Naturforsch., **31b**, 993 (1976).
63. US P.3742003 (1973).
64. B.P.1228874 (1971); Chem.Abs., **75**, 36330 (1971).
65. B.P.1228873 (1971).
66. L.W.Breed and R.L.Elliott, J.Organometal.Chem., 11, 447 (1968).
67. US P.3414584 (1968); Chem.Abs., 70, 87947 (1969).
68. H.Bürger, R.Mellies, and K.Wiegel, J.Organometal. Chem., **142**, 55 (1977).
69. U.Wannagat, J.Herzig, and H.Bürger, J.Organometal. Chem., **23**, 373 (1970).
70. D.Mootz, J.Fayos, and A.Zinnius, Angew.Chem., **84**, 27 (1972).
71. R.P.Bush and C.A.Pearce, J.Chem.Soc.A, 808 (1969).
72. K.A.Andrianov, Zh.S.Syrtsova, V.M.Kopylov, and T.Augustiniene, Khim.Geterotsikl.Soed., 751 (1972).
73. K.A.Andrianov, Zh.S.Syrtsova, V.M.Kopylov, and T.Augustiniene, Symposium, "Khimiya i Khimichiskaya Tekhnologiya" (Chemistry and Chemical Engineering), Izd.MITKhT im.Lomonosova, Moscow, 1972, p.234.
74. K.A.Andrianov and N.V.Delazari, Izv.Akad.Nauk SSSR, Ser.Khim., 2169 (1961).
75. K.A.Andrianov and N.V.Delazari, Izv.Akad.Nauk SSSR, Ser.Khim., 2748 (1972).
76. L.W.Breed, W.L.Budde, and R.L.Elliott, J.Organometal.Chem., **6**, 676 (1966).
77. BRD P.1187615 (1965); Chem.Abs., 63, 9986 (1965).
78. P.Geymayer and E.G.Rochow, Angew.Chem., **77**, 618 (1965).
79. W.Fink, Helv.Chim.Acta, **51**, 1011 (1968).
80. French P.1546594 (1968); Chem.Abs., 71, 50203 (1969).
81. B.P.1203622 (1970); Chem.Abs., **72**, 32015 (1970).
82. French P.1519953 (1969); Chem.Abs., 71, 50206 (1969).
83. US P.3539609 (1970); Offic.Gaz.U.S., **880**, No.2 (1970).
84. J.Silbiger, J.Fuchs, and N.Gesundheit, Inorg. Chem., **6**, 399 (1967).
85. W.Fink, Helv.Chim.Acta, **51**, 978 (1968).
86. U.Wannagat, E.Bogusch, and P.Geymayer, Monatsh. Chem., **102**, 1825 (1971).
87. L.W.Breed, R.L.Elliott, and J.C.Wiley, J.Organometal.Chem., 24, 315 (1970).
88. BRD P.2226069 (1973); Chem.Abs., 78, 159838 (1973).
89. US P.3755397 (1973).
90. B.P.1339374 (1973); Abridgments of Specificat. 1973.
91. French P.2140123 (1972); Bull.Offic.Propr.Industr., 1972.
92. K.A.Andrianov, N.A.Tebeneva, et al., Dokl.Akad. Nauk SSSR, **222**, 1101 (1975).
93. U.Wannagat, E.Bogusch, and F.Höfler, J.Organometal.Chem., 7, 203 (1967).
94. J.Silbiger and J.Fuchs, Inorg.Chem., **4**, 1371 (1965).
95. U.Wannagat, P.Geymayer, and E.Bogusch, Monatsh. Chem., **95**, 801 (1964).
96. U.Wannagat and E.Bogusch, Monatsh.Chem., 102, 1806 (1971).
97. French P.93608 (1970); Chem.Abs., 72, 32015 (1970).
98. J.R.Van Wazer and K.Moedritzer, J.Chem.Phys., **41**, 3122 (1964).
99. U.Wannagat, Angew.Chem., 77, 626 (1965).
100. L.W.Breed and J.C.Wiley, Inorg.Chem., 11, 1634 (1972).
101. L.W.Breed, R.L.Elliott, and J.C.Wiley, J.Organometal.Chem., **31**, 179 (1971).
102. E.Bogusch, Dissertation Technische, Hochschule Graz, 1966.
103. H.Bürger, E.Bogusch, and P.Geymayer, Z.anorg. Chem., **349**, 124 (1967).
104. P.Geymayer and E.Rochow, Sci.Foundation Grant NSF-GP-2007, 44 (1965).
105. V.N.Bochkarev, A.A.Bernadskii, Yu.M.Varezhkin, M.M.Morgunova, and D.Ya.Zhinkin, Symposium, "Khimiya Elementoorganicheskikh Soedinenii" (The Chemistry of Organoelemental Compounds), Izd. Nauka, Leningrad, 1976, p.31.
106. U.Wannagat, P.Schmidt, and M.Schulze, Angew. Chem., **79**, 409 (1967).
107. U.Wannagat, M.Schulze, and H.Bürger, Z.anorg. Chem., **375**, 157 (1970).
108. U.Wannagat, H.Moretto, and P.Schmidt, Z.anorg. Chem., **385**, 164 (1971).
109. U.Wannagat, H.Moretto, P.Schmidt, and M.Schulze, Z.anorg.Chem., **381**, 288 (1971).
110. H.Moretto, P.Schmidt, and U.Wannagat, Z.anorg. Chem., **394**, 125 (1972).
111. French P.1425306 (1964); Chem.Abs., **65**, 12366 (1966).
112. BRD Appl.1570912 (1969); Auszüge Offenlegungsschr., **2**, 2209 (1969).
113. BRD P.1813177 (1969); Chem.Abs., 71, 102005 (1969).
114. W.Fink, Helv.Chim.Acta, **52**, 2261 (1969).
115. W.Fink, Angew.Chem., 81, 499 (1969).
116. K.A.Andrianov, M.I.Shkol'nik, Zh.S.Syrtsova, K.I.Petrov, V.M.Kopylov, M.G.Zaitseva, and E.A.Koroleva, Dokl.Akad.Nauk SSSR, **223**, 347 (1975).

Translated from *Uspekhi Khimii*, **49**, 2344-2376 (1980) U.D.C. 541.124

Kinetics and Mechanism of the Reaction of Ozone with Double Bonds

S.D.Razumovskii and G.E.Zaikov

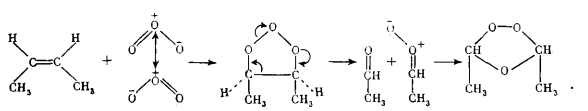
Analysis of the results of recent studies has shown that the reaction of ozone with the double bonds of organic compounds apparently takes place not by a synchronous addition mechanism but through a reversible stage involving the formation of an intermediate complex of ozone with the double bond. The subsequent stages of the reaction involve the formation of a primary ozonide, its decomposition into two fragments, their combination, and a number of other transformations. The properties of the intermediate products, the relationship between the structure of the original alkenes and their reactivity towards ozone, the influence of the nature of the solvent on the direction and rate of the reaction, and the practical application of the reaction of ozone with double bonds in research and chemical technology have been examined. The bibliography contains 205 references.

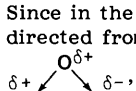
CONTENTS

I. Introduction 1163
II. Mechanism of the reaction of ozone with double bonds 1163
III. Kinetics of the reaction of ozone with unsaturated compounds 1165
IV. Intermediate stages in the addition of ozone to alkenes 1171
V. The use of the reaction of ozone with unsaturated compounds in research and technology 1176

I. INTRODUCTION

The reaction of the double bond with ozone is one of the most specific reactions of unsaturated organic compounds. It is widely used in preparative synthesis, qualitative and quantitative analysis[1], and chemical technology[2,3]. At the start of the present century, this reaction was used to establish the structure of macromolecular compounds[4], and it is still often used to study the positions of C=C bonds in macromolecules[5,6]. A few years ago, it seemed that the mechanism of the reaction of ozone with a double bond had been fairly well established[2,3,7]. In monographs and reviews, this reaction is dealt with as a classical example of synchronous 1,3-dipolar addition[8-11]:

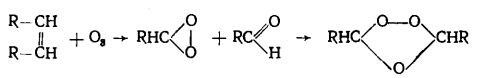


Recent studies have shown, however, that the reaction does not take place synchronously, but involves the reversible formation of an intermediate complex, which has been identified by kinetic and spectroscopic methods. The term 1,3-dipolar addition, introduced by Huisgen[8], is inappropriate when applied to ozone. Huisgen[8] assigned to ozone the structure $\overset{+}{O}-O=\overset{-}{O}$, which does not correspond to present-day views of the electronic structure of the ozone molecule[12-14]. Since in the ozone molecule the dipole moment vector is directed from the central oxygen atom to the terminal atoms  , there should be 1,2- and not 1,3-dipolar addition. However, the fact that most alkenes have zero dipole moment, the low value of the dipole moment of ozone (0.53 *D*), the insensitivity of the reaction to polar factors[15], and even, on the contrary, the decrease in the reaction rate with change in the electronegativity of one of the atoms at the double bond[16], indicate that the term "dipolar addition" does not correspond to the character of the reaction being considered.

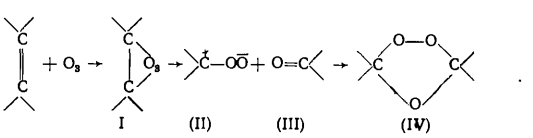
II. MECHANISM OF THE REACTION OF OZONE WITH DOUBLE BONDS

1. Development of Views of the Reaction Mechanism

At an early stage in the studies, Harries[17], Staudinger[18], and Rieche[19] suggested that the reaction involves the formation of a cyclic peroxide

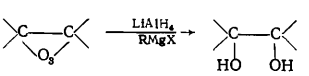


Later, Criegee[20,21] proposed a scheme showing better agreement with known facts about the reaction mechanism:



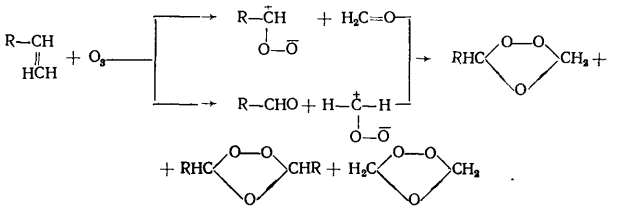
I (II) (III) (IV)

In this scheme, the primary product of the reaction is the so-called molozonide (I), which is unstable at ordinary temperatures and decomposes rapidly to the "zwitterion" (II) and a carbonyl compound (aldehyde or ketone (III)). These intermediate compounds can combine again (after preliminary rotation through 180°) and form a normal ozonide ("iso-ozonide" (IV)). By carrying out the reaction at low temperatures, it is possible to decrease the reaction rate at the molozonide stage, and to observe its transformation into other products[22], for example its reduction to the glycol[23]:

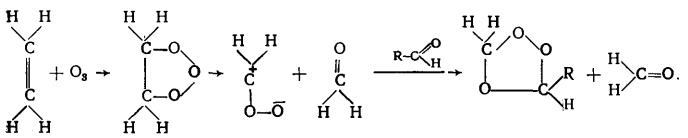


The conjugated formation of the zwitterion–carbonyl compound pair follows from many characteristic features of the reaction. In particular, it is known that the action of ozone

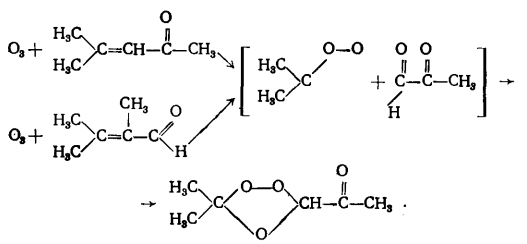
on unsymmetrical alkenes gives the crossed ozonides[24]:



When introduced into a system in which an alkene and ozone are reacting, an aldehyde enters the molecule of the ozonide formed; simultaneously, a carbonyl-containing compound, which is a fragment of the intermediate molozonide, is detected in the system[25]:



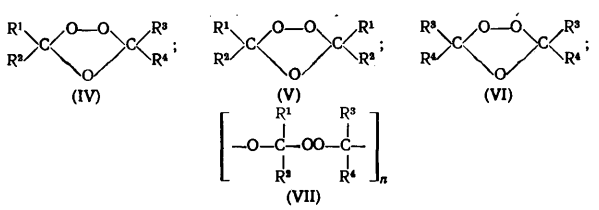
A very elegant confirmation of Criegee's mechanism is provided by the formation of a single final ozonide by the reaction of ozone with two different original alkenes—mesityl oxide and 2,3-dimethylcrotonaldehyde[26]:



Other schemes[24,27] have been proposed in addition to Criegee's scheme, but they have not been adequately confirmed[28,29].

2. Reaction Products

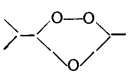
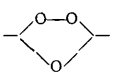
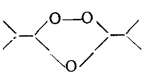
The products of the reaction of ozone with alkenes in solution (in an inert solvent) usually consist of a mixture of the normal ozonide (IV), the crossed ozonides (V) and (VI), and the polymeric ozonides (VII):

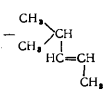


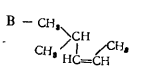
which in accordance with accepted nomenclature can be called 1,2,4-trioxolanes. The reaction mixture contains small quantities of alcohols[30], aldehydes and ketones[31], acids[32], and frequently alkenes oxides[33–36], the concentration of which may be high (up to 90%) in some cases.

Gas chromatography has established the existence of the *cis*- and *trans*-isomers of the normal and crossed ozonides[37,38], which are fairly effectively separated on polyester phases (Table 1) and give different absorption bands in the infrared and PMR spectra[39]. The ratio of the *cis*- and *trans*-isomers in the reaction products is fairly sensitive to the nature of the solvent, the original concentration of the alkene, and the temperature of the experiment.

Table 1. Composition of ozonides, %, from gas–liquid chromatography[24].

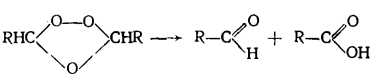
Ozonide	Formula	A	B
Normal			
cis-		32	4.2
trans-		34	4.4
Crossed			
cis-		2.3	5.19
trans-		3.7	6.1
Crossed			
cis-		5.5	12.5
trans-		5.5	6.5

Note: A—original alkene 

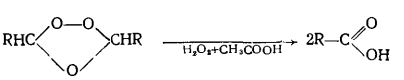
B – 

In early studies of the infrared spectra of ozonides, the maxima in the range 1705–1740 cm^{-1}, due to the absorption by the $>C=O$ group of the decomposition products, were erroneously assigned as characteristic bands of the trioxolane ring[40]. Most ozonides have characteristic absorption bands in the range 980–1100 cm^{-1}.[39,41–43].

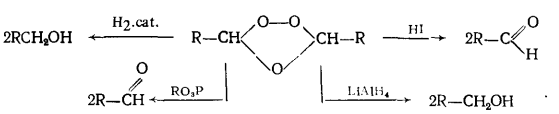
The most typical reactions of ozonides are: thermal decomposition[44,45]



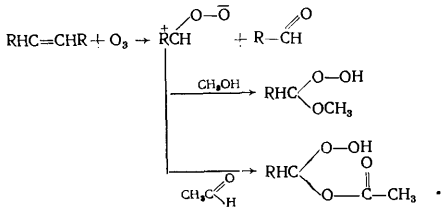
oxidation[46]



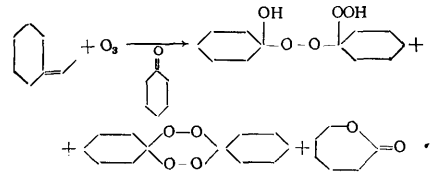
and reduction[46]



When the reaction is carried out in the presence of alcohols, acids, and various other compounds, the products are not ozonides but peroxo-compounds of different character[3,27,46]:



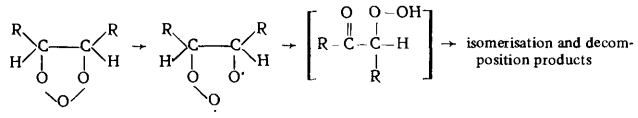
The composition of the peroxo-compounds obtained has not been studied in detail[52,53], but it is known that they are unstable, and capable of further reaction, for example with accompanying carbonyl compounds[54]. When the reaction was carried out in a ketone as solvent, the yield of ozonide decreased from 86.6% to 2.9%, and the chief products were peroxides and lactones[55]



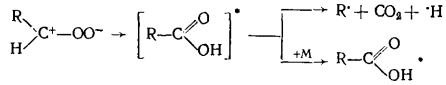
3. Characteristic Features of the Reaction in the Gaseous Phase

The study of the reaction of ozone with alkenes in the gaseous phase has shown that ozonides, which are the chief products of the reaction in solution, are formed in very small quantities in the gaseous phase. The mixture containing CO, CO_2, H_2O, hydrocarbons, acids, and aldehydes, produced by the splitting of the alkene at the C=C bond and further decomposition of the fragments[56–59]. Mass spectrometry has shown that the reaction products contain compounds having mass numbers up to five original molecular units (in particular, for butenes, $M \geq 200$).[60] In the case of halogen-substituted alkenes, the formation of oxides as chief reaction products has been noted[36]. Matrix isolation techniques have shown that the products of the reaction of ozone with ethylene contain not only CO, CO_2, H_2O, CH_2O, HCOOH, CH_3OH, CH_3CHO, and also $\overline{CH_2OCH_2}$, but also the unstable formaldehyde and glyoxal[61]. The reaction is accompanied by chemiluminescence[62], so that it rapidly found practical application in apparatus for determining the concentration of ozone in samples of atmospheric air[63]. The luminescence is due to the presence of the excited species H_2CO (^1A) and OH ($X^2\Pi_i$; $v \leq 9$ and $A^2\Sigma^+$).[64,65]

In the proposed reaction schemes, the change in the composition of the products and the formation of excited intermediate species are attributed to radical processes, which begin with the homolytic rupture of the O–O bond of the molozonide[56,66–68]



or as a result of the isomerisation of the zwitterion[44]:



The stoichiometry of the alkene + ozone reaction varies from 1 : 1.4 to 1 : 2, depending on the conditions; when these prevent secondary reactions, the observed stoichiometric ratio is close to 1 : 1.

III. KINETICS OF THE REACTION OF OZONE WITH UNSATURATED COMPOUNDS

1. Gaseous Phase

The reaction of ozone with alkenes takes place readily at all temperatures studied, from −180 °C [43,69] to 300 °C.[70] Its rate is generally limited by the rate of supply of reagents to the reaction site. The elementary reaction of ozone with the double bond of an alkene obeys a bimolecular law[71], whereas the overall process may be described by more complex relationships. In particular, in the gaseous phase there is difference between the kinetics of the reaction in the presence and absence of oxygen[56,58,59,72]. Thus for example, the kinetics of the reaction of ozone with tetrafluoroethylene are described by the relationship[73]:

$$d[O_3]/d\tau = k_1[O_3][C_2F_4] + k_2[O_3]^2[C_2F_4],$$

where

$$\lg k_1 = (8.2 \pm 0.5) - (9500 \pm 700)/2.3\,RT;$$
$$\lg k_2 = (14.6 \pm 0.4) - (10100 \pm 600)/2.3\,RT$$

(k_1 and k_2 in litre mole^{-1} s^{-1} units), and the reaction of ozone with allene is described by the relationship[74]:

$$d[O_3]/d\tau = k'_1[O_3][C_3H_4] + k'_2[C_3H_4][O_3]^2/[O_3]_0,$$

where

$$\lg k'_1 = (6.0 \pm 0.7) - (5500 \pm 1000)/2.3\,RT;$$
$$\lg k'_2 = (6.9 \pm 0.7) - (6200 \pm 800)/2.3\,RT.$$

In both cases the second term takes account of the reaction of the intermediate products with ozone, responsible for its chain decomposition.

Table 2. Rate constants (10^{-3} k, litre mole^{-1} s^{-1}) for the reaction of ozone with alkenes in the gaseous phase at 25 °C.[56,57,71,74–80]

Alkene	Data from Ref.75	Data from Ref.76	Data from Refs.56,57,77–79	Alkene	Data from Refs.57,71, 77, 80
Ethylene	1.6±0.2	1.8	1.6[77]; 0.8[78]; 1.02[57]	Propene	7.1[57]
But-1-ene	6.2	3.9	—	Allene	0.09[74]
trans-But-2-ene	260±40	3	29[78]	Butadiene	4.5[57]
cis-But-2-ene	200	17	63[56]	1,1-Dichloroethylene	0.0022[71]
Isobutene	14±2	3.6	3.7[78]; 0.49[79]; 5.4[56]	1,2-Dichloroethylene	0.24[79]
2-Methylbut-2-ene	450	—	—	Tetrafluoroethylene	31[80]
Trimethylethylene	—	12	—	Hexafluoropropene	1.3[80]
Cyclopentene	—	4.6	61[77,78]	Octafluorobutene	1.6[80]
Pent-1-ene	—	3.9	3.2[77]; 4.5[78]		

Table 2 gives the rate constants for the reaction of ozone with alkenes having different structures. The data in Table 2 do not make it possible to establish a relationship between

the structure of an alkene and the rate of its reaction with ozone; moreover, the data given by different authors sometimes differ considerably (for example for *cis*- and *trans*-but-2-ene). The temperature dependence of the reaction rate has been used to find the activation energies of the process and the pre-exponential factors for a number of alkenes (Table 3). The high rate constants and low activation energies readily explain why the unsaturated components of a contaminated atmosphere are decomposed to the extent of more than 50% by atmospheric ozone, despite the fact that both the ozone and the unsaturated hydrocarbons are present in the atmosphere in small quantities[61,83]. This reaction, together with the reaction of ozone with SO_2 and NO_x, facilitates the formation of photochemical smog in large cities, and usually appears as one of the key reactions in the overall model describing the dynamics of the urban atmosphere[84,85].

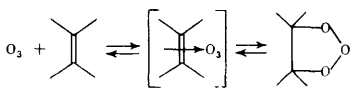
Table 3. Parameters of the Arrhenius equation for the reaction of ozone with alkenes in the gaseous phase*.

Alkene	$10^{-5}A_0$, litre mole^{-1} s^{-1}	E, kcal mole^{-1}
Ethylene	0.0016[77]; 16[75]; 54[81]; 3.2[79]	4.2±0.4[77]; 4.0±0.4[75]; 2.6[81]; 4.9[79]
Propene	0.00037[81]; 2.9[79]	1.9[81]; 3.9[79]
Butene	18	1.7
trans-But-2-ene	3.6[75]; 2.6[79]; 35	0.2±0.3[75]; 2.3[79]; 1.1
cis-But-2-ene	19	0.96
Isobutene	14[75]; 19	2.8[75]; 1.7
2,3-Dimethylbut-2-ene	17	0.82
Hex-1-ene	0.061[77]	

*The values without references are taken from Ref. 82.

2. Kinetics of the Reaction in Solution

In the examination of the reaction in the gaseous phase, it was noted that the reaction of ozone with a double bond is often complicated by side reactions. For the reaction in solution, in the case of simple alkenes, a stoichiometric reagent ratio of 1 : 1 is typical, and more than 95% of the products are formed by a single reaction path. This means that the rate of consumption of the starting materials characterises the reactivity of the ozone–alkene system. Experiments at low temperature, where the intermediate products can accumulate in large quantities and, after evaporation of the system, can regenerate the starting materials to be observed:



have shown that the contribution of the back reactions may be neglected. In a first approximation, the kinetics of the reaction in solution are described by a bimolecular law (Fig. 1).

The published reaction rate constants have been obtained by three methods: by measuring the relative rate of consumption of the alkene being studied, relative to a standard compound[86]; by measuring the rate of absorption of ozone from a gas stream[32]; and by the stopped-flow method[87]. The reaction rate constants in solution are more than an order of magnitude greater than those for the gaseous phase. This may be due to the experimental difficulty of measuring the rates of the rapid gas-phase reactions. Theory does not yet give an unambiguous answer to the question of the ratio of the rate constants in bimolecular reactions in the liquid and gaseous phases[88,89], although it can explain the decrease in the rate constant. For slow processes, such as, for example, the reactions of ozone with saturated hydrocarbons, the rate constants are similar for the solution and the gaseous phase[90].

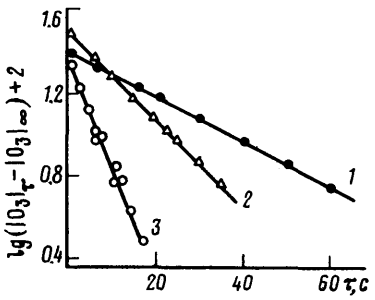
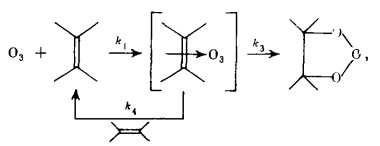


Figure 1. Kinetics of the reaction of ozone with vinylidene chloride in CCl_4 at 20 °C and different initial concentrations of vinylidene, M: *1*) 1×10^{-3}; *2*) 2×10^{-3}; *3*) 5×10^{-3}.

A study of the dependence of the reaction rate on the concentration of the alkenes over a wide concentration range showed that the kinetics of the reaction are described only approximately by the bimolecular law. The experimental data show best agreement with the scheme[3,91]:



in which a new reaction has been introduced—the reaction of the intermediate ozone–alkene complex with another alkene molecule, leading to decomposition of the complex to the starting materials. The observed rate constant k_{obs} is related to the rate constants of the first and subsequent stages by the equations ([Alkene] is the concentration of the alkene):

$$k_{obs} = k_1 k_3/(k_3 + k_4[\text{Alkene}])$$

or

$$1/k_{obs} = 1/k_1 + k_4[\text{Alkene}]/k_1 k_3.$$

Fig. 2 gives as an example the time dependence of the concentration of ozone in the gas stream at the outlet from a reaction vessel containing a solution of acrylic acid (AC), and the dependence of $1/k_{obs}$ on [AC], calculated from these data[32]. The values obtained are $k_1 = 4.2 \times 10^3$ litre mole^{-1} s^{-1} and $k_4/k_3 \doteq 8 \times 10^6$.

This characteristic feature of the reaction must be borne in mind when comparing the results of different studies or when examining the influence of the characteristic features of the structure of alkenes on their reactivity towards ozone.

The temperature dependence of the reaction rate in solution has been studied only for fumaric and maleic acids and maleic anhydride[91]; in the range 17–42 °C, the activation energies are 3, 6, and 6 kcal mole^{-1}, and the pre-exponential factors 1.6×10^6, 77.2×10^6, and 9.7×10^6 litre mole^{-1} s^{-1}

respectively. The rates of the reactions of non-substituted alkenes with ozone are greater by 2–3 orders of magnitude than that for fumaric acid, and the activation energies are 0.5–2 kcal mole^{-1}, which explains the weak influence of temperature on the reaction rate.

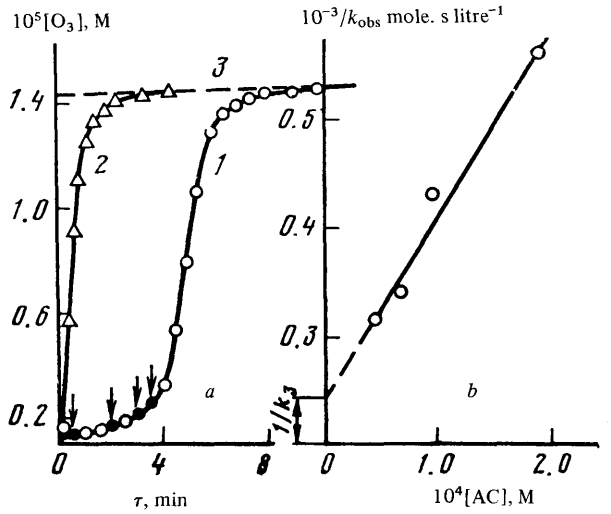


Figure 2. Time dependence of the concentration of ozone at the outlet from the reaction vessel (*a*) and plot of $1/k_{obs}$ against the concentration of acrylic acid (*b*): *1*) 2×10^{-4} M acrylic acid; *2*) CH_3COOH; *3*) concentration of ozone at the inlet to the reaction vessel, CH_3COOH, 20 °C. The arrows indicate the points used to calculate k_{obs}.

The experimental activation energies typical of the reactions of ozone with unsaturated compounds lie in a range which is not favourable for interpretation; their orders of magnitude do not differ greatly from those of many contributions which are usually difficult to incorporate and which are neglected at values of $E_{expt} \geq 10$ kcal mole^{-1} [92] (these contributions include the energy of reorientation of the solvation layers, the thermal energy of the molecules, etc.). Finally, in the range of these values it is in general difficult to expect that E_{expt} will be independent of temperature, since by definition, $E_{expt} = E_0 + 1/2RT$, where E_0 is the height of the potential barrier at 0 K.

Table 4 shows that low-molecular-weight alkenes having a terminal double bond (hex-1-ene, oct-1-ene, and octadec-1-ene) react with ozone at similar rates. On going to compounds having a C=C bond in the interior of the molecule (hex-2-ene, methyl oleate), there is a considerable increase in the reaction rate. Increase in the number of alkyl substituents on the carbon atoms at the double bond leads to an increase in the reaction rate (compare, for example, hex-1-ene and 2-methylpent-2-ene, acrylic and methacrylic acids, polybutadiene and polyisoprene). C_5–C_{12} cycloalkenes having one C=C bond react at similar rates, irrespective of the size of the ring, and, apparently, slightly less rapidly than a compound having a $\diagdown\!\!\diagup C{=}C \diagdown\!\!\diagup$ bond in an open chain (for cyclohexene, $k_1 = 4 \times 10^5$, compared with 1×10^6 for methyl oleate). The introduction of a phenyl substituent leads to an increase in the reaction rate, and not to a decrease, which might have been expected from the direction of the inductive effect of the phenyl ring. Increase in the number of phenyl groups (styrene–stilbene–1,1,4-tetraphenylbutadiene) has almost no influence on the reaction side.

Table 4. Rate constants for the reaction of ozone (litre mole^{-1} s^{-1}) with different unsaturated compounds in CCl_4 at 20 °C.[93]

Compound	$10^{-5}k_1$	Compound	$10^{-5}k_1$	Compound	k_1
Ethylene	0.4	Norbornene	5	Maleic acid	7.8
But-1-ene	1.3	Styrene	3	Fumaric acid	1.5
cis-But-2-ene	1.63	Stilbene	1.8	Maleic anhydride	14.1
Isobutene	0.97	1,4-Diphenylbutadiene	0.9	2,6-Dimethylhept-2-ene-carboxylic acid	2800
1,3-Butadiene	7.4	1,1,4,4-Tetraphenyl-butadiene	0.8	Vinyl chloride	1180
Pent-1-ene	1.4			Allyl chloride	8500
2-Methylbut-2-ene	5	Acenaphthene	2.2	Bis-1,2-dichloro-ethylene	35.7
Hex-1-ene	1.4	Acrylic acid	0.042		
Hex-2-ene	5	Methacrylic acid	0.078	Vinylidene chloride	22.1
2-Methylpent-2-ene	5	Methyl methacrylate	0.078	Trichloroethylene	3.6
Oct-1-ene	1.3	Oleic acid	10	Tetrachloroethylene	1.0
Octadec-1-ene	1.8	Methyl oleate	10	2-Bromopropene	2800
Cyclopentene	4	Polybutadiene	0.6	Acrylonitrile	100
Cyclohexene	4	Squalene	7.5	Tetracyanoethylene	0.4
Cyclododecene	4	Natural rubber	4.4	1,1,2-Triphenyl-2-nitroethylene	3.6
Cyclododeca-*trans*-1,5,9-triene	3.5	Gutta percha (*trans*-polyisoprene)	2.7		
		Polychloroprene	0.042	1,1-Diphenyl-2,2-dinitroethylene	0.7

The reaction of ozone with an unsaturated compound can be regarded as the reaction of an electrophile with a donor. Thus the introduction into the molecule of electronegative substituents such as Br, $Cl-C\overset{O}{\diagup\!\!\diagdown}OH$, and NO_2 decreases the electron density in the π-bond and leads to a significant decrease in the rate of the reaction with the corresponding compound. Comparison of macromolecular compounds with their low-molecular-weight analogues readily shows that the reaction rate constants of the polymeric products are lower (compare polybutadiene with methyl oleate and cyclododeca-*trans*-1,5,9-triene or polyisoprene with squalene and 2-methyl-2-ene).[94] A distinct difference is also observed between *cis*- and *trans*-isomers (maleic and fumaric acids, cyclohexene and cyclododeca-*trans*-1,5,9-triene, gutta percha and natural rubber).

The ozone molecule is small, so that steric factors do not play a significant role in the reaction. In only one of the cases in Table 4 is it possible to establish anomalies in the rate which might be attributed to steric effects. Comparison of the reaction rate constants of acrylic, methacrylic, and 2,6-dimethylhept-2-enecarboxylic acids (4.2×10^3, 7.8×10^3, and 2.8×10^3 litre mole^{-1} s^{-1} respectively) with allowance for the inductive effect of the substituents (the method for taking account of this effect is described below) shows that in the absence of steric hindrance, the reaction rate constant for 2,6-dimethylhept-2-enecarboxylic acid should be 7.8×10^3–1×10^4 litre mole^{-1} s^{-1}, whereas the experimental value is smaller by a factor of three.

3. Correlation Between the Structure of an Unsaturated Compound and the Rate of Its Reaction with Ozone

Table 4 shows that the rates of the reactions of ozone with alkenes have structures which differ considerably. For example, for oleic acid and tetracyanoethylene the values differ by more than six orders of magnitude. It is therefore very important to establish the quantitative relationship between the structure of an alkene and its reactivity to ozone, so that this relationship can be used for approximate estimates in work with new substances.

The first attempt in this direction was made by Cvetanovic and Williamson[86], who found a linear relationship between the logarithm of the rate constant and the ionisation potential of chlorinated ethylenes (Fig.3). In spite of the existence of a comparatively simple relationship, this approach cannot be regarded as successful, chiefly because a change in the potential by a small amount ($\lesssim$0.1 V) is accompanied by a change of several orders of magnitude in the reaction rate, and this makes the practical application of the observed relationship difficult. Moreover, the ionisation potential is a generalised characteristic of the molecule as a whole, and in the case of complex molecules, this relationship is not fulfilled in simple form. Distant parts of the molecule, which do not influence the reactivity of the C=C bond, make their contribution to the overall value of the potential.

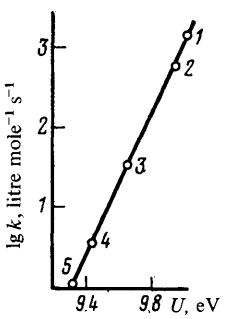


Figure 3. Plot of lg k against the ionisation potential for chlorinated ethylenes: *1*) C_2H_3Cl; *2*) *trans*-1,2-$C_2H_2Cl_2$; *3*) *cis*-1,2-$C_2H_2Cl_2$; *4*) C_2HCl_3; *5*) C_2Cl_4.

The rule that there is a linear relationship between the free energy changes, which establishes a semi-quantitative relationship between the rate constants and the inductive effects of a substituent at the reactive centre of molecules[95,96], is fulfilled for the decomposition of molozonides[97] and ozonides[98], and slightly less satisfactorily for the reaction of ozone with substituted alkenes[93]:

$$\lg(k_i/k_0) = \rho\sigma_{lit},$$

where k_0 and k_i are the rate constants for the reactions of ozone with the C=C bond of a compound taken as standard and the compound containing the substituent being studied, X_i; σ_{lit} is the inductive constant of the substituent, taken from published data, and ρ a proportionality coefficient, called the "sensitivity of the series". The standard compound chosen was ethylene, for which there are no substituents apart from hydrogen at the C=C bond. The plot of $\lg(k_i/k_0)$ against σ_{lit}, constructed from the data in Table 4, is given in Fig.4. In the set of compounds given, a significant deviation from the overall linear relationship is shown by the compounds containing phenyl substituents (styrene, stilbene), and maleic and fumaric acids. Since the rates of the reactions of ozone with acids and their methyl esters are identical (oleic acid and methyl oleate, methacrylic acid and methyl methacrylate), the values of σ_{lit} for the methyl esters were taken as equal to σ_{lit} for the acids (0.265).

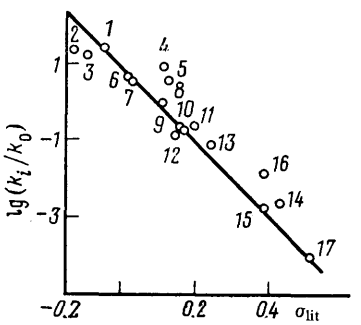


Figure 4. Plot of $\lg(k_i/k_0)$ against the inductive constant of the substituent[93]: *1*) methyl oleate, *2*) methylpent-2-ene, *3*) hex-2-ene, *4*) styrene, *5*) stilbene, *6*) hex-1-ene, *7*) octadec-1-ene, *8*) ethylene, *9*) methyl methacrylate, *10*) methacrylic acid, *11*) allyl chloride, *12*) 2-bromopropene, *13*) acrylic acid, *14*) acrylonitrile, *15*) maleic acid, *16*) fumaric acid, *17*) 1,1,2-triphenyl-2-nitroethylene.

Allowance for the spatial arrangement of the substituents and for electrostatic interactions might apparently improve the agreement between experiment and the model, but even as a first approximation it can be seen that the published values of σ_{lit} can be used to estimate the probable rates of the reactions of ozone with different unsaturated compounds. A negative sign for the coefficient ρ indicates that the reaction of ozone with the C=C bond is electrophilic.

An interesting and as yet insufficiently clear question is the relationship between the reactivities of different groups in a molecule and the degree of deformation of the valence bonds. This deformation may be due to different factors (mechanical forces, steric factors, etc.). The alkenes given in Table 4 include compounds in which the C=C bond is strained for some reason. These include cycloalkenes having large rings (cyclododecene and cyclododecatriene), various norbornenes, and acenaphthene, and unsaturated compounds having bulky substituents at the C=C bond, for example 2,6-dimethylhept-2-enecarboxylic acid in Table 4. Compounds having strained bonds are more reactive than alkenes having an unstrained bond[99]. This is revealed, for example, in the fact that they readily react with diazomethane, whereas alkenes having unstrained C=C bonds do not react in this way. The decrease in the strain in the series of cycloalkenes $C_4 > C_5 > C_6$ coincides with the decrease in the yields of the corresponding pyrazolines[100].

Table 5 gives the published[101] rate constants for the reactions of C_5–C_{12} *cis*-cycloalkenes with ozone. There is a clear relationship between the size of the ring and the rate of the reaction of the compound with ozone. As expected, the reactivity shows a better correlation not with the excess energy of the molecule as a whole but with that fraction of

the strain corresponding to the double bond[101]. Analysis showed[101] that the chief contribution to the change in the reactivity on going from one ring to another is made by the steric factor, determined by the difference between the hybridisation of the carbon atoms at the double bond in the original state and in the activated complex.

Table 5. Rate constants for the reaction of O_3 with *cis*-cycloalkenes (0 °C, CCl_4) and the excess strain of the cycloalkene and the double bond, kcal mole^{-1}.

Ring	$10^{-5}k$, litre mole^{-1} s^{-1}	Cycloalkene	C=C
C_5	4.1	5.9	+2.3
C_6	0.96	0	0
C_7	2.5	5.2	+0.7
C_8	6.0	5.8	−1.6
C_9	3.1	9.4	−0.6
C_{10}	0.73	6.6	−0.7
C_{12}	0.59	—	

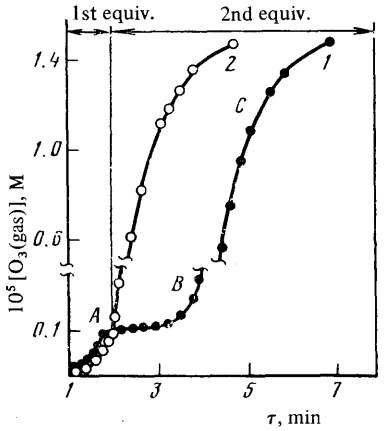
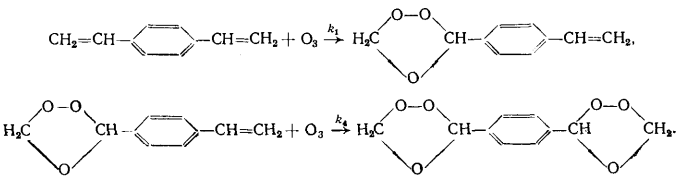


Figure 5. Plot of $[O_3(gas)]$ against reaction time for *p*-divinylbenzene (*1*) and styrene (*2*); *1*) 6×10^{-5} M, *2*) 1×10^{-4} M, CCl_4, 20 °C.

If the alkene molecule contains not one but several C=C bonds, the C=C bonds at a sufficient distance from one another react as independent kinetic units, and the addition of ozone at one of them has little influence on the reactivity of its neighbours. The inductive effect of a substituent usually decreases by a factor of 2.7 through each carbon atom of a saturated hydrocarbon chain[102], so that these influences are of little significance after only 3–4 carbon atoms. In the case of conjugated C=C bonds (1,3-dienes, *p*-divinylbenzenes, etc.), the difference in reactivities due to the structure of the original alkene may be increased by the positive inductive effect of the ozonide formed at a neighbouring group. This can be clearly seen for the case of divinylbenzene (DVB):

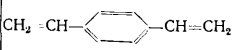
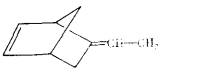
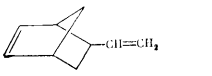
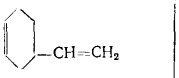
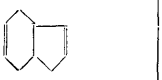
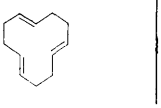


The fact that the reaction takes place in two stages is reflected in the form of the plot of $[O_3(gas)]$ against τ in a bubbler reaction vessel, shown in Fig.5; typical curves for styrene and divinylbenzene are given for comparison. The relationships obtained can be used to calculate rate constants. The rate constant for the reaction of the second double bond of DVB with ozone, k_4, is calculated along section AB using the equation:

$$k_4 = \frac{\omega([O_3]_0 - [O_3(g)]}{\alpha[DVB]''[O_3(g)]}$$

where $[O_3]_0$ and $[O_3(gas)]$ are the concentrations of ozone in the gas flow at the inlet and outlet of the reaction vessel; α the solubility coefficient of ozone; [DVB]" the current concentration of double bonds in the solution; and ω the specific rate of supply of the gas mixture.

Table 6. Rate constants for the reaction of ozone with di- and trialkenes in CCl_4 at 20 °C, litre mole^{-1} s^{-1}.

Compound	Formula	$10^{-5}k_1$	$10^{-5}k_4$
Divinylbenzene		2.1	0.22
Ethylidenenorbornene		3.6	2
Vinylnorbornene		3.3	0.82
Vinylcyclohexene		1.4	0.8
Tetrahydroindene		1.4	1.4
Cyclododeca-1,5,9-triene		3.5	3.5

The values of k_1 are found from the equation

$$k_1 = \frac{\omega([O_3]_0 - [O_3(g)]) - \alpha k_4[O_3(g)][DVB]_0}{\alpha[DVB]'[O_3(g)]},$$

where $[DVB]_0$ is the initial concentration of divinylbenzene, and [DVB]' the current concentration of DVB molecules having two double bonds. The calculations are possible when k_1 and k_4 differ significantly, and this is the case for divinylbenzene and many other alkenes (Table 6).

For divinylbenzene it is easily possible to follow the change in the reaction rate constant after the addition of one ozone molecule and to show how this change agrees with the general principles of the theory. The rate constant for the reaction of ozone with one C=C bond of the original divinylbenzene, because of the conjugation of the bonds, should be lower than that for styrene, as observed experimentally. When ozone attacks the first bond, the conjugation is broken, so that it might seem that the subsequent stage of the reaction should proceed at a rate close to that observed for styrene (3×10^5 litre mole^{-1} s^{-1}), but the products of the addition of ozone, that is the ozonides, have an appreciable inductive influence on the reaction, so that the second stage is much slower than the first.

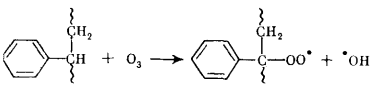
Comparison of the rate constants for the reactions of ozone with ethylidene- and vinylnorbornenes indicates that the initial attack is directed at the double bond in the side chain, since changes in its structure influence k_1, whereas the values of k_4 for the two isomers are identical. The separation of the bonds from one another, and the identical configurations of the immediate environments, make the C=C bonds in cyclododeca-1,5,9-triene equivalent, as shown by the fact that the rate constants for all three stages are identical.

The study of the kinetics of the reactions of ozone with macromolecular compounds is of exceptional interest, since this reaction is the chief cause of the cracking of rubber articles[103]. At the same time, the study of the kinetics of the reactions of ozone with the C=C bonds in macromolecules may give valuable information on the specific influence of the polymeric state on the course of chemical reactions. This question has been attracting considerable attention in recent years[104,105]. Flory[106] put forward the principle that the reactivity of the terminal group or any other group of a polymeric molecule is independent of its length. It is known, however, that certain reactions of polymers take place much more slowly than the reactions of the low-molecular-weight analogues (for example, catalytic hydrogenation), whereas a number of enzyme reactions take place extremely rapidly, but are not shown by the low-molecular-weight compounds[107].

In polymers, approach of the functional groups is possible, and this has a considerable influence on the kinetics of the reactions of these groups[104]. The coiled or straight forms of the macromolecule may create different conditions for the encounter between the reagent and the reacting parts of the macromolecule[108]. The applications of Flory's principle to reactions in which there is no specific interaction between the groups which have approached one another, or hindrance caused by diffusion, have been refined[109]. One of the greatest difficulties in this field is that there are no simple reactions which might serve as models for the study of the specific properties of a macromolecule. In this respect, the reaction of ozone with C=C bonds is exceptionally convenient: it takes place over a wide temperature range, the nature of the solvent has no influence on the reaction rate, and the mechanism of the reaction has been well studied and is the same for low-molecular-weight and macromolecular compounds.

Table 4 gives the rate constants for the reactions of ozone with polymeric compounds and their low-molecular-weight analogues. A good correlation is observed between the reactivities of the monomer and the polymer. In the macromolecular series, the reactivity decreases with change in the inductive effects of the substituents from electronegative to electropositive. It is well known that polychloroprene rubbers are more stable to ozone ageing than butadiene or polyisoprene rubbers. Attempts have been made to relate this increase in stability to a lower reaction rate; the imperfect methods used, however, did not make it possible to detect differences in the rates[110]. The data given in Table 4 show that high stability does in fact correspond to a lower reactivity.

As in the case of the low-molecular-weight alkenes, the *cis*-isomers (natural rubbers) react more rapidly than the *trans*-isomers (gutta percha). The effects associated with change in the length of the macromolecule or the extent to which it is coiled are apparently small, and could not be detected[111,112]. A noteworthy feature is that in all cases the reaction rate constant is smaller by a factor of 1.5–3 than that for the corresponding low-molecular-weight analogue. This characteristic feature cannot be attributed to the specific features of the electrophilic addition of ozone to the C=C bond. The reactions of ozone with the saturated polymers polystyrene and polyisobutene (which take place by a free-radical mechanism[111]):

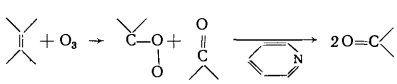


are also slower than those of the low-molecular-weight analogues. The accuracy of the experiment does not make it possible to determine whether the decrease in the rate constant is due to the pre-exponential factor or to the exponential term of the Arrhenius equation (by putting $A_{mon} = A_{pol}$ for $k_{mon}/k_{pol} = 2$, we should have obtained the difference $E_{mon} - E_{pol} = 0.5$ kcal mole^{-1}); simple examination shows, however, that the reacting part of the polymer chain should have a lower mobility, since it is joined to extremely long chains. This may decrease the probability of a favourable orientation at the moment of encounter with the reagent.

4. Influence of Solvent on the Mechanism and Kinetics of the Addition of Ozone to the C–C Bond

Many compounds, for example alcohols and acids, can react with the intermediate species, chiefly the zwitterion, altering the direction of the reaction[27,46].

As noted above, in the presence of alcohols and acids, hydroxyalkyl- and hydroxyacylhydroperoxides are formed instead of ozonides[26,113]. When pyridine is used[114], reduction of the zwitterion to the corresponding carbonyl derivative probably takes place:



Saturated hydrocarbons, chloroform, and other halogen derivatives, used as solvents, apparently do not take part in the intermediate stages of the process, although it has been reported that they influence the yield of monomeric and polymeric ozonides[115,116].

An increase in the yield of acids when ozonisation is carried out in esters has been noted[117]. The chemical and physical properties of the system can be altered, sometimes radically, by using a suitable solvent. For example, in the presence of organic acids, gels are not formed in the ozonisation of cyclic alkenes, and the peroxide products of the ozonisation more readily undergo further transformation. In spite of their obvious importance, however, the problems of the influence of the solvent on the mechanisms of the reactions taking place have as yet been little studied, the published data are only preliminary, and the nature of the peroxide compounds and their interconversion, which has been observed by thin-layer chromatography[54], have not been established.

There are particularly few data on the influence of the medium on the rate of the reaction of ozone with alkenes. Only two papers have been published[15,87], giving different results. Razumovskii and Berezova[15] compared the influence of CCl_4, $C_{10}H_{22}$, CH_3COOH, H_2O, and a $CH_3COOH-H_2O$ binary mixture on the rate of the reaction of ozone with acrylic acid; the dielectric constant ranged from 2 to 80; in all cases the reaction rate constant was independent of the nature of the solvent. Henry and coworkers[87] studied the rate of the reaction of ozone with substituted stilbenes in solvents of different polarity (from CCl_4 to CH_3CN); in all cases, the reaction rate increases by a factor of 2–3 on going from CCl_4 ($\varepsilon = 2.24$) to CH_3CN ($\varepsilon = 37.4$). Since Razumovskii and Berezova[15] studied a wider range of ε and used a relatively unreactive alkene (which reduced the experimental difficulties), and since for the closest analogue of the reaction—the reaction of ozone with a C≡C bond—it has also been found that the polarity of the medium has no influence on the reaction rate[118], it may be assumed that the reaction rate depends little or not at all on the solvent.

The fact that the polarity of the solvent has no influence on the reaction rate is in good agreement with the suggestion that the reaction involves a weak intermediate complex in which there is no appreciable transfer of electron density from one partner to the other, so that there is no significant rearrangement of the solvation layer.

IV. INTERMEDIATE STAGES IN THE ADDITION OF OZONE TO ALKENES

The intermediate stages of the reaction of ozone with unsaturated compounds, and the properties and structure of the labile intermediate products, are being studied intensively[28,29,32,119–127]. It still cannot be said that all the characteristic stages of the process are known, but the key reactions have been determined.

This section will examine the qualitative and quantitative characteristics of the stages of the scheme[1] given below. In the reaction of ozone with alkenes in solution, the first stage of the reaction is apparently the formation of a complex of ozone with the C=C bond of the alkene[28,91]. Its formation has been detected from the colour of the solution[7,28], the kinetic characteristics of the reaction[3,91], and the PMR and infrared spectra[43]. In the complex, both partners retain character and can be separated by decomposing the complex. At a low temperature, the reaction can be held at the stage of complex formation, appreciable quantitaties of which can be accumulated[7,119]. This means that the principal activation barrier to the reaction lies on the reaction coordinate after complex formation, as represented schematically in Fig.6. The complex has characteristic adsorption bands in the range 700–1000 cm^{-1}, which disappear rapidly with increase in temperature[119,120].

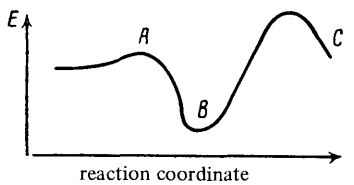
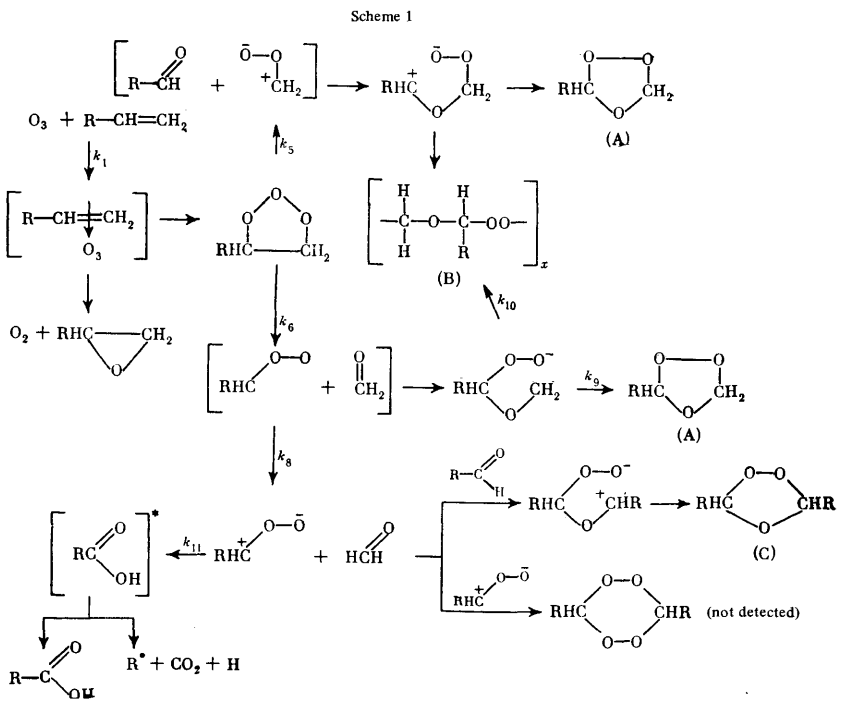
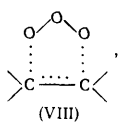


Figure 6. Change in the potential energy of the system in the transformation of the original reagents into the primary ozonide; *B* corresponds to the formation of the complex.

Scheme 1

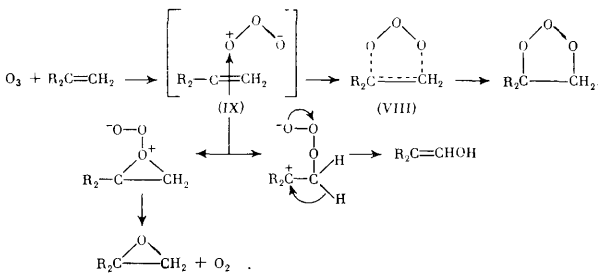


Only tentative conclusions can be reached about the structure of the complex formed. There are serious objections to structure (VIII)



(VIII)

which would correspond to the idea of synchronous 1,3-dipolar addition. It does not explain the mechanism of formation of ozides and vinyl alcohols by the action of ozone on branched alkenes[128]. A scheme including the intermediate formation of a π-complex with a terminal oxygen atom in ozone (IX) has been proposed:

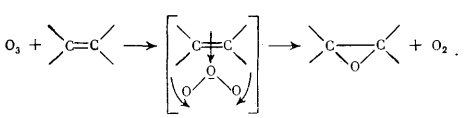


The qualitative character of the data makes it impossible to determine whether (VIII) is formed from (IX) or whether they accumulate in parallel, as suggested by Hull and coworkers[129]. Moreover, the polar structure assigned to (IX) contradicts the above conclusion that the medium does not influence the reaction rate[15]. The kinetic data indicate that in the transition state *A* (Fig.6) and the first intermediate complex, which has a similar structure (corresponding to the minimum *B* in Fig.6), the displacement of charges is slight, so that the solvation does not differ significantly for the original state and the transition state. Quantum-mechanical calculations also show that the formation of open complexes of type (IX) is unfavourable[127]. If it is assumed that the occupied molecular orbitals of ozone in the ground state $^1A_1$ have the configuration

$$O_3[(\text{core})(4b_2)^2(6a_1)^2(1a_2)^2],$$

and that the lowest unoccupied molecular orbital is $2b_1$,[12] it is found that in electrophilic reactions the largest coefficient of the AO corresponds to the central oxygen atom. In other words, electrostatic and polarisation factors favour the formation of a complex in which the optimum overlap of the π-orbital of the alkene and the lowest unoccupied molecular orbital of ozone corresponds to the crossed structure of the complex (Fig.7).

The formation of both the molozonide (for transverse displacements of the original components) and other products from the crossed complex can readily be represented. In particular, the deformation vibrations of the terminal oxygen atoms can probably lead to the formation of oxides:



The next intermediate product in order of relative stability is the molozonide, which can be accumulated in the system and studied. In most cases, the molozonide retains the stereoisomerism of the original alkene[130,131]. The *trans*-ozonide is much more stable than the *cis*-molozonide: the former can be observed in the system as far as −60 °C, whereas the second decomposes rapidly even at −130 °C;[38,119] the *cis*- and *trans*-isomers also differ in various other properties. Table 7 gives as an example the PMR spectra of the isomeric molozonides obtained from different alkenes.

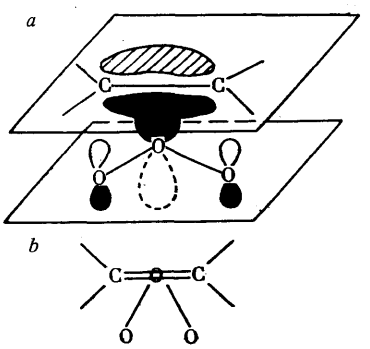


Figure 7. Schematic representation of the ozone–alkene complex: *a*) in the axonometric projection, *b*) view from above.

Table 7. Characteristic absorption bands in the PMR spectra (σ, p.p.m.) of the *cis*- and *trans*-molozonides and normal ozonides from the *cis*- and *trans*-molozonides in CF_2Cl_2 at −130 °C.[131]

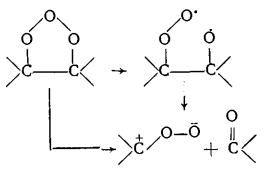
Original alkene	Molozonide	Ozonide
cis-But-2-ene	4.52 (u)*	5.05 (q)*
trans-But-2-ene	4.12 (q)	5.00 (q)
cis-Pent-2-ene	4.35 (m)*	4.93 (m)*
trans-Pent-2-ene	4.08 (m)	4.95 (u)
trans-Hex-3-ene	4.07 (t)	—

Symbols: q = quartet, m = multiplet, u = unresolved, t = triplet; the asterisks mark the data for the *cis*-molozonides.

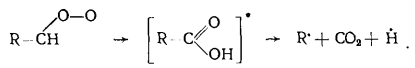
The molozonides have characteristic absorption bands in the range 700–1000 cm^{-1}, which are observed at low temperatures (between −175 °C and −100 °C),[119,121] but which disappear rapidly with increase in temperature to values between −80 °C and −60 °C. The strength of the C–O bond in the molozonide has been estimated as 45 kcal $mole^{-1}$.[132] The molozonides can be reduced to the corresponding diols by the action of an alkylmagnesium bromide or other reducing agents on the products of the reaction of ozone with the alkene at low temperature[123,133]. The first proof that the reaction involves the formation of molozonides involved this reaction.

The molozonide is unstable, and readily decomposes to give two fragments—the zwitterion and a carbonyl compound. It may be assumed that the reaction involves the intermediate rupture of one of the O–O bonds and the formation of a

biradical

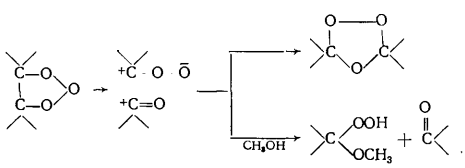


which decomposes rapidly to give the zwitterion and the carbonyl compound. This scheme has been used[66] to explain the high concentrations of free radicals in the reaction of ozone with alkenes in the gaseous phase. Although it has been reported that free radicals have been detected in the reaction of ozone with branched alkenes in solution[134], the accumulated experience in the study of this reaction nevertheless suggests that its principal direction is the direct conversion of the molozonide into two fragments without detectable radical states. The most probable route for the formation of radicals in solution is the isomerisation of the zwitterion and the subsequent decomposition of the excited molecules[44]:



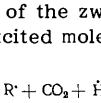
Since conditions in the gaseous phase are not more favourable than those in solution for the stabilisation of free radicals, yet the rates of the processes of energy dissipation are nevertheless greatly reduced, it is more logical to attribute the increase in the concentration of radicals in the gaseous phase to transformation of the zwitterion and to assume that the mechanism of the decomposition of the molozonide is the same for the liquid and gaseous phases, and involves a non-radical route.

The kinetics of the decomposition of the molozonide have been studied in solution by a chemical method[22] and by PMR spectroscopy[135]. In the chemical method, specimens removed at measured time intervals were mixed with alcohol. The molozonide which had not reacted at this moment was converted to the methoxyhydroperoxide in the presence of alcohol:

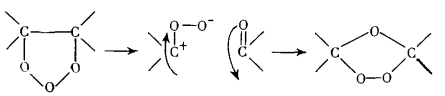


The concentration of the methoxyhydroperoxide in the reaction products gave a measure of the concentration of the molozonide.

The results obtained by the two methods showed good agreement: at -100 °C, the rate constant of the monomolecular decomposition ($k_5 \cong k_6$, see scheme 1) is equal to ~0.1 s^{-1}; the activation energy of the reaction is ~7–8 kcal $mole^{-1}$. The value of the activation energy can be used for a rough estimation of the energy of the O–O bond in the molozonide, which should differ from the activation energy by the difference in the free energies of solvation of the original molozonide and the transition state ($D_{O-O} \cong E$ + 5–10 ≅ 12–17 kcal $mole^{-1}$). The zwitterion formed as a result of the decomposition is an extremely reactive compound, about which very little is known; it can be represented as an aldehyde oxide[38] or as a methylene peroxide[136]. The description of the structure of this intermediate species in the usual symbols presents certain difficulties. It is isoelectronic with ozone, and is apparently a valence-saturated compound, although it is strongly polarised, in view of the difference in the electronegativities of oxygen and carbon.

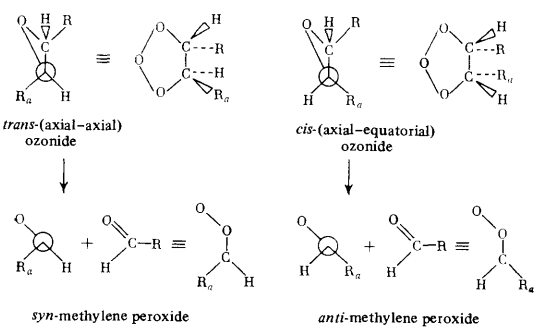
Quantum-mechanical calculations show that the cyclic structure of the zwitterion is energetically more favourable than the open structure[137]. This brings the discussion back to Harries' ideas[17], but at a different qualitative level. A recent study of the reaction of ozone with ethylene in the gaseous phase detected species having a mass number of 46, but the position of their peak did not coincide with that for formic acid[138]. The microwave spectra of this system showed bands at 29.938 GHz and 30.872 GHz, assigned to dioxiran H_2C-OO.[139] For alkenes unsymmetrical with respect to the C=C bond, conditions can be created for the preferential formation of the zwitterion at one of the carbon atoms, depending on the nature of the substituents. In particular, substituents having a positive inductive effect (CH_3, RCH_2, etc.) increase the probability of formation of the zwitterion at the given carbon atom[140], whereas substituents having a negative inductive effect (Cl,  , etc.) decrease it. The ratio of the probabilities is described by a relationship of the Hammett type[140]. When both carbon atoms have substituents, the probability of the addition of two oxygen atoms depends on the difference in the inductive constants of the substituents.

The pair (zwitterion and carbonyl compound) formed by the decomposition of the molozonide can combine again extremely rapidly, forming the ozonide (the arrows show the directions of the rotations of the fragments):

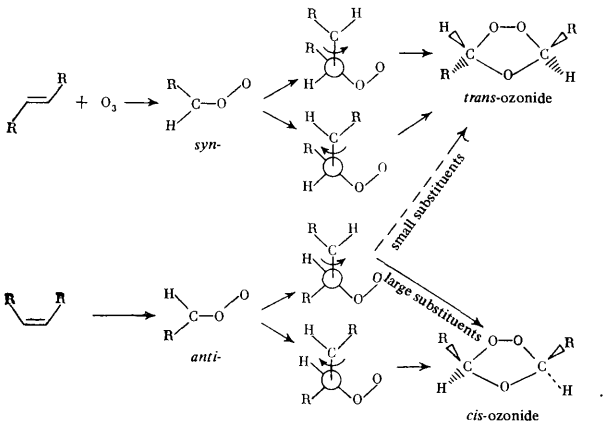


The formation of this compound is preceded by a change in the relative orientation of the fragments (rotation through 180°).

The composition of the final products usually carries valuable information on the processes preceding their formation. Thus analysis of the ratio of the *cis*- and *trans*-isomers in the ozonisation products showed that the zwitterion as it were "remembers" the structure of the original alkene. In spite of the free rotation at the stage of carbonyl formation, the preservation of the structure of the original alkene by the final ozonides is preferred[24,38,141]. This is attributed to the high barrier to rotation in the zwitterion (~29 kcal [136]), which fixes the *syn*- or *anti*-form of the zwitterion:



In the subsequent addition of the carbonyl, a difference betwen the structures of the substituents, together with the *syn*- or *anti*-form of the zwitterion, leads to the formation of *cis*- or *trans*-ozonides[136]:



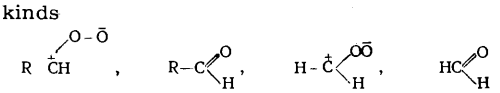
The recently detected influence of complex-forming species on the stereospecificity of the formation of ozonides was explained similarly[126]. A large amount of data has been published on the composition of ozonides[3,7,27,142–149], but only a few papers give a material balance of the principal components[32,41]. Table 8 gives the compositions of the reaction mixtures for several simple alkenes. Judging from the reaction products, most of the zwitterions are able to react with "their own" carbonyl compounds, with which they were formed from the molozonide, that is a clearly defined cage effect is observed[20,144].

Table 8. Composition of the reaction mixture after the ozonisation of the alkenes[32].

Component	Propene	Pent-1-ene	Hex-1-ene	Hex-1-ene
	−78° C			0° C
Normal ozonide (a)	73	67	70	75
Polymeric ozonide (B)	7	8	7	3
Crossed ozonide (C)	20	25	23	22
including:				
macromolecular ozonide	10	15	11	12
ethylene ozonide	10	10	12	10

Note; A, B, and C correspond to the final products of scheme 1, page 1171.

The decomposition of an unsymmetrical alkene gives species of four kinds

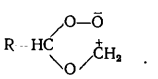


(X) (XI) (XII) (XIII)

in approximately equal proportions (allowance for the inductive effect of the substituent makes it possible to define this more accurately[140]). All the cages of the combination of (X) with (XIII) and of (XI) with (XII), giving A (scheme 1), and of (X) with (XI) and of (XII) with (XIII), giving C, are equally probable. The ratio ([A] + [B] − 0.5[C])/1.5 characterises the fraction of the transformation in the cage, which for all alkenes is close to 0.7. This indicates that the rate of reaction (7) in scheme 1 is comparable with the rate at which the particles leave the "cage". The duration of the existence of the pair of particles in the "cage" can be estimated from Einstein's equation[145,146] $\tau = \frac{1}{6}r^2/D$. For small molecules, $r = 4 \times 10^{-8}$ cm, $D = 10^{-5}$ cm s^{-1}; if it is assumed that the molecules can collide 10–100 times before moving apart, then $\tau = 10^{-11}$–10^{-10} s. For the present case, in the selection of the values of τ, it is also necessary to take account of the fact that an appreciable proportion of the zwitterions reacted outside the cage, forming crossed ozonides. This makes it possible to assume that the value of τ is close to the lower limit of the lifetime of the cage or even lower (10^{-9} s), so that

$$k_7 = 1/\tau = 1 \cdot 10^9 \ s^{-1}.$$

The activation energy of reaction (7) is low, since the cage effect was observed at all temperatures studied (from 30 °C to −78 °C), and the concentrations of the carbonyl compounds and bipolar ions were very low in all cases. Approximately 30% of the total quantity of molozonide decomposition products are able to leave the cage before the start of the reaction; an appreciable proportion leave with an unclosed ring:



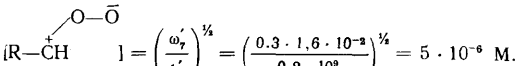
(XIV)

These reactive species move freely in the solution, and are subsequently converted into crossed and polymeric ozonides.

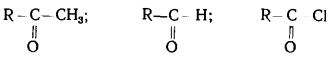
A certain concentration of alkenes and carbonyl compounds is established in the solution. Estimation of this concentration (from the quantity of formaldehyde carried away by the bubbline gas) showed that it is much lower than 10^{-3} M. It can be estimated from the following: $k_8 = 0.3 \times 10^9$; $k_7 = 0.3 \times 10^9$. Since ω_8 is the rate of diffusion, in this case it is possible to use the regular features of diffusion kinetics[147]. The published experimental data[32] then give

$$k_8 k_7/(k_8 + k_7) = k_7', \text{ from which } k_7' = 0.2 \cdot 10^8 s^{-1},$$

and



The nature of the substituents at the carbonyl group has a significant influence on the rate of its reaction with the zwitterion. The direction of the influence is the opposite of that observed in the reaction of ozone with the double bond or in the decomposition of the molozonide. Electron-donor substituents decrease the reaction rate, and electron-acceptor substituents increase it. Thus in the series of compounds



the rate of the reaction with the zwitterion increases[3]; the reaction rate constants in the cage, k_7, are 0.3×10^9, 1.0×10^9, and 4.2×10^9 s^{-1} respectively. The zwitterion in solution may react not only with the carbonyl group but also with another zwitterion[7].

In a number of cases, ozonide formation has not been observed at all, and dimeric peroxides and ketones have been obtained[55]. Dimeric peroxides have not yet been detected, however, in the ozonisation products of simple alkenes having an open chain. The formation of polymeric ozonides can be represented as follows: the primary association of the

zwitterion with the carbonyl compound takes place at high rates and without a significant heat change, whereas ring closure is associated with a considerable increase in the order of the system and hence with a decrease in its entropy. The rate of this process is apparently lower than that of the preceding process, and several of these unclosed rings are able to combine with one another before the ring closes. The polymeric ozonides are cyclic formations including an average of about three monomeric units in the case of alkenes having a normal structure[41,148]. The action of ozone on cycloalkenes gives macromolecular three-dimensional products, exhibiting typical properties of polymers[148].

To estimate the probable values of k_9 and k_{10} (see scheme 1), it is possible to make three assumptions: 1) $k_9 \geq k_7$; in this case, k_{10} takes a value $\geq 1 \times 10^{12}$ litre mole^{-1} s^{-1}, which is unlikely; 2) $k_{10} \cong k_7$; in this case,

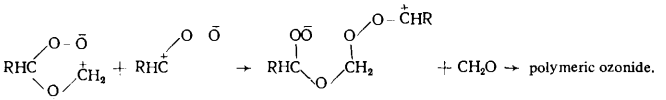
$$[\mathrm{XIV}] \simeq \left(\frac{1.6 \cdot 10^{-2} \cdot 0.1}{10^9}\right)^{1/2} \simeq 1.3 \cdot 10^{-6}\ \mathrm{M},$$

$$k_9 \simeq 1.6 \cdot 10^{-2}/1.3 \cdot 10^{-6} \simeq 10^{-4}\ c^{-1},$$

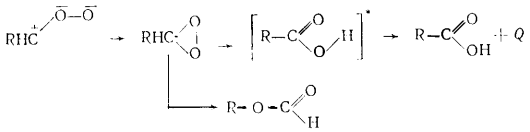
which is quite probable; and 3) both k_9 and k_{10} differ considerably from k_7; in this case it can be established from the experimental data that for −78 °C

$$k_{10}[(\mathrm{XIV})]/k_9 = 0{,}1.$$

The kinetic scheme shows that a decrease in the reaction temperature, an increase in the reaction rate, and the use of polar solvents facilitating an increase in the concentration of (XIV) should increase the formation of the polymeric ozonide. The zwitterion and the carbonyl compound leaving the cage and passing into the solution may also be involved in the formation of polymeric ozonides:



The zwitterion undergoes isomerisation comparatively readily. This reaction provides the principal channel for the formation of acids in the thermal decomposition of ozonides[44]. The isomerisation probably takes place via the cyclic form of the zwitterion:



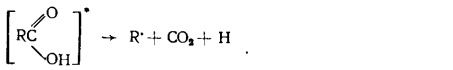
The quantity of free acids formed in the reaction of ozone with the alkene can be used as a measure of the contribution of this reaction to the transformation balance[32].

The unimolecular rate constant for the isomerisation of the zwitterion can be found from the relationship

$$k_{11} = [\mathrm{Acid}]k_7^{1/2}/[\mathrm{Ozonide}]^{1/2}.$$

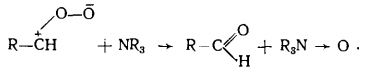
According to published data[32], $k_{11} = (1 \pm 0.8) \times 10^7 \exp\left[\frac{(-6600 \pm 800)}{RT}\right]$ s^{-1}.

The isomerisation of the zwitterions is accompanied by the liberation of 60–80 kcal of energy, which initially is concentrated in the newly formed bonds. The acid molecule is therefore in an excited state (marked by an asterisk in scheme 1) and can decompose relatively easily, for example[44]:



The decomposition takes place more rapidly under conditions in which the dissipation of the energy and the thermalisation of the "hot" molecules are hindered. Thus in the gaseous phase, this process becomes predominant[56–60], whereas in solution at room temperature or lower temperatures, its contribution usually does not exceed 1–3%.[32]

The reaction in the second direction—the splitting of the C–C bond with the formation of esters of formic acid—is slower by about three orders of magnitude, and is observed in the reaction of ozone with branched alkenes[149]. The zwitterion may react with added ammonia, pyridine, or tetracyanoethylene[150]:



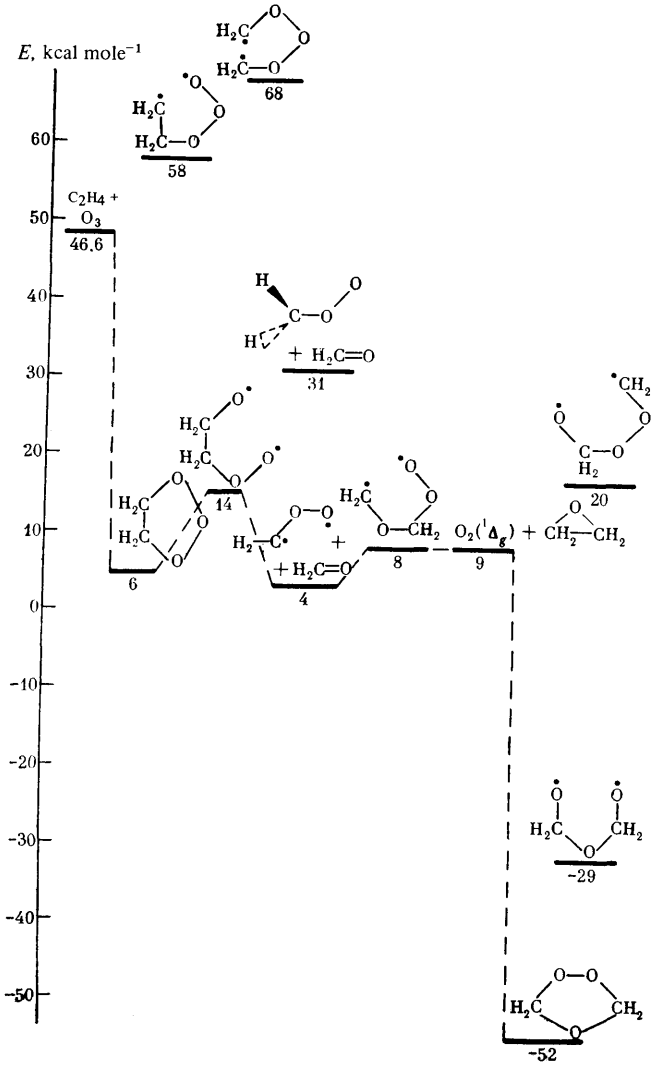
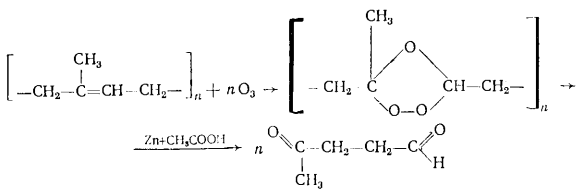


Figure 8. Thermochemistry of ozonisation.

Fig.8 gives the results of thermochemical calculations which make it possible to show the positions of the intermediate species on the reaction coordinate (marked by the broken line relative to the initial and final stages)[136]. In addition to the labile intermediate products mentioned in the text, the diagram shows species whose possible formation has been discussed in the literature. Unfortunately, Fig.8 does not give the complex of ozone with the alkene, for which thermochemical data are not yet available.

V. THE USE OF THE REACTION OF OZONE WITH UNSATURATED COMPOUNDS IN RESEARCH AND TECHNOLOGY

Comparison of the rate of the reaction of ozone with the double bond and with the $-CH_2-$ group of the saturated parts of the alkene molecule shows that they differ by 4–8 orders of magnitude[151]. This makes it possible to use ozone in analysis to determine the number of double bonds and their position in the molecule of an organic compound. Mention must first be made of the classical work of Harries, who determined the structure of various natural polymers, in particular natural rubber[4]:



Subsequently, the rupture of a double bond by ozone has been used repeatedly in the study of the structure of various new polymers and copolymers[5,152–158]. This question has been the subject of several reviews[4,46,104].

The use of ozone to study the processes associated with the formation of unstable products, for example keto–enol tautomerism, has proved extremely effective[1,159].

In the early nineteen-thirties, a process for obtaining high-octane petrol by the dimerisation of propene and butenes was widely developed; the positions of the double bonds in the isomeric dimers were determined from the composition of the ozonisation products[160]. This method proved extremely useful in the study of the structure of lipids, fats, steroids, and other natural compounds[53,161,162].

The combination of ozonisation methods with gas–liquid chromatography increased considerably the possible use of ozone in determining the structure of unsaturated compounds, since it became possible to analyse ultramicro-quantities of the products (~10^{-3}–10^{-6} M). The procedure for these determinations has been described by a number of authors[163,164].

The determination of the position of a C=C bond in the molecule of an organic compound is now well established. It is often necessary to determine the positions of several C=C bonds present together (for example, the 1,2- and 1,4-structures in polybutadienes) and the nature of the terminal groups of the macromolecules of synthetic polymers, to distinguish double and triple bonds, etc. In these cases it is necessary to make a more complete study of the composition of the reaction products or to combine the results of the study of the composition of the reaction products with kinetic data[5].

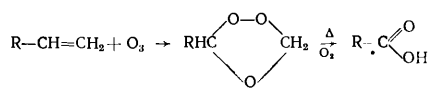
A large proportion of present-day processes in organic synthesis, petroleum chemistry, and polymer chemistry are based on various transformations of compounds containing a double bond. The use of ozone has made it possible to develop control systems which are very rapid and have a very high sensitivity (as far as 10^{-8} M double bonds in the specimen)[165]. They have proved to be particularly effective in the determination of the quality of new saturated copolymers containing small quantities of added dienes, for example the ethylene–propene–diene copolymer (SKEPT), in which the concentration of unsaturated units in the molecule is 0.5–2%, which lies at the limit of the sensitivity of the methods previously used.

In the analysis of the products of the incomplete hydrogenation of fats (margarines), compounds containing halogen atoms or aromatic rings at a double bond, and new polymeric materials such as acrylates or urethanes, the usual iodometric or infrared spectroscopic methods are ineffective, whereas the use of ozone gives good results[151,166,167].

The concentration of ozone in the layers of the atmosphere close to the earth's surface is usually low (10^{-10}–10^{-9} M), but it increases considerably in industrial centres. Ozone plays an important role in the production of photochemical smog, so that the monitoring of atmospheric ozone is included in all ecological programmes[85]. Various methods have been proposed for determining ozone in air[3,168–171]. One of the best methods is that based on the measurement of the intensity of the chemiluminescence produced when ethylene is mixed with a portion of the air being studied[62,63].

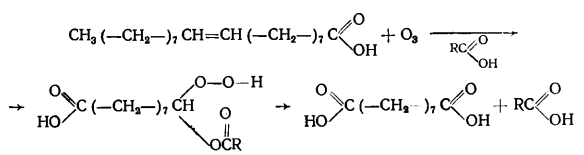
The reaction of ozone with double bonds has also found application in the preparation of many oxygen-containing compounds[26,172–175]. According to published data, a number of technological assemblies are now operating, and new ones are being devloped[26,174,176,177]. The principal direction in this work at present involves the preparation of expensive products from scarce raw material. In these processes, the high selectivity of the reactions of ozone has made it possible to achieve maximum yields.

Ozonisation provides the simplest method of obtaining various acids[178–180]:



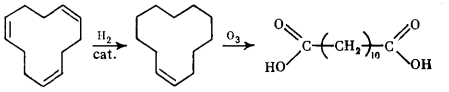
The demand for organic acids is extremely large; they are obtained from plant and animal products or by oxidising saturated petroleum hydrocarbons. The last reaction gives acids containing considerable quantities of undesirable functional groups (keto- and hydroxyacids, lactones, etc.) and having a wide fractional composition. The quality of the acids obtained by ozonisation is much better, and their composition is determined by the original alkene[180,181].

Several methods have been published for preparing adipic[182–184], azelaic[26,185–187], and other dicarboxylic acids[188–191]. The industrial production of azelaic acid is based on the treatment of oleic acid with ozone in nonanoic acid:

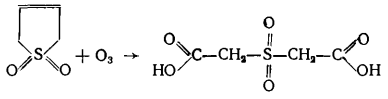


The development of methods for the cyclo-oligomerisation of divinyl[192] and the selective hydrogenation of dimers and

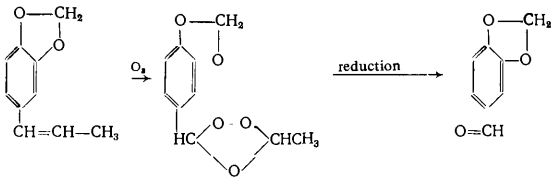
trimers to monocycloalkenes[193,194] makes promising the synthesis of octane dicarboxylic and dodecanedicarboxylic acids[113]:



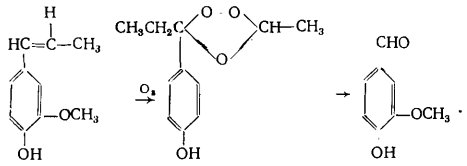
The synthesis of dicarboxylic acids containing heteroatoms in the molecule has been reported[195,196]:



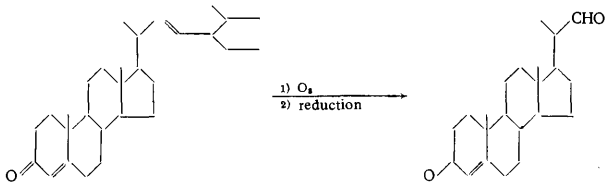
Various aromatic aldehydes have been obtained in good yields, for example heliotropine, used in perfumery and cosmetics[197]:



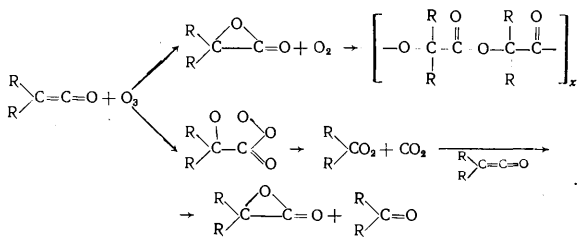
and of vanillin from isoeugenol[198]:



Various steroids in which the double bond in the ring is stabilised by substituents having an appreciable electron affinity give good yields (up to 94%) of aldehydes as a result of bond rupture in the side chain[26,174,199]:



The reaction of ozone with ketenes giving α-lactones, which polymerise spontaneously to give complex polyesters[200,201]. The mechanism of the reactions taking place can be represented by the following scheme:



The synthesis of biologically active compounds, for example glutamic acid from cyclopentadiene[202], various hormones such as cortisone and progesterone from ergosterol (protovitamin D),[203] keto steroids[204], steroids containing heteroatoms[205], and intermediate α,ω-dialdehydes of given stereoisomeric form in the synthesis of tellergons[91], has been described.

REFERENCES

1. J.Houben and T.Weyl, "Die Methoden der Organischen Chemie" (Translated into Russian), Izd.Khimiya, Moscow, 1964.
2. R.Criegee, Chem.Ztg., **99**, 138 (1975).
3. S.D.Razumovskii and G.E.Zaikov, "Ozon i ego Reaktsii s Organicheskimi Soedineniyami" (Ozone and Its Reactions with Organic Compounds), Izd.Nauka, Moscow, 1974.
4. C.D.Harries, Untersuchungen über die natürlichen und künstlichen Kautschukarten, Berlin, 1919.
5. S.D.Razumovskii, G.M.Bantsyrev, M.I.Cherkashin, G.E.Zaikov, and A.A.Berlin, Vysokomol.Soed., **13**, 211 (1971).
6. A.A.Lapshova, G.S.Kupreeva, M.P.Strukova, and L.N.Chechetkina, Zhur.Anal.Khim., **32**, 1816 (1977).
7. Ozone Reaction with Organic Compounds, Adv.Chem. Ser., **112**, Washington, 1972.
8. R.Huisgen, Angew.Chem., Int.Ed., **2**, 563 (1963).
9. R.Breslow, "Organic Reaction Mechanisms" (Translated into Russian), Izd.Mir, Moscow, 1968, p.161.
10. T.S.Smirnova, in collected papers, "Sovremennye Problemy Organicheskoi Khimii" (Present-Day Problems of Organic Chemistry), Izd.Leningrad.Gos.Univ., 1969, p.254.
11. R.Huisgen, J.Org.Chem., **41**, 403 (1976).
12. D.Grimbert and A.Devaquet, Mol.Phys., **27**, 831 (1974).
13. G.C.Carney, S.R.Langhoff, and L.A.Curtiss, J.Chem. Phys., **66**, 3724 (1977).
14. W.A.Goddard III, T.H.Dunning, W.J.Hunt, and P.J.Hay, Acc.Chem.Res., **6**, 368 (1973).
15. S.D.Razumovskii and L.V.Berezova, Izv.Akad.Nauk SSSR, Ser.Khim., 223 (1974).
16. S.D.Razumovskii and G.E.Zaikov, Zhur.Org.Khim., **8**, 468 (1972).
17. C.Harries, Ber., **38**, 1195 (1905).
18. H.Staudinger, Chem.Ber., **58**, 1088 (1925).
19. A.Rieche, Peroxide und Ozonide, Berlin, Erlangen, 1931.
20. R.Criegee, Record of Chem.Progess, **18**, 111 (1957).
21. R.Criegee, in Peroxide Reaction Mechanisms, Pergamon Press, New York–London, 1962, p.29.
22. S.D.Razumovskii and L.V.Berezova, Izv.Akad.Nauk SSSR, Ser.Khim., 207 (1968).
23. F.L.Greenwood and B.J.Haske, J.Org.Chem., **30**, 1276 (1965).
24. R.W.Murray, R.D.Youssefyeh, and P.R.Story, J.Amer. Chem.Soc., **89**, 2429 (1967).
25. R.P.Lattimer and R.L.Kuczkowski, J.Amer.Chem.Soc., **96**, 6205 (1974).
26. Organic Ozone Reaction and Techniques, Wellsbach Corpor.Ozone Processes Divis., Philadelphia, p.26.
27. A.T.Menyailo and M.V.Pospelov, Uspekhi Khim., **36**, 663 (1967) [Russ.Chem.Rev., No.4 (1967)].
28. N.L.Bauld, J.A.Thompson, C.E.Hudson, and P.S.Bailey, J.Amer.Chem.Soc., **90**, 1822 (1968).
29. R.P.Latimer, R.L. Kuczkowsky, and C.W.Gillies, J.Amer.Chem.Soc., **96**, 348 (1974).

30. R.C.Fuson, M.D.Armstrong, W.E.Wallace, and J.W.Kneisley, J.Amer.Chem.Soc., **66**, 1274 (1944).
31. G.Komppa and R.H.Roschier, Ann., **470**, 129 (1929).
32. S.D.Razumovskii, Izv.Akad.Nauk SSSR, Ser.Khim., 335 (1970).
33. E.H.Farmer and R.C.Pitkethly, J.Chem.Soc., 287 (1938).
34. P.D.Bartlett and R.M.Stiles, J.Amer.Chem.Soc., **77**, 2806 (1955).
35. E.Mathias, Canad.J.Chem., **52**, 3852 (1974).
36. C.W.Gillies, J.Amer.Chem.Soc., **97**, 1276 (1975).
37. R.Criegee and G.Schröder, Chem.Ber., **93**, 689 (1960).
38. P.S.Bailey, T.M.Ferrell, A.Rustaiyan, S.Seyhan, and L.E.Unruh, J.Amer.Chem.Soc., **100**, 894 (1978).
39. G.Schröder, Chem.Ber., **95**, 733 (1962).
40. L.J.Bellamy, "Infrared Spectra of Complex Molecules" (Translated into Russian), Inostr.Lit., Moscow, 1967, p.47.
41. S.D.Razumovskii, L.V.Berezova, N.D.Gil'chenok, O.M.Oranskaya, Yu.N.Yur'ev, and V.K.Tsyskovskii, Zhur.Org.Khim., **2**, 1942 (1966).
42. G.A.Niazashvili, S.D.Razumovskii, and I.A.Tutorskii, Vysokomol.Soed., **13B**, 211 (1971).
43. I.S.Hisatsune, L.H.Kolopajlo, and J.Heicklen, J.Amer. Chem.Soc., **99**, 3704 (1977).
44. S.D.Razumovskii and Yu.N.Yur'ev, Zhur.Org.Khim., **3**, 251 (1967).
45. Yu.N.Yur'ev and S.D.Razumovskii, Zhur.Org.Khim., **10**, 1145 (1974).
46. P.S.Bailey, Chem.Rev., **58**, 925 (1958).
47. J.A.Sousa and A.L.Bluhm, J.Org.Chem., **25**, 108 (1960).
48. N.D.Gil'chenok, S.D.Razumovskii, and V.K.Tsyskovskii, in collected papers, "Kataliticheskie Reaktsii v Zhidkoi Faze" (Collected Papers on Catalytic Reactions in the Liquid Phase), Izd.Nauka, Alma-Ata, 1967, p.183.
49. O.Lorenz and C.R.Parks, J.Org.Chem., **30**, 1976 (1965).
50. P.R.Story, C.E.Bishop, J.R.Burgess, R.W.Murray, and R.D.Youssefyeh, J.Amer.Chem.Soc., **90**, 1907 (1968).
51. V.N.Odinokov, V.R.Akhunova, R.S.Bakeeva, R.I.Talaeva, A.V.Semenovskii, A.M.Moiseenkov, and G.A.Tolstikov, Zhur.Org.Khim., **13**, 532 (1977).
52. D.G.M.Diaper, Oxid.Comb.Rev., **6**, 145 (1973).
53. J.L.Sebedio and R.G.Ackman, Canad.J.Chem., **56**, 2480 (1979).
54. E.S.Zelikman, L.V.Berezova, and Yu.N.Yur'ev, Zhur. Org.Khim., **12**, 770 (1976).
55. D.R.Kerur and D.G.M.Diaper, Canad.J.Chem., **51**, 3110 (1973).
56. B.J.Finlayson, J.N.Pitts, and R.Atkinson, J.Amer. Chem.Soc., **96**, 5356 (1974).
57. F.S.Toby, S.Toby, and H.E.O'Neal, Int.J.Chem. Kinetics, Symposium, **1**, 25 (1975).
58. C.W.Blume, I.S.Hisatune, and J.Heicklen, Int.J. Chem.Kinetics, **8**, 235 (1976).
59. D.A.Hanse, and J.N.Pitts, Chem.Phys.Letters, **35**, 569 (1975).
60. H.R.Schulten and U.Schurath, J.Phys.Chem., **70**, 51 (1975).
61. H.Kühne, Ber.Bunsenges.Phys.Chem., **82**, 15 (1978).
62. G.W.Nederbragt, A.van der Horst, and J.Van Duijn, Nature, **206**, 87 (1965).
63. G.J.Warren and G.Babcock, Pribory dlya Nauchnykh Issledovanii, No.12, 123 (1970).
64. B.J.Finlayson, J.N.Pitts, and H.Akimoto, Chem.Phys. Letters, **12**, 495 (1973).
65. W.A.Kummer, J.M.Pitts, and R.P.Steer, Environ.Sci. Technol., 5, 1045 (1971).
66. H.E.O'Neal and C.Blumstein, Int.J.Chem.Kinetics, **5**, 495 (1973).
67. J.T.Herron and R.E.Huie, J.Amer.Chem.Soc., **99**, 5430 (1977).
68. J.T.Herron and R.E.Huie, Int.J.Chem.Kinetics, **10**, 1019 (1978).
69. F.L.Greenwood, Tetrahedron, **21**, 631 (1965).
70. C.E.Thorp, A.Heights, and A.J.Gaynor, US P.2 857 410 (1956); Chem.Abs., **53**, 9067 (1959).
71. L.A.Hull, I.S.Hitatsune, and J.Heicklen, Canad.J. Chem., **51**, 1504 (1973).
72. S.M.Japar, C.H.Wu, and H.Niki, J.Phys.Chem., **80**, 2057 (1976).
73. F.S.Toby and S.Toby, J.Phys.Chem., **80**, 2313 (1976).
74. F.S.Toby and S.Toby, Int.J.Chem.Kinetics, **6**, 417 (1974).
75. J.J.Bufalini and A.P.Altschuller, Canad.J.Chem., **43**, 2243 (1965).
76. T.Vrbaski and R.J.Cvetanovic, Canad.J.Chem., **38**, 1053 (1960).
77. R.D.Cadle and C.Shadt, J.Amer.Chem.Soc., **74**, 6002 (1952).
78. P.L.Hanst, E.R.Stephens, W.E.Scott, and R.C.Doerr, Atmospheric Ozone-Olefin Reaction, Philadelphia, Publ.The Franklin Institute, 1958.
79. K.H.Becker, U.Schurath, and H.Seitz, Int.J.Chem. Kinetics, **6**, 725 (1974).
80. J.Heicklen, J.Phys.Chem., **70**, 477 (1966).
81. J.T.Herron and R.E.Huie, J.Phys.Chem., **78**, 2085 (1974).
82. R.E.Huie and J.T.Herron, Int.J.Chem.Kinetics, Symposium, **1**, 165 (1975).
83. P.A.Leighton, Photochemistry of Air Pollution, Acad. Press, New York, 1961.
84. T.E.Graedel, L.A.Farrow, and T.A.Weber, Armos. Environ., **10**, 1095 (1976).
85. J.G.Calvert and R.D.McQuigg, Int.J.Chem.Kinetics, Symposium, **1**, 113 (1975).
86. D.G.Williamson and R.J.Cvetanovic, J.Amer.Chem.Soc., **90**, 3668, 4248 (1968).
87. H.Henry, M.Zador, and S.Fliszar, Canad.J.Chem., 51, 3309 (1973).
88. S.W.Benson, "Foundations of Chemical Kinetics" (Translated into Russian), Izd.Mir, Moscow, 1964, p.434.
89. E.T.Denisov, Zhur.Fiz.Khim., **49**, 2473 (1975) [Russ. J.Phys.Chem., No.10 (1975)].
90. S.D.Razumovskii and G.E.Zaikov, Izv.Akad.Nauk SSSR, Ser.Khim., 1963 (1975).
91. S.D.Razumovskii, S.K.Rakovski, and G.E.Zaikov, Izv.Akad.Nauk SSSR, Ser.Khim., 1766 (1974).
92. E.F.Caldin, J.Chem.Soc., 3345 (1959).
93. S.D.Razumovskii and G.E.Zaikov, Zhur.Org.Khim., **8**, 464 (1972).
94. S.D.Razumovskii, L.M.Reutova, G.A.Niazashvili, I.A.Tutorskii, and G.E.Zaikov, Dokl.Akad.Nauk SSSR, **194**, 1127 (1970).
95. Yu.A.Zhdanov and V.I.Minkin, "Korrelyatsionnyi Analiz v Organicheskoi Khimii" (Correlation Analysis in Inorganic Chemistry), Izd.Rostov.Gos.Univ., 1968.
96. C.D.Johnson, "The Hammett Equation" (Translated into Russian), Izd.Mir, Moscow, 1977,
97. S.D.Razumovskii and Yu.N.Yur'ev, Tetrahedron Letters, 3939 (1967).

98. E.Barnatek, P.Kolasker, and T.Ledaal, Tetrahedron, Letters, 1317 (1969).
99. N.S.Zefirov and V.I.Sokolov, Uspekhi Khim., **36**, 243 (1967) [Russ.Chem.Rev., No.2 (1967)].
100. H.Paul, I.Sange, and A.Kausmann, Chem.Ber., **98**, 1789 (1965).
101. A.A.Popov, S.D.Razumovskii, V.M.Parfenov, and G.E.Zaikov, Izv.Akad.Nauk SSSR, Ser.Khim., 282 (1975).
102. J.Hine, Physical Organic Chemistry, Pergamon Press, New York–London, 1962, p.87.
103. Yu.S.Zuev, "Razrushenie Polimerov pod Deistviem Agressivnykh Sred" (The Breakdown of Polymers Under the Influence of Aggressive Media), Izd. Khimiya, Moscow, 1972.
104. T.Alfrey, in "The Chemical Reactions of Polymers" (Translated into Russian), Izd.Mir, Moscow, 1967, p.9.
105. N.A.Plate, A.D.Litmanovich, and O.V.Noa, "Makromolekulyarnye Reaktsii" (Macromolecular Reactions), Izd.Khimiya, Moscow, 1987.
106. P.J.Flory, Principles of Polymer Chemistry, New York, 1953, p.41.
107. A.M.Kotliar and H.Morawetz, J.Amer.Chem.Soc., 77, 3692 (1955).
108. A.N.Glazer and E.L.Smith, J.Biol.Chem., **236**, 2948 (1961).
109. A.A.Berlin, A.A.Sayadyan, and N.S.Enikolopyan, Vysokomol.Soed., **11A**, 1893 (1969).
110. Yu.S.Zuev and V.F.Molofeevskaya, in collected papers, "Starenie i Zashchita Reziny" (Collected Papers on the Ageing and Protection of Rubber), Goskhimizdat, Moscow, 1960, p.27.
111. S.D.Razumovskii, O.N.Karpukhin, A.A.Kefeli, T.V.Pokholok, and G.E.Zaikov, Vysokomol.Soed., 13A, 782 (1971).
112. A.A.Kefeli, S.D.Razumovskii, and G.E.Zaikov, Vysokomol.Soed., **13A**, 803 (1971).
113. Yu.N.Yur'ev, V.P.Kapralov, and E.S.Zelikman, "Materialy II Vsesoyuznoi Mezhvuzovskoi Konferentsii po Ozonu" (Proceedings of the Second All-Union Intercollegiate Conference on Ozone), Izd.Moskov.Gos. Univ., Moscow, 1977, p.154.
114. G.Slomp and J.L.Johnson, J.Amer.Chem.Soc., **80**, 915 (1958).
115. R.W.Murray, R.D.Youssefyeh, and G.J.Williams, Tetrahedron, **24**, 4347 (1968).
116. O.S.Privett and E.C.Nickell, J.Amer.Oil Chem.Soc., **43**, 393 (1966).
117. V.N.Odinokov, L.P.Zhemaiduk, and G.A.Tolstikov, Izv.Akad.Nauk SSSR, Ser.Khim., 1900 (1976).
118. D.J.Miller, T.E.Nemo, and L.A.Hull, J.Org.Chem., **40**, 2675 (1975).
119. L.A.Hull, I.C.Hisatsune, and J.Heicklen, J.Amer. Chem.Soc., **94**, 4856 (1972).
120. I.C.Hisatsune, L.H.Kolopajlo, and J.Heicklen, J.Amer. Chem.Soc., **99**, 3704 (1977).
121. W.G.Alcock and B.Mile, Chem.Comm., 575 (1973); 5 (1976).
122. G.Klopman and C.M.Joiner, J.Amer.Chem.Soc., **97**, 5287 (1975).
123. W.R.Wadt and W.A.Goddard III, J.Amer.Chem.Soc., **97**, 3004 (1975).
124. P.S.Bailey, J.W.Ward, T.P.Carter, E.C.Nieh, C.M.Fischer, and A.I.Y.Khashab, J.Amer.Chem.Soc., **96**, 6136 (1976).
125. H.Kühne and H.H.Guenthard, J.Chem.Phys., **80**, 1238 (1976).
126. P.S.Bailey, A.Rustaiyan, and T.M.Ferrell, J.Amer. Chem.Soc., **98**, 638 (1976).
127. P.C.Hiberty, J.Amer.Chem.Soc., **98**, 6088 (1976).
128. P.S.Bailey, J.A.Thompson, and B.A.Shoulders, J.Amer.Chem.Soc., **88**, 4098 (1966).
129. G.Klutsch and S.Fliszar, Canad.J.Chem., **50**, 2841 (1972).
130. L.J.Durham and F.L.Greenwood, Chem.Comm., 24 (1968).
131. L.J.Durham and F.L.Greenwood, J.Org.Chem., **33**, 1629 (1968).
132. S.W.Benson, "Thermochemical Kinetics" (Translated into Russian), Izd.Mir, Moscow, 1971, p.252.
133. F.L.Greenwood, J.Org.Chem., **29**, 1321 (1964).
134. P.S.Bailey, F.E.Potts III, and J.W.Ward, J.Amer. Chem.Soc., **92**, 230 (1970).
135. L.J.Durham and F.L.Greenwood, J.Org.Chem., **34**, 3363 (1969).
136. L.B.Harding and W.A.Goddard III, J.Amer.Chem.Soc., **100**, 7180 (1978).
137. T.K.Ha, H.Kühne, S.Vaccani, and H.H.Guenthard, Chem.Phys.Letters, **24**, 172 (1974).
138. R.I.Martinez, R.E.Huie, and J.T.Herron, Chem.Phys. Letters, **51**, 457 (1977).
139. F.J.Lovas and R.D.Suenram, Chem.Phys.Letters, **51**, 453 (1977).
140. S.D.Razumovskii and Yu.N.Yur'ev, Zhur.Org.Khim., **4**, 1716 (1968).
141. P.S.Bailey and T.M.Ferrell, J.Amer.Chem.Soc., **100**, 899 (1978).
142. G.Riezebos, J.C.Grimmelikhuysen, and D.A.van Dorp, Rec.trav.chim., **82**, 1234 (1963).
143. R.W.Murray and R.Hagen, J.Org.Chem., 36, 1098 (1971).
144. L.D.Loan, R.W.Murray, and P.R.Story, J.Amer.Chem. Soc., **87**, 137 (1965).
145. R.M.Noyes, J.Chem.Phys., **22**, 1349 (1954).
146. Kh.S.Bagdasar'yan, "Teoriya Radikal'noi Polimerizatsii" (The Theory of Radical Polymerisation), Izd.Akad. Nauk SSSR, Moscow, 1959.
147. D.A.Frank-Kamenetskii, "Diffuziya i Teploperedacha v Khimicheskoi Kinetike" (Diffusion and Heat Transfer in Chemical Kinetics), Izd.Akad.Nauk SSSR, Moscow, 1947, p.32.
148. S.D.Razumovskii, G.A.Niazashvili, I.A.Tutorskii, Yu.N.Yur'ev, and G.E.Zaikov, Vysokomol.Soed., **13A**, 195 (1971).
149. S.D.Razumovskii and Yu.N.Yur'ev, Zhur.Org.Khim., **4**, 1884 (1968).
150. R.Criegee and P.Guenther, Chem.Ber., **96**, 1564 (1963).
151. Z.G.Zemskova, D.M.Lisitsyn, N.G.Matveeva, S.D.Ravumovskii, and A.A.Berlin, Vysokomol.Soed., **14A**, 2257 (1972).
152. E.N.Alekseeva and R.M.Belitskaya, Zhur.Obshch. Khim., **11**, 358 (1941).
153. N.G.Kasatkina and S.V.Dolgoplosk, Zhur.Obshch. Khim., **29**, 377 (1959).
154. A.I.Yakubchik, N.G.Kasatkina, and T.E.Pavlovskaya, Zhur.Obshch.Khim., **27**, 1487 (1957).
155. A.I.Yakubchik, N.G.Kasatkina, and T.E.Pavlovskaya, Rubber Chem.Technol., **32**, 284 (1959).
156. A.I.Yakubchik, A.I.Spasskova, A.G.Zak, and E.D.Potatskaya, Zhur.Obshch.Khim., **28**, 3090 (1958).
157. C.S.Marvel and R.E.Light, J.Amer.Chem.Soc., **72**, 3887 (1950).
158. G.S.Whitby, "Synthetic Rubber" (Translated into Russian), Goskhimizdat, Moscow, 1957.
159. C.Weygand, Ann., **459**, 121 (1927).

160. F.C.Whitmore and J.M.Church, J.Amer.Chem.Soc., **54**, 3710 (1932).
161. O.S.Privett and E.C.Nickell, J.Amer.Oil.Chem.Soc., **39**, 414 (1962).
162. V.Koman and D.Anderle, Chem.Zvesti, **20**, 358 (1966).
163. B.Smith, R.Ohlson, and A.M.Olson, Acta Chem. Scand., **16**, 1463 (1962).
164. J.S.Belew, Oxidation, Vol.1, Wiley, New York, 1969, p.259.
165. Soviet Instruments and Science Devices, Editorials Advertisements, Vol.3, No.1, p.42 (1942).
166. I.S.Ungar and G.A.Lutz, Rubber Chem.Technol., **34**, 205 (1961).
167. K.F.Guenther, G.Sosnovsky, and R.Brunier, Anal. Chem., **36**, 2508 (1964).
168. T.N.Merenishcheva, V.F.Plekhotkin, and V.G.Pimkin, "Metody Opredeleniya Ozona v Otkhodyashchikh Gazakh i Stochnykh Vodakh" (Methods for the Determination of Ozone in Effluent Gases and Liquids), NIITEKhIM, Moscow, 1973.
169. D.Chamberlin and R.E.Sanders, ASTM Sec.Techn. Publ., 1974, 555, p.112; Chem.Abs., **77**, 10 550 (1974).
170. A.G.Stepanova, E.A.Bozhevol'nov, I.V.Ardisonov, and V.S.Gritsenko, Zhur.Anal.Khim., **30**, 1238 (1975).
171. R.T.Menzies and M.S.Shumate, Science, **184**, 570 (1974).
172. R.Criegee, Chimia, **22**, 392 (1968).
173. C.Bischoff and A.Rieche, Z.Chem., No.3, 97 (1965).
174. Ozone Chemistry and Technology, Adv.Chem.Ser., Vol.21, Washington, 1958.
175. Yu.N.Yur'ev, "Reaktsiya Ozona s Olefinami (Obzor)" (The Reaction of Ozone with Alkenes. A Review), NIITEKhIM, Moscow, 1976.
176. Yu.M.Emel'yanov, Priroda, No.12, 67 (1965).
177. Yu.N.Yur'ev, "Materialy II Vsesoyuznoi Mezhvuzovskoi Konferentsii po Ozonu" (Proceedings of the Second All-Union Intercollegiate Conference on Ozone), Moskov. Gos.Univ., 1977, p.152.
178. F.Asinger, Chem.Ber., **75**, 656 (1942).
179. A.Greiner and U.Müller, J.Prakt.Chem., **15**, 313 (1962).
180. S.D.Razumovskii, L.V.Berezova, S.G.Dembovitskaya, A.S.Zhelunya, and V.K.Tsyskovskii, Khim.Prom., 651 (1968).
181. O.R.Kaliko, A.T.Menyailo, G.G.Filina, and M.V.Pospelov, Khim.Prom., 884 (1971).
182. S.D.Razumovskii, L.V.Berezova, and V.K.Tsyskovskii, "Neftekhimiya i Neftekhimicheskaya Promyshlennost'. Sbornik" (Collected Papers on Petroleum Chemistry and the Petrochemical Industry), Izd.Khimiya, Leningrad, 1965, No.2, p.27.
183. P.S.Bailey, Ind.Eng.Chem., **50**, 993 (1958).
184. A.T.Menyailo, I.E.Pokrovskaya, and A.K.Yakovleva, Neftekhimiya, 7, 70 (1967).
185. Chem.Eng., **68**, 80 (1961).
186. S.D.Razumovskii, B.A.Brunshtein, and V.K.Tsyskovskii, USSR P.210 853 (1967); Byul.Izobr., No.7 (1968).
187. Yu.N.Yur'ev, L.V.Berezova, and S.D.Razumovskii, Zhur.Prikl.Khim., **43**, 627 (1970).
188. M.Fremery and E.K.Fields, J.Org.Chem., **28**, 2537 (1963).
189. J.E.Franz, W.S.Knowles, and C.Osuch, J.Org.Chem., **30**, 4328 (1965).
190. J.R.Geigy A.-G., Dutch P.6 511 374 (1966); Chem. Abs., **65**, 2129 (1966).
191. A.I.Volozhin, E.T.Krut'ko, L.I.Vorob'eva, and S.D.Razumovskii, USSR P.555 087 (1975); Byul. Izobr., No.15 (1977).
192. L.I.Zakharkin and V.V.Guseva, Uspekhi Khim., **47**, 1774 (1978) [Russ.Chem.Rev., No.10 (1978)].
193. Bull.Soc.Chem.Japan, **40**, 2818 (1967).
194. E.P.Tepenitsyna and M.I.Farberov, Izv.Vys.Ucheb. Zaved., Khim.i Khim.Tekhnol., **10**, 338 (1967).
195. S.D.Razumovskii and V.K.Tsyskovskii, USSR P. 183 742 (1965); Byul.Izobr., No.14 (1966).
196. R.C.Slagel, J.Org.Chem., **31**, 593 (1966).
197. M.Indo, Nippon Kagaku Zasshi, **80**, 537 (1959).
198. M.Indo, Nippon Kagaku Zasshi, 81, 1106, 1109 (1960).
199. F.W.Heyl and M.E.Herr, US P.2 601 287 (1952); Chem. Abs., **46**, P9808 (1952).
200. R.Wheland and P.D.Bartlett, J.Amer.Chem.Soc., **92**, 6057 (1970).
201. J.K.Crandall, S.A.Sojka, and J.B.Komin, J.Org. Chem., **39**, 2172 (1974).
202. J.L.Purvis, US P.2 833 786 (1958); Chem.Abs., **52**, 14 664 (1958).
203. P.Bladon, H.B.Henbest, E.R.H.Jones, and G.W.Wood, J.Chem.Soc., 4890 (1952).
204. J.C.Lacquesy and J.F.Patoiseau, Tetrahedron Letters, 1499 (1977).
205. R.J.Chorvat and R.Pappo, J.Org.Chem., **41**, 2684 (1976).

Institute of Chemical Physics,
Academy of Sciences of the USSR,
Moscow

Translated from *Uspekhi Khimii*, **49**, 2377 - 2388 (1980) U.D.C. 539.27

Internuclear Distances in Carbaboranes

V.S.Mastryukov, O.V.Dorofeeva, and L.V.Vilkov

Structural data for different carbaboranes, investigated in the solid and gas phases, have been compiled and arranged systematically. The subdivision of bonds into polyhedral and exopolyhedral, proposed previously, is illustrated by additional examples. It is shown that the concept of the coordination number helps to discover the rules governing the variation of the polyhedral C - C and B - C distances. Since this approach proved to be relatively ineffective in relation to B - B bonds, an attempt was made to estimate the influence of electronic factors on these distances on the basis of a modified inductive rule. This has shown that the polyhedral and exopolyhedral C - X and B - X distances in carbaboranes obey different rules.
The bibliography includes 66 references.

CONTENTS

I. Introduction 1181
II. C-C bonds 1181
III. Polyhedral C-B bonds 1182
IV. Polyhedral B-B bonds 1185
V. Exopolyhedral B-X bonds 1186

I. INTRODUCTION

Vigorous studies in the field of boron hydrides led at the end of the 1950s and the beginning of 1960 to the discovery of a new class of organic derivatives of boron—carbaboranes. The structural basis of carbaboranes consists of fragments of polyhedral boranes incorporating carbon atoms as an intrinsic component of the skeleton, in contrast, for example, to alkylboranes, in which carbon is a substituent. After a short time, this field of chemistry developed so actively that the possibilities for the synthesis of new compounds now appear almost unlimited. Interest in carbaboranes is to a large extent due to the fact that, both experimentally and theoretically, they occupy a strategically important position at the junction of many fields of chemistry: those of boron hydrides, organoelemental compounds, transition metal complexes, and metallic clusters. These common features were manifested particularly strikingly in the middle of the 1960s when metallocarbaboranes were discovered.

closo-Carbaboranes, forming closed polyhedral structures, were initially investigated in greatest detail. The inclusion of carbon atoms in the boron hydride skeleton is accompanied by the disappearance of hydrogen bridge atoms and greatly increases the thermal and chemical stabilities of the initial systems. The majority of studies were carried out on $C_2B_{10}H_{12}$ and $C_2B_5H_7$ and were designed to synthesise thermostable polymers. However, other ways of using carbaboranes were also found. Even before the polyhedral structure of carbaboranes was demonstrated by direct structural methods, their structure had been correctly predicted on the basis of indirect considerations. Both certain experimental methods (infrared spectroscopy, NMR, and mass spectrometry) and theoretical ideas, to a large extent developed by the American investigator Lipscomb†, played an important role here. In particular, one of the simple fundamental ideas was the observed analogy between the structures of *closo*-carbaboranes $C_2B_{n-2}H_n$ and the isoelectronic $B_nH_n^{2-}$ ions, for example, $C_2B_4H_6$ and $B_6H_6^{2-}$, etc. The vigorous development of the chemistry of carbaboranes would have been impossible without the exact knowledge of their structure. The majority of structural results for substituted carbaboranes were obtained by single crystal X-ray diffraction. The structure of volatile lower carbaboranes was established mainly by gas electron diffraction and microwave spectroscopy.

Data on the structure of carbaboranes are usually included in reviews on their chemical properties. As a result, extensive structural data have accumulated, the compilation and systematic arrangement of which are both urgently required and desirable. Furthermore, there is a possibility of surveying these experimental data and examining them from a single standpoint, for example in terms of coordination numbers (C.N.).

The stereochemistry of carbon with C.N. = 2, 3, and 4 has been studied in detail in relation to organic compounds. An expansion of the coordinating capacity of carbon has been observed in carbaboranes, where C.N. = 4, 5, and 6 are encountered. In the present review we attempted to compare these two ranges of C.N. on the basis of carbaborane data obtained in the gas and crystalline phases. The polyhedral and exopolyhedral bonds formed by carbon are considered separately; next, bonds involving boron atoms are analysed by analogy. The classification of exopolyhedral distances as an independent group, which we proposed on the basis of geometrical considerations[1], has been confirmed independently in the study of the photoelectron spectra of carbaboranes[2].

One cannot assume *a priori* that a fairly formal characteristic of the atom such as its coordination number will exert a unique or even a decisive influence on the lengths of all the bonds involving the given atom. In particular, this applies to systems with a considerable delocalisation of electrons, to which carbaboranes belong. Such cases may require an additional allowance for electronic factors.

II. C–C BONDS

Stoichev's rule, expressing the dependence of the C–C bond length on the number of bonds or atoms attached to

†Lipscomb also played an important role in the experimental determination of the structures of numerous boron hydrides and carbaboranes by X-ray diffraction. His work in this field was recognised by the award of the Nobel prize in 1976.

it, is well known in the stereochemistry of organic compounds:

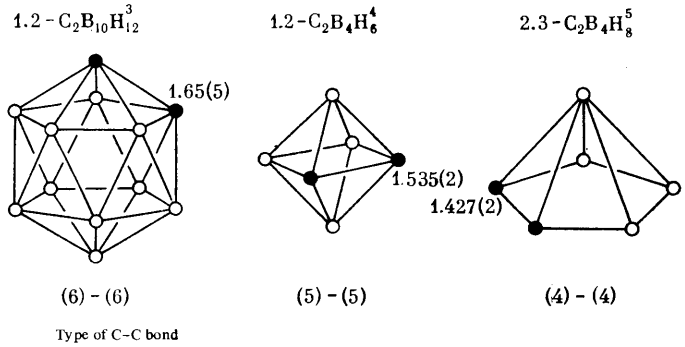
$$r(C-C) = 1.299 + 0.040\,n(\text{Å});\ n = 2-6, \qquad (1)$$

where n is equal to the sum of the C.N. of the atoms forming the bond minus two.

This equation reproduces satisfactorily the C–C bond lengths in diacetylene ($n = 2$), vinylacetylene ($n = 3$), butadiene ($n = 4$), propene ($n = 5$), and ethane ($n = 6$), constituting a convincing illustration of the usefulness of the concept of the coordination number. Numerous attempts have been made at a theoretical justification of Stoichev's rule (these include the theory of orbital hybridisation, allowance for the influence of the delocalisation of electrons, steric effects, electronegativity, amount of ionic character of the bond, etc), but as yet there is no unanimous view on this subject.

The problem arises of the possibility of extrapolating Stoichev's equation to higher C.N. for carbon atoms, characteristic of carbaboranes. We have shown[1] that, for the C–C bond of the type (6)–(6) (the C.N. of the carbon atoms are indicated in brackets), Eqn.(1) leads to 1.699 Å, which agrees, within the limits of the errors of the individual measurements, with the value 1.655 Å found for 1,2-$C_2B_{10}H_{12}$ (Bohn and Bohn[3]) and its derivatives.

Analogous treatment yields 1.619 and 1.539 Å for bonds of the type (5)–(5) and (4)–(4) respectively, which differ appreciably from the experimental data quoted below:



Such a marked discrepancy led us to compile additional literature data for the structures of carbaboranes, which are listed in the Table. The coordination numbers for all the bonds, with the exception of those of the (6)–(6) type, are indicated here as superscripts; for C–B bonds, the C.N. of the carbon atoms is given first. Additional alphabetic subscripts are used only for B–B bonds and correspond to their classification in relation to carbon atoms (see below).

The majority of the compounds investigated are *closo*-carbaboranes; the letters (*n*) and (*a*) denote *nido*- and *arachno*-carbaboranes respectively. Carbaboranes with heteroatoms (1-$CH_3GaC_2B_4H_6$, 1,12-$CHPB_{10}H_{10}$, etc.) are not included in the Table.

The results for C–C bonds are presented in a graphical form in Fig.1. Inspection of this figure permits the following observations.

1. The length of polyhedral C–C bonds in *closo*- and *nido*-carbaboranes varies linearly with the C.N. of the carbon atoms, which is described by the empirical equation

$$r(C-C) = 1.074 + 0.058\,n(\text{Å});\ n = 6, 8, 9, 10. \qquad (2)$$

Evidently the observed relation for carbaboranes lies below that for hydrocarbons and the straight lines corresponding to Eqns.(1) and (2) diverge appreciably in the region of low C.N., which also accounts for the unsatisfactory estimates of the lengths of bonds of the type (4)–(4) and (5)–(5) in carbaboranes by Eqn.(1).

2. Extrapolation of Eqn.(2) to the region of small C.N., shown by a dashed line, yields satisfactory estimates of the lengths of the C=C and C≡C multiple bonds. This phenomenon is especially interesting in the light of the fact that a considerable amount of double-bond character has been postulated for the (4)–(4) bond in $C_2B_4H_8$ and $C_4B_2H_6$.[7,8,50]

3. The exopolyhedral C–C_e bonds form a special group of distances, depending little on the immediate environment, which is described by the empirical equation

$$r(C-C_e) = 1.510 + 0.002\,n(\text{Å});\ n = 6, 7, 8, 10. \qquad (3)$$

These distances vary on average from 1.52 to 1.53 Å with increase of n from 6 to 10, i.e. they are almost constant and intersect the bond corresponding to Eqn.(2) in the region of bonds of the type (6)–(4).

Overall, the data for the exopolyhedral C–X distances in carbaboranes are few and are in essence limited to C–C distances. However, for X = I or Si, the substituent is seen to exert a considerable influence, since the C–I bonds in 1,7-$C_2I_2B_{10}H_{10}$ [51] and 1,12-$C_2I_2B_{10}H_{10}$ [28] are much shorter and the C–Si bond in 1,2-$C_2(CH_3)[Si(CH_3)_3]B_{10}H_{10}$ [37] is much longer than might have been expected on the basis of stereochemical analogies. The structural data for C–H bonds are not very accurate and are therefore not discussed here. One should only note that the high vibration frequencies of the C–H bonds, characteristic of ethylenic and aromatic compounds, are also characteristic of carbaboranes: with increase of the C.N. of the carbon atom, the frequencies diminish[52].

III. POLYHEDRAL C–B BONDS

In the most symmetrical *closo*-carbaboranes the polyhedral C–B bonds depend only on the C.N. of the carbon atom n_C (Mastryukov et al.[1]):

$$r(C-B) = 1.249 + 0.077\,n_C(\text{Å});\ n_C = 4, 5, 6. \qquad (4)$$

When data for 1,10-$C_2B_8H_{10}$ were published[23], it became possible to estimate the influence of the C.N. of the boron atom for a constant C.N. of the carbon atom. The C–B bond lengths are indicated below for symmetrical *closo*-carbaboranes having C_2B_4, C_2B_8, and C_2B_{10} skeletons with an indication of the C.N. of the atoms forming the bond:

C(5)–B(5)	C(5)–B(6)	C(6)–B(6)
1.634 (4)[12]	1.602 (2)[23]	1.710 (11)[3]

This comparison shows that, when the C.N. of the boron atom is altered, there is a smaller change in the C–B bond lengths than after the alteration of the C.N. of the carbon atom. This justifies the choice of n_C as the variable quantity in Eqn.(4). On the other hand, when one employs the atomic radii of boron proposed by Brown and Lipscomb[53], then the C–B(6) bond should be longer by 0.070 Å than the C–B(5) bond.

A more complex picture arises for the C–B bonds when account is taken of less symmetrical *closo*-carbaboranes and data for *nido*-carbaboranes are included (see Table). It then becomes clear that Eqn.(4) is applicable only to the most symmetrical *closo*-carbaboranes. It can be assumed that the wide variety of C–B bonds is best characterised by the simplest relation in the form of Eqn.(4), taking into account

The bond lengths in carbaboranes (in Å).

No.	Molecule	C–C (polyhedral)	C–C (exopolyhedral)	C–B (polyhedral)	B–B (polyhedral)	Method	Refs
1	1,5-$C_2B_3H_5$	—	—	1.556[4]–[5]	1.853[5]–[5], i	E	6
2	2,3-$C_2B_4H_8$ (*n*)	1.419[4]–[4]	—	1.500[4]–[5], 1.750[4]–[6]	1.714[c], 1.772[5]–[6], g, 1.790[5]–[6], b	X	7
	»	1.427[4]–[4]	—	1.538[4]–[5], 1.764[4]–[6]	1.695[c], 1.816[5]–[6], b, 1.821[5]–[6], g	E	5
3	2,3-$C_2(CH_3)_2B_4H_6$ (*n*)	1.431[4]–[4]	1.516[4]–[4]	1.520[4]–[5], 1.763[4]–[6]	1.705[c], 1.768[5]–[6], g, 1.778[5]–[6], b	X	7
4	$C_4B_2H_6$ (*n*) *	1.424[4]–[4], 1.436[4]–[4]	—	1.541[4]–[4], 1.697[4]–[6], 1.709[4]–[6]	1.886[4]–[6], i	M	8
5	CB_5H_9 (*n*)	—	—	position of C atom not determined	1.759[5]–[6], b, 1.781[b], 1.782[5]–[6], d, 1.830[a]	M	10
6	1,2-$C_2B_4H_6$	1.535[5]–[5]	—	1.618[5]–[5], 1.621[5]–[5]	1.723[5]–[5], g, 1.745[5]–[5], e	E	4
	»	1.540[5]–[5]	—	1.605[5]–[5], 1.627[5]–[5]	1.721[5]–[5], g, 1.752[5]–[5], e	M	11
7	1,6-$C_2B_4H_6$ **	—	—	1.633[5]–[5]	1.720[5]–[5], i	E	6
	»	—	—	1.634[5]–[5]	1.724[5]–[5], i	E	12
8	CB_5H_7	—	—	1.60[5]–[6], 1.63[5]–[5]	1.70[5]–[6], b,d 1.72[5]–[5],d, 1.87[d] 1.89[b]	M	14
	»	—	—	1.602[5]–[6], 1.660[5]–[5]	1.686[5]–[6],d, 1.690[5]–[6], b, 1.756[5]–[5],d, 1.910[b], 1.921[d]	E	4
9	2,4-$C_2B_5H_7$	—	—	1.546[5]–[5], 1.563[5]–[5], 1.708[5]–[6]	1.651[5]–[5], f, 1.815[5]–[6],h, 1.818[5]–[6], i	M	15
	»	—	—	1.537[5]–[5], 1.558[5]–[5], 1.717[5]–[6]	1.659[5]–[5], f, 1.772[5]–[6],h, 1.852[5]–[6], i	E	16
10	1,7-$C_2(CH_3)_2B_6H_6$	—	1.521[5]–[4]	1.500[5]–[5], 1.595[5]–[6], 1.695[5]–[6], 1.697[5]–[6]	1.696[5]–[6],f, 1.772[5]–[6],f, 1.806[5]–[6],d, 1.842[h] 1.894[i], 1.902[f]	X	17
11	1,6-$C_2B_7H_9$	—	—	position of C atoms not determined	1.712[5]–[6], b, 1.784[d],1.805[i], 1.976[h], 1.995[f]	M	18
12	1,6-$C_2(CH_3)_2B_7H_7$	—	1.529[5]–[4]	1.595[5]–[6], 1.615[5]–[6]	1.698[5]–[6], b, 1.764[i], 1.772[d], 1.969[h], 1.984[f]	X	19
13	5,9-$C_2(CH_3)_2B_7H_{11}$ (*a*)	—	1.559[5]–[4]	1.672[5]–[6], 1.704[5]–[5], 1.706[5]–[6]	1.714[f], 1.725[a], 1.730[5]–[6],h, 1.777[b], 1.779[d], 1.819[b], 1.823[b]	X	20
14	1,2-$C_2(CH_3)_2B_7H_9$ (*n*)	1.55[5]–[5]	1.50[5]–[4]	1.60[5]–[5], [5]–[6], 1.65[5]–[6], 1.67[5]–[6], 1.75[5]–[5]	1.69[a], 1.75[5]–[6], b, 1.78—1.81	X	21
15	1,6-$C_2(CH_3)_2B_8H_8$	—	1.505[5]–[4], 1.527[6]–[4]	1.597[5]–[6], 1,600[5]–[6], 1,632[6]–[5] 1.751, 1.776	1.681[5]–[6], b, 1.694[5]–[6],d, 1.783[h] 1.797[f], 1.812[h] 1.828[b], 1.831[d], 1.861[i]	X	22
16	1,10-$C_2B_8H_{10}$	—	—	1.602[5]–[6]	1.829[f], 1.850[d]	E	23
17	6,9-$C_2(CH_3)_2B_9H_9$	—	1.52[5]–[4]	1.60[5]–[6], 1.67[5]–[7], 1.70[5]–[6]	1.78[b] 1.80[b], 1.82[d], 1.85[a], 1.87[f], 2.06[6]–[7], h	X	24
18	11-CH_3-2,7-$C_2B_9H_{12}$ (*n*)	1.606[5]–[6]	—	1.621[5]–[6], 1.657[5]–[6], 1.660, 1.677, 1.682, 1.707[5]–[6], 1.791	1.734[b], 1.746[a], 1.752[a], 1.755[c], 1.774[b], 1.776 g, 1.784[a], 1.786[b], 1.792[b], 1.796[b], 1.800 g, 1.836 g, 1.849[b], 1.856[c], 1.920[a]	X	25
19	$C_4(CH_3)_4B_8H_8$ (i)	1.49[5]–[5]	1.52[5]–[4]	1.62—2.15 (cf. 1.78[5]–[6])	1.68—1.86 (cf. 1.78)	X	26
20	1,12-$C_2B_{10}H_{12}$	—	—	1.710	1.772[f], 1.792d	E	3
21	(1,12-$C_2B_{10}H_{11})_2$	—	—	1.709	1.756[f], 1.777d	X	27
22	1,12-$C_2I_2B_{10}H_{10}$	—	—	1.708	1.775[f], 1.777d	E	28
23	1,2-$C_2B_{10}H_{12}$	1.653	—	1.711 ***	1.798, 1.802 ***	E	3
24	(1,2-$C_2B_{10}H_{11})_2$	—	1.522	1.722	1.768, 1.777	X	29
25	1,2-$C_2H_2B_{10}Cl_8H_2$	1.67	—	1.70, 1.73	1.75[c], 1.76[b], 1.78[b], 1.79[d], 1.81[a,g], 1.82[a]	X	30
26	1,2-$C_2(CH_2Br)_2B_{10}H_{10}$	1.64	1.52[6]–[4]	1.71, 1.73	1.75[b], 1.76[c], 1.77[a], 1.78 g, 1.79[d], 1.81[a]	X	31
27	1,2-$C_2H_2B_{10}Br_2H_8$	1.63	—	1.71, 1.73	1.73[a,c], 7.74[b], 1.76 b,g, 1.78[a], 1.80[d]	X	32
28	1,2-$C_2(CH_3)_2B_{10}Br_4H_6$	1.65	1.51[6]–[4]	1.71, 1.73	1.76[b], 1.77[c], 1.78[a,d,g], 1.79 a,b	X	33
29	1,2-$C_2H_2B_{10}Br_3H_7$	1.65	—	1.70, 1.71	1.74[c,g], 1.78[b], 1.80[a,b,d]	X	34
30	(1,2-$C_2B_{10}H_{10}CO)_2$	1.645	1.520[6]–[3]	1.715, 1.745	1.760[c], 1.767[b], 1.771[d], 1.781[b], 1.782[a], 1.785[a], 1.792g	X	35
31	1,2-$C_2B_{10}(CH_3)_4H_8$	1.663	1.504[6]–[4]	1.706, 1.757	1.767[d], 1.768[b], 1.771[b], 1.774[a], 1.777[c], 1.785g	X	36
32	1,2-$C_2H(C_4H_9)B_{10}H_{10}$	1.670	1.562[6]–[4]	1.714	1.766—1.791 (cf. 1.777)	X	37
33	1,2-$C_2(CH_3)[Si(CH_3)_3]B_{10}H_{10}$	1.669	1.524[6]–[4]	1.718	1.766—1.790 (cf. 1.777)	X	37
34	C_6H_5CO-1,2-$C_2B_{10}H_{11}$	1.62	—	1.71	1.76—1.81 (cf. 1.78)	X	38
35	1,2-$C_2(CH_3)_2B_{10}(C_6H_5)H_9$	1.70	1.52[6]–[4]	1.69	1.71—1.86 (cf. 1.76)	X	39
36	1,2-$C_2H_2B_{10}(CH_3C_6H_4)H_9$	1.62	—	1.69	1.69—1.86 (cf. 1.78)	X	39
37	$(CH_3)_2Ge(1,2\text{-}C_2B_{10}H_{10})_2PC_6H_5$	1.678	—	1.722	1.762—1.794 (cf. 1. 778)	X	40
38	$(CH_3)_2Sn(1,2\text{-}C_2B_{10}H_{10})_2$, $CHOCH_3$	1.71	1.51[6]–[4]	1.73	1.66—1.99 (cf. 1.81)	X	40
39	$CH_2(1,2\text{-}C_2B_{10}H_{10})_2PCH_3$	1.655	1.518[6]–[4]	1.724	1.754—1.798 (cf. 1.770)	X	41
40	$(1,2\text{-}C_2B_{10}H_{10})_2AsCH_3$	1.650	1.529	1.729	1.73—1.81 (cf. 1.772)	X	41
41	1,7-$C_2B_{10}H_{12}$	—	—	1.720****	1.791, 1.817, 1.831[i] ****	E	3
42	1,7-$C_2H_2B_{10}Br_2H_8$	—	—	1.64, 1.68, 1.74	1.70[b], 1.72[h] 1.77[a], 1.80[b], 1.81[f], 1.83[d], 1.89[i]	X	42
43	1,7-$C_2H_2B_{10}Cl_{10}$	—	—	1.70	cf. 175	X	43
44	1,7-$C_2H_2B_{10}H_7CH_3Cll$	—	—	1.69, 1.71, 1.74	1.78[b,f,h] 1.80[b], 1.83[d], 1.87[a], 1.93[i]	X	44
45	1,7-$C_2H_2B_{10}Br_3H_7$	—	—	1.71, 1.72	1.73[b], 1.75[a,f] 1.76[h], 1.79[b], 1.80[d] 1.82[i]	X	45
46	1,7-$C_2(CH_3)_2B_{10}Cl_2H_8$	—	1.56[6]–[4]	1.72, 1.73	1.74[h], 1.76[b], 1.79[d,f], 1.81[b,i], 1.84[a]	X	46
47	1,7-$C_2H(CH_3)B_{10}Br_3H_7$	—	1.49[6]–[4]	1.73–1.75 (equality of all bond lengths in icosahedron was assumed)		X	47
48	1,7-$C_2H_2B_{10}Cl_3H_7$	—	—	1.680, 1.689, 1.691	1.757[f], 1.761[h] 1.765[i], 1.772[b], 1.774[d], 1.776[b], 1.791[a]	X	48
49	1,7-$C_2(C_6H_5)B_{10}H_{10}$	—	1.52[6]–[3]	1.70, 1.74	1.75[i], 1.78[h], 179[b,f], 180[a,b,d]	X	49

Remarks: Research techniques used: E = electron diffraction; X = X-ray diffraction; M = microwave spectroscopy.

*An electron diffraction study of $C_4B_2(CH_3)_6$ has also been carried out[9]. These data are unreliable, since they differ markedly from the results for the unsubstituted molecule.

**The 2-Cl-1,6-$C_2B_4H_5$ molecule has been investigated by the microwave method[13]. These results have not been included in the Table because of their low accuracy.

***The values for two types of C–B bonds in *ortho*-carbaborane and its derivatives (Nos.23–40) are presented: C(1)–B(3) and C(1)–B(4) (the atoms are always numbered in accordance with Bohn and Bohn[3]) or average values are given. The values for seven types of B–B bonds are quoted: B(3)–B(4)(g); B(4)–B(5)(d); B(3)–B(8)(c); B(4)–B(8)(b); B(4)–B(9)(b); B(8)–B(9)(a); B(9)–B(12)(a); otherwise the average values for some of them are given.

****The values for three types of C–B bonds in *meta*-carbaborane and its derivatives (Nos.41–49) are quoted: C(1)–B(2), C(1)–B(4), and C(1)–B(5), or their average values are given. Seven types of B–B bonds are quoted: B(2)–B(3)(i); B(2)–B(6)(h); B(4)–B(5)(d); B(4)–B(8)(f); B(4)–B(9)(b); B(5)–B(9)(b); B(9)–B(10)(a); otherwise the average values of some of them are given.

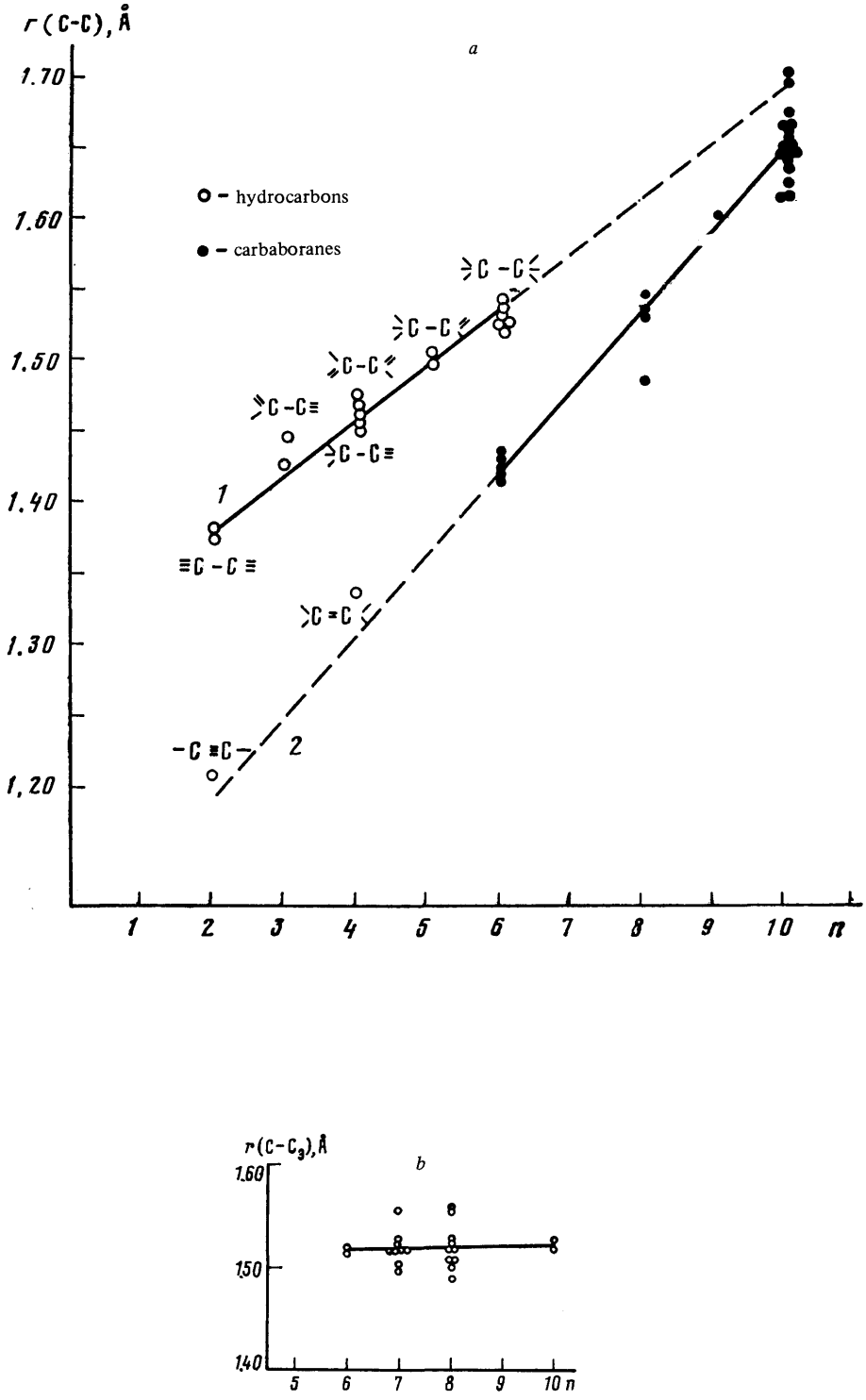


Figure 1. Variation of the C–C bond lengths in carbaboranes and hydrocarbons with the number n of neighbouring bonds: *a*) continuous line *1* corresponds to the variation of the bond lengths in hydrocarbons [see Eqn.(1)] and line *2* corresponds to the variation of the polyhedral distances in carbaboranes [see Eqn.(2)]; the dashed line represents the extrapolation of Eqn.(1) to the region of high C.N. of the carbon atom and the extrapolation of Eqn.(2) to the region of low C.N. of the carbon atom; *b*) variation of the exopolyhedral distances in carbaboranes [see Eqn.(3)].

the deviations from the latter, which in the case of *closo*-carbaboranes are indicated in Fig.2.

IV. POLYHEDRAL B–B BONDS

The uncertain role of the C.N. of the boron atom in C–B bonds becomes still more appreciable on passing to B–B bonds even in the simplest *closo*-carbaboranes with the following skeletons:

C_2B_3	C_2B_4	C_2B_5		C_2B_8	C_2B_{10}
(5) — (5)	(5) — (5)	(5) — (5)	(5) — (6)	(6) — (6)	(6) — (6)
1.853 (2)	1.724 (9)	1.659 (10)	1.772 (11)	1.850 (5)	1.792 (7)
			1.852 (11)	1.829 (4)	1.772 (13)

(for the corresponding references, see Table). The B–B bond lengths apparently depend to a large extent on electronic factors which are weakly related (or not related at all) to the C.N. One may note, by analogy, that in the stereochemistry of organic compounds not all the changes in C–C bond lengths depend on the C.N.: the most evident exceptions are cyclic hydrocarbons and sterically hindered molecules[54].

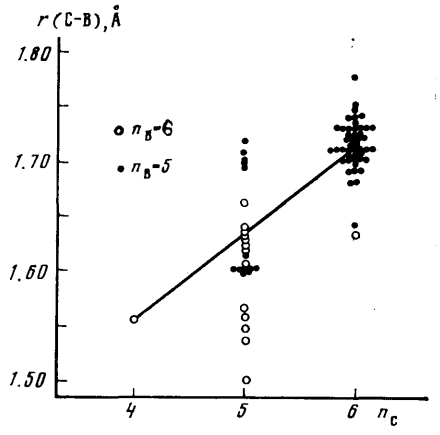


Figure 2. Variation of the C–B bond lengths in *closo*-carbaboranes with the C.N. of the carbon atom n_C. Different designations have been used for different C.N. of the boron atom (n_B). The straight line corresponds to Eqn.(4).

The anomalously long B–B bond in 1,5-$C_2B_3H_5$ [6] agrees with the quantum-chemical description of this molecule[55], which is represented as a bicyclic system consisting of three C–B–C bonds and without B–B bonds. For the remaining cases, a gradual increase of the B–B distances with increasing C.N. of the boron atoms can be seen. This agrees qualitatively with the proposed[53] atomic radii of boron with different coordination, but quantitative estimates are relatively inaccurate even in those cases where the geometry has been optimised[55,56].

As a result of structural studies on carbaboranes, attempts have been made to specify the rules concerning the B–B distances.

1. In molecules of *p*-carbaborane 1,1,2-$C_2B_{10}H_{12}$ and its derivatives[3,27,28] and also in 1,10-$C_2B_8H_{10}$ [23] the B–B bonds at the bases of the pyramids are longer than the equatorial bonds.

2. The B–B distance included between two carbon atoms is longest in the molecules of certain small carbaboranes[15–17,22] and also in *m*-carbaborane 1,7-$C_2B_{10}H_{12}$ and its derivatives[3,42,44,45].

3. In the molecules of *o*-carbaborane 1,2-$C_2B_{10}H_{12}$ and its derivatives[3] there is a tendency towards an increase in the length of the B–B bonds near carbon atoms.

Although the proposed rules are not general (exceptions are known[18,19,34,46,48,49]), they are of considerable interest. They can be related to the distribution of charges on the boron and carbon atoms, which obey the so-called inductive rule[57]. According to this rule, boron atoms become electropositive when they are linked to carbon atoms. The inductive rule acquires a geometrical aspect when account is taken of the fact that the bond between two electropositive boron atoms should be weak and long and that an increase of the negative charge on the atoms should be accompanied by a strengthening and shortening of the bonds. Hence it follows that the longest B–B bonds are to be expected in the vicinity of carbon atoms and that the shortest B–B bonds are those at the maximum remove from them.

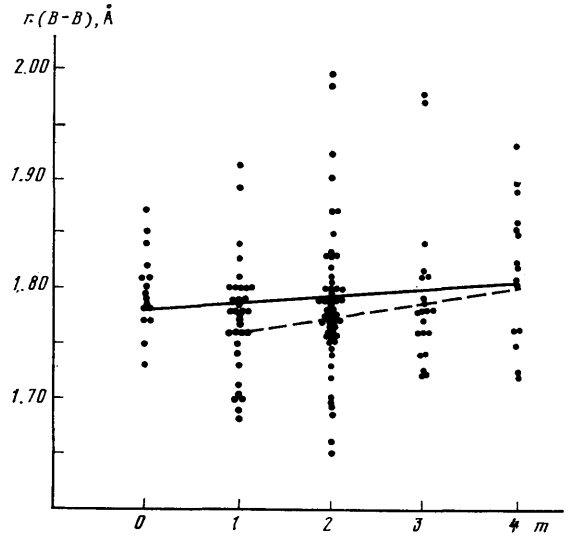
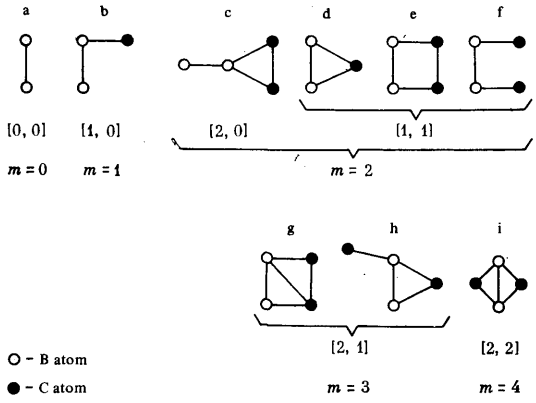


Figure 3. Variation of the B–B bond lengths in *closo*-carbaboranes with the overall number *n* of attached carbon atoms. The continuous line corresponds to Eqn.(5). The dashed line represents the corresponding relation for unsubstituted carbaboranes $C_2B_nH_{n+2}$.

As a result of this approach, it becomes clear that the empirical relations noted above are a direct consequence of a modified inductive rule. Furthermore, there is a possibility of a more detailed quantitative test of the applicability of this rule to the carbaboranes investigated. For this purpose, all the B–B bonds listed in the Table have been classified in terms of the [*k*, *l*[types; the numerals in square brackets show to how many carbon atoms each boron atom is linked.

The comparison of different B–B bonds is based on the overall characteristic $m = k + l$:



The results of a quantitative treatment of data for *closo*-carbaboranes alone are presented in Fig.3 and are described by the equation

$$r(\text{B—B}) = 1.780 + 0.006\,m(\text{Å});\ m = 0,\ 1,\ 2,\ 3,\ 4. \qquad (5)$$

For each type of B–B bond, there is a considerable scatter of values, but the average bond length is in all cases close to 1.80 Å. In order to eliminate the possible influence of substituents on the distribution of electron density in the skeleton, a calculation was performed taking into account only data for unsubstituted carbaboranes $C_2B_nH_{n+2}$. The final relation changed insignificantly, as shown by the dashed line in Fig.3.

Thus the analysis showed that the modified inductive rule is of limited applicability, being valid only for some molecules. In the remaining cases there are appreciable infringements of this rule, as a result of which the average B–B distances are almost independent of the distance from the carbon atoms in the molecules of *closo*-carbaboranes.

V. EXOPOLYHEDRAL B–X BONDS

The B–Hal bonds proved to be most thoroughly investigated among the exopolyhedral bonds formed by boron atoms in carbaboranes. Compared with, for example, the C–I bond mentioned above, their specific features consist in the fact that all the B–Hal distances in the carbaboranes investigated[13,30,32–34,42,43–48], where Hal = Cl, Br, or I, are greater by 0.01–0.1 Å than the corresponding distances in the simplest compounds of the type $BHal_3$.[58]# This is consistent with the fact that the electron-accepting properties of the C_2B_{10} carbaborane nucleus are manifested much more weakly in relation to the substituents attached to the boron atoms than in relation to the substituents at the carbon atoms[59]. It is also of interest to note that, in contrast to the C–H bonds (see above), the B–Cl vibration frequencies in carbaboranes are lower than in the B_2Cl_4 and BCl_3 molecules[60].

#The only exception is the B–Cl distance in the $1,7\text{-}C_2H_2B_{10}H_7CH_3ClI$ molecule (1.69 Å),[44] which is somewhat smaller than in BCl_3.

The B–C distances in the four carbaboranes investigated[25,36,39] are 1.55–1.60 Å, which is close to the B–C distances in the $B(CH_3)_3$ (1.578 Å)[61] and $1\text{-}CH_3B_5H_9$ (1.595 Å)[62] molecules and to values expected on the basis of Eqn.(4) (Fig.2) for the polyhedral C–B bonds with $n_C = 4$. For $1,2\text{-}C_2B_{10}$. $.(CH_3)_4H_8$, this distance is significantly longer (1.68 Å).[44]

The B–B distance between the two carbaboranyl systems in $(1,2\text{-}C_2B_{10}H_{11})_2$ is 1.660 Å,[27] which is appreciably smaller than the polyhedral distances of the same type, but is close to the corresponding distance (1.686 Å)[63] between the *closo*-borane fragments in $10,10'\text{-}\{B_{10}H_8[S(CH_3)_2]\}_2$ and to the distance (1.678 Å)[64] in its analogue $2,2'\text{-}(1\text{-}B_9H_8S)_2$.

---o0o---

It is seen from the foregoing that individual aspects of the geometrical structures of carbaboranes have now been investigated in fair detail. This applies primarily to the structure of *closo*-carbaboranes and especially to the structure of the icosahedral carbaboranes with the C_2B_{10} skeleton. The accumulated data permit a classification of the internuclear distances and make it possible to discover certain rules in the variation of the polyhedral bonds in carbaboranes. The exopolyhedral C–X and B–X bonds have been studied much less, although they undoubtedly merit a special systematic investigation.

During the preparation of this article, two reviews devoted to the chemistry of carbaboranes were published[65,66], which demonstrates yet again the vigorous development of this field of chemistry.

REFERENCES

1. V.S.Mastryukov, L.V.Vilkov, and O.V.Dorofeeva, J.Mol.Struct., **24**, 217 (1975).
2. T.P.Fehlner, Inorg.Chem., **14**, 934 (1975).
3. R.K.Bohn and M.D.Bohn, Inorg.Chem., **10**, 350 (1971).
4. E.A.McNeill and F.R.Scholer, Inorg.Chem., **14**. 1081 . (1975).
5. E.A.McNeill and F.R.Scholer, J.Amer.Chem.Soc., **99**, 6243 (1977).
6. E.A.McNeill, K.L.Gallaher, F.R.Scholer, and S.H.Bauer, Inorg.Chem., **12**, 2108 (1973).
7. F.P.Boer, W.E.Streib, and W.N.Lipscomb, Inorg. Chem., **3**, 1666 (1964).
8. J.P.Pasinski and R.A.Beaudet, J.Chem.Phys., **61**, 683 (1974).
9. J.Haase, Z.Naturforsch., **28a**, 785 (1973).
10. C.-C.S.Cheung and R.A.Beaudet, Inorg.Chem., **10**, 1144 (1971).
11. R.A.Beaudet and R.L.Poynter, J.Chem.Phys., **53**, 1899 (1970).
12. V.S.Mastryukov, O.V.Dorofeeva, L.V.Vilkov, A.V.Golubinskii, A.F.Zhigach, V.T.Laptev, and A.B.Petrunin, Zhur.Strukt.Khim., **16**, 171 (1975).
13. G.L.McKown and R.A.Beaudet, Inorg.Chem., **10**, 1350 (1971).
14. G.L.McKown, B.P.Don, R.A.Beaudet, P.J.Vergamini, and L.H.Jones, Chem.Communs., 765 (1974).
15. R.A.Beaudet and R.L.Poynter, J.Chem.Phys., **43**, 2166 (1965).
16. E.A.McNeill and F.R.Scholer, J.Mol.Struct., **27**, 151 (1975).
17. H.Hart and W.N.Lipscomb, Inorg.Chem., **7**, 1070 (1968).
18. K.-K.Lau and R.A.Beaudet, Inorg.Chem., **15**, 1059 (1976).

19. T.F.Koetzle, F.E.Scarbrough, and W.N.Lipscomb, Inorg.Chem., **7**, 1076 (1968).
20. D.Voet and W.N.Lipscomb, Inorg.Chem., **6**, 113 (1967).
21. J.C.Huffman and W.E.Streib, Chem.Communs., 665 (1972).
22. T.F.Koetzle and W.N.Lipscomb, Inorg.Chem., **9**, 2279 (1970).
23. E.G.Atavin, V.S.Mastryukov, A.V.Golubinskii, and L.V.Vilkov, J.Mol.Struct., **65**, 259 (1980).
24. C.Tsai and W.E.Streib, J.Amer.Chem.Soc., **88**, 4513 (1966).
25. Yu.T.Struchkov, M.Yu.Antipin, V.I.Stanko, V.A.Brattsev, N.I.Kirillova, and S.P.Knyazev, J.Organomet.Chem., **141**, 133 (1977).
26. D.P.Freyberg, R.Weiss, E.Sinn, and R.N.Grimes, Inorg.Chem., 16, 1847 (1977).
27. N.I.Kirillova, A.I.Klimova, Yu.T.Struchkov, and V.I.Stanko, Zhur.Strukt.Khim., **17**, 675 (1976).
28. A.Almenningen, O.V.Dorofeeva, V.S.Mastryukov, and L.V.Vilkov, Acta Chem.Scand., A**30**, 307 (1976).
29. L.H.Hall, A.Perloff, F.A.Mauer, and S.Block, J.Chem.Phys., **43**, 3911 (1965).
30. J.A.Potenza and W.N.Lipscomb, Inorg.Chem., 3, 1673 (1964).
31. D.Voet and W.N.Lipscomb, Inorg.Chem., **3**, 1679 (1964).
32. J.A.Potenza and W.N.Lipscomb, Inorg.Chem., **5**, 1471 (1966).
33. J.A.Potenza and W.N.Lipscomb, Inorg.Chem., **5**, 1483 (1966).
34. J.A.Potenza and W.N.Lipscomb, Inorg.Chem., 5, 1478 (1966).
35. R.W.Rudolph, J.L.Pflug, C.M.Bock, and M.Hodgson, Inorg.Chem., **9**, 2274 (1970).
36. N.I.Kirillova, M.Yu.Antipin, Yu.V.Gol'tyapin, Yu.T.Struchkov, and V.I.Stanko, Izv.Akad.Nauk SSSR, Ser.Khim., 859 (1978).
37. N.I.Kirillova, T.V.Klimova, Yu.T.Struchkov, and V.I.Stanko, Izv.Akad.Nauk SSSR, Ser.Khim., 2481 (1979).
38. A.V.Astakhin, V.N.Kalinin, V.V.Romanov, A.I.Gusev, N.I.Kobel'kova, and K.I.Zakharkin, Zhur.Strukt.Khim., **19**, 555 (1978).
39. V.N.Kalinin, N.I.Kobel'kova, A.V.Astakhin, A.I.Gusev, and L.I.Zakharkin, J.Organomet.Chem., **149**, 9 (1978).
40. N.G.Bokii, A.I.Yanovskii, Yu.T.Struchkov, N.F.Shemyakin, and L.I.Zakharkin, Izv.Akad.Nauk SSSR, Ser.Khim., 380 (1978).
41. A.I.Yanovskii, N.G.Furmanova, Yu.T.Struchkov, N.F.Shemyakin, and L.I.Zakharkin, Izv.Akad.Nauk SSSR, Ser.Khim., 1523 (1979).
42. H.Beall and W.N.Lipscomb, Inorg.Chem., 6, 874 (1967).
43. J.A.Potenza and W.N.Lipscomb, Proc.Nat.Acad.Sci. U.S.A., **56**, 1917 (1966).
44. N.I.Kirillova, Yu.V.Gol'tyapin, Yu.T.Struchkov, and V.I.Stanko, Zhur.Strukt.Khim., **17**, 681 (1976).
45. A.A.Sayler and H.Beall, Canad.J.Chem., **54**, 1771 (1976).
46. H.V.Hart and W.N.Lipscomb, Inorg.Chem., 12, 2644 (1973).
47. I.S.Astakhova, Yu.T.Struchkov, V.I.Stanko, and N.S.Titova, Zhur.Strukt.Khim., 10, 1063 (1969).
48. N.I.Kirillova, A.I.Klimova, Yu.T.Struchkov, and V.I.Stanko, Zhur.Strukt.Khim., 17, 892 (1976).
49. A.V.Astakhin, V.V.Romanov, A.I.Gusev, V.N.Kalinin, L.I.Zakharkin, and N.G.Los', Zhur. Strukt.Khim., 18, 406 (1977).
50. D.S.Marynick and W.N.Lipscomb, J.Amer.Chem. Soc., **94**, 8692 (1972).
51. V.S.Mastryukov, L.V.Vilkov, A.V.Golubinskii, E.L.Osina, and E.G.Atavin, Zhur.Strukt.Khim., 19, 763 (1978).
52. L.A.Leites and L.E.Vinogradova, J.Organomet. Chem., **125**, 37 (1977).
53. L.D.Brown and W.N.Lipscomb, Inorg.Chem., **16**, 2989 (1977).
54. L.V.Vilkov, V.S.Mastryukov, and N.I.Sadova, "Opredelenie Geometricheskogo Stroeniya Svobodnykh Molekul" (Determination of the Geometrical Structure of Free Molecules), Izd.Khimiya, Leningrad, 1979.
55. C.-C.S.Cheung, R.A.Beaudet, and G.A.Segal, J.Amer.Chem.Soc., **92**, 4158 (1970).
56. M.J.S.Dewar and M.L.McKee, J.Amer.Chem.Soc., **99**, 5231 (1977).
57. F.P.Boer, J.A.Potenza, and W.N.Lipscomb, Inorg. Chem., **5**, 1301 (1966).
58. L.V.Vilkov, L.S.Khaikin, A.F.Zhigach, and V.N.Siryatskaya, Zhur.Strukt.Khim., 9, 889 (1968).
59. R.N.Grimes, "Carboranes" (Translated into Russian), Izd.Mir, Moscow, 1974, Chapters 6 and 7.
60. L.A.Leites, L.E.Vinogradova, V.T.Aleksanyan, and S.S.Bukalov, Izv.Akad.Nauk SSSR, Ser.Khim., 2480 (1976).
61. L.S.Bartell and B.L.Carroll, J.Chem.Phys., 42, 3076 (1965).
62. J.D.Wieser, D.C.Moody, J.C.Huffman, R.L.Hilderbrandt, and R.Schaeffer, J.Amer.Chem.Soc., **97**, 1074 (1975).
63. O.P.Anderson and A.P.Schmitt, Inorg.Chem., **16**, 1630 (1977).
64. W.R.Pretzer, T.K.Hilty, and R.W.Rudolph, Inorg. Chem., **14**, 2459 (1975).
65. V.I.Stanko, V.A.Brattsev, and S.P.Knyazev, Uspekhi Khim., **48**, 241 (1979)[Russ.Chem.Rev., No.2 (1979)].
66. E.V.Leonova, Uspekhi Khim., 49, 283 (1980)[Russ. Chem.Rev., No.2 (1980)].

Faculty of Chemistry, Lomonosov
Moscow State University

The High Temperature Institute,
USSR Academy of Sciences, Moscow

Translated from *Uspekhi Khimii*, 49, 2389 - 2417 (1980) U.D.C. 547.979.733:541.49

The Formation, Structure, and Properties of the Extracomplexes of Porphyrins

B.D.Berezin and O.I.Koifman

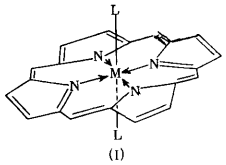
The results of studies on the extracomplexes of metalloporphyrins namely the conditions of their formation, structure, spectroscopy, kinetics, and thermodynamics, are considered.
The bibliography includes 245 references.

CONTENTS

I.	Introduction	1188
II.	General principles of the formation of extracomplexes of metalloporphyrins	1188
III.	Stereochemistry of the extracomplexes of metalloporphyrins	1190
IV.	Physical properties of the extracomplexes	1191
V.	Kinetics of the formation of the extracomplexes	1193
VI.	Thermodynamics of the extracoordination reaction	1194

I. INTRODUCTION

Extracoordination in metalloporphyrins is one of the most important properties of compounds of this class[1]. Extracoordination is understood as additional coordination by a stable planar complex species (for example, a metalloporphyrin) or ligands occupying the fifth, sixth, etc. coordination sites in the inner coordination sphere of the metal and located above and below the plane of the initial stable complex; this results in the formation of the extracomplex (I)



(I)

If the extraligands in (I), i.e. the additional ligands, add to the fifth and sixth coordination sites along the z axis perpendicular to the plane of the molecule of the complex, the resulting complex has come to be referred to in coordination chemistry as an axial complex and the ligands are referred to as axial ligands. Numerous extracomplexes of porphyrins in which the ligands are not axial have now been obtained; consequently, the concepts of the "extracomplex" and "extracoordination" are wider than those of the "axial complex" and "axial coordination".

Depending on the nature of the metalloporphyrin (MP) and the nature and concentration of the extraligand, monoligand (LMP) or biligand (L_2MP) extracomplexes of metalloporphyrins are formed as a rule:

$$MP + L \rightleftharpoons LMP + L \rightleftharpoons L_2MP. \quad (1)$$

The molecules of water, organic solvents, nitrogen-containing heterocycles, aliphatic and aromatic amines, polypeptides, and proteins are most frequently used as the extraligands, while the acido-ligands are halide, acetate and other carboxylate, CN^-, OH^-, O^{2-}, HO_2^-, etc. ions.

Much attention is being devoted nowadays to experimental and theoretical studies to extracomplexes and the phenomenon of extracoordination to metalloporphyrins. The great interest in the extracomplexes of porphyrins is due to the fact that the most important biological functions of metalloporphyrins such as photosynthesis, the fixation and transport of oxygen by blood haemoglobin, and other enzymatic processes are associated primarily with the extracoordination of H_2O, O_2, H_2O_2, nitrogen-containing heterocycles, proteins, and other molecules. It is most likely that the catalytic activity of MP in both enzyme and chemical catalysis is due to the possibility of the formation of mono- and bi-ligand extracomplexes. Extracoordination ensures that the reacting molecules in the extracomplex are linked to one another. The ready reversibility of the formation of the extracomplex, and the possibility of chemical and photochemical oxidation-reduction reactions involving the complex.

It has been established[2] that chlorophyll strongly coordinates one water molecule to form an aquo-extracomplex. In combination with a protein molecule, which can also be part of the extracomplex, this complex is involved in the first (photophysical) stage of photosynthesis (and possibly also in the photochemical water oxidation stage).

The physical chemistry of extracoordination has been investigated for a long time, starting with the first studies by Williams[3]. However, until the 1970's the majority of the investigations were not systematic. From the 1970's the number of investigations of the extracomplexes of porphyrins (of their structure, spectroscopy, the thermodynamics of their formation, etc.) increased sharply. This review represents an attempt to survey the extensive data on extracomplexes which have accumulated hitherto: the conditions of their formation, structure, spectroscopy, kinetics, and thermodynamics; it deals only with the most fundamental studies.

II. GENERAL PRINCIPLES OF THE FORMATION OF EXTRACOMPLEXES OF METALLOPORPHYRINS

Depending on the strength of the metal–porphyrin coordination interaction, which is determined by the degree of covalence of the N–N dative bonds, i.e. the electronic structure of the porphyrin, the structure and charge of the cation, as well as steric factors, metalloporphyrins can be divided into coordination-saturated and coordination-unsaturated[1]. The former have a 2+ charge on the metal ion and form extremely stable covalent dsp^2-hybrid complexes (Cu^{2+}, Pt^{2+}, Pd^{2+}). Ions forming part of the coordination-saturated MP do not have low-energy non-bonding orbitals; their effective charge is low and they show little tendency to combine with extraligands regardless of the nature of the porphyrin molecule and the solvent. Naturally in the gas phase

the addition of extraligands to them takes place nevertheless[4], because the absolute coordination saturation of atomic-molecular species is virtually impossible. There are data[5] indicating the formation of very unstable monoligand extracomplexes by the porphyrin complexes of copper and nickel in solution.

Coordination-unsaturated porphyrin complexes contain ions which, having a formal 2+ charge, do not tend to undergo dsp^2-hybridisation (Zn^{2+}, Fe^{2+}, Cr^{2+}, Mn^{2+}), have unstable oxidation states (Co^{2+}, Re^{2+}), form predominantly ionic complexes with a weakly neutralised charge (Be^{2+}, Mg^{2+}, Cd^{2+}, Hg^{2+}, Ca^{2+}, Ga^{2+}), and all have a formal charge greater than two (Co^{3+}, Ru^{3+}, Al^{3+}, Ga^{3+}, Fe^{3+}, Mn^{3+}, Os^{4+}, Sn^{4+}, Ti^{4+}, VO_2^{2+}, UO_2^{2+}).[1] The subdivision of the central atoms in the MP into two groups—with coordination numbers of 5 and 6—of the kind carried out by Falk[6] cannot be regarded as desirable. The point is that, as a result of the strong saturation of the chemical affinity of the metal by the porphyrin molecule in the case of Mn^{2+} and in addition by the counterion in the case of Mn^{3+} the energy of subsequent coordination of extraligands usually proves to be so low that the degree of the overall extrainteraction cannot be measured and assessed quantitatively by the existing spectroscopic and thermodynamic methods. The nature of the extraligand plays a considerable role in the coordination of extracomplexes; extraligands containing N, O, P, and S atoms, and, as already mentioned, acido-ligands as the electron-donating species are mainly investigated nowadays. The formation of extracomplexes is naturally regulated by the thermodynamics of their formation.

1. Synthesis of Extracomplexes

The synthesis of extracomplexes of porphyrins and phthalocyanines has been described in many studies. The formation of extracomplexes of iron[7-31], cobalt[32-38], manganese[39,40], rhenium and technetium[41-43], rhodium[43-46], ruthenium[43,47,48], iridium[49], osmium[49], chromium[37], yttrium, lutetium, and thorium[50,51], and almost all the lanthanides except cerium and promethium[52] has been studied. Fairly detailed information about the extracomplexes synthesised and isolated in a crystalline state has been given in a review[53].

The formation of anionic extracomplexes of porphyrins, incorporating cations with a charge greater than two, takes place spontaneously in the synthesis of metalloporphyrins from porphyrin (H_2P) and a salt:

$$H_2P + MX_{(n+2)} \rightarrow (X)_nMP + 2HX \qquad (2)$$

($n = 1,2,3,4$; X = any singly charged anion). The anion X can then be substituted by any other anion on treatment of the extracomplex $(X)_nMP$ with solutions of salts or acids[20,36,37,54]. In the presence of water there is a possibility of hydrolysis:

$$MP \quad MP \qquad (3)$$

In many instances there is a possibility of the formation of a μ-oxo-dimer:

$$2OHMP \rightleftharpoons MPO\text{-}MP + H_2O \qquad (4)$$

or an oxo-extracomplex:

$$(OH)_2MP \rightleftharpoons O = MP + H_2O. \qquad (5)$$

Complexes of Al^{3+}, Ga^{3+}, Cr^{3+}, Sn^{4+}, Si^{4+}, and Ge^{4+} are formed readily in reaction (3).[53] Reaction (4) is preferred for Sc^{3+}, Fe^{3+}, and In^{3+}, which is attributed[55] to the ease of displacement of the metal atom from the plane of the porphyrin molecule (see Section III), but the metals in the first list are also capable of forming μ-oxo-dimers. Complexes of Ti^{4+}, V^{4+}, Nb^{5+}, Mo^{5+}, W^{5+}, Re^{5+}, and Os^{6+} are formed via reaction (5).[53]

If a coordination-unsaturated MP and an extraligand are the initial reactants, the extracomplex is formed in a homogeneous phase when solutions of the metalloporphyrin and the extraligand in a weakly coordinating solvent are mixed; the concentration of the extraligand should usually greatly exceed that of the MP. Depending on the nature of the MP and the extraligand, the equilibration time varies from several minutes to several days. The extracomplexes of metalloporphyrins containing a readily oxidisable metal atom are obtained in an inert gas; the solvent is slowly evaporated in order to obtain solid complexes—in some cases *in vacuo*[23,24]. Thus, in order to obtain $L_2Fe^{+}PP$ (H_2PP = protoporphyrin) with a series of substituted imidazoles as the extraligands L, a suspension of protohaemin in a solution of the extraligand is shaken for 50 h.[10] The extracomplexes of iron-phthalocyanine FePc with amines[13], LCoPc, and L_2CoPc (L = pyridine or 4-methylpyridine) have been obtained similarly[32,33].

The extraligand can also be introduced into the complex in a chromatographic process. The presence of water in chromatography on Al_2O_3 or silica gel frequently leads to the substitution of the extraligand or to hydrolysis with subsequent reactions (3), (4), and (5).[53]

The extraligands and solvents employed must be carefully purified. It has been noted[53] that the most suitable solvents are methylene chloride and chloroform, which should be freed from alcohols and hydrochloric acid (otherwise alkoxo- and chloro-extracomplexes are formed). It has been observed[56,57] that *ortho*-substituted pyridines form extracomplexes only in the presence of negligible amounts of sterically unhindered pyridines as impurities.

The addition of gaseous NO as extraligand to ClFeTPP (H_2TPP = tetraphenylporphin) has been described[9,12]. A convenient method has been developed for the synthesis of porphyrin extracomplexes from metal acetylacetonates and octaethylporphin in quinoline and in imidazole and phenol melts[37]. The yield of extracomplexes varies from 55 to 85%, phenol constituting the most favourable reaction medium. The synthesis of Cr^{3+} complexes in diethylene glycol led to the formation of extracomplexes with unidentified extraligands, which forced the authors[37] to recrystallise the extracomplex. We may note that crystallisation is sometimes used as a method of obtaining extracomplexes[58].

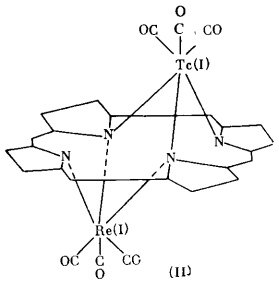
Complexes with tetra-arylporphyrins in which β-diketones serve as the extraligands have been obtained from lanthanide β-diketonates[52].

Metal carbonyls were used for the first time to synthesise extracomplexes of metalloporphyrins by Tsutsui et al.[59] The development of these methods is an important achievement in the synthetic chemistry of MP and their extracomplexes. New metalloporphyrins with chromium, molybdenum, technetium, ruthenium, rhodium, rhenium, and iridium have been obtained by the reaction of metal carbonyls and metal carbonyl halides with porphyrins[42,46,48,49,60-77]. With the exception of chromium and molybdenum complexes, the carbonyl groups used as extraligands are firmly retained at the central atom[43] and the number of carbonyl groups located on one side of the plane of the MP molecule varies from one for Ru and Ir to two for Rh [44,45] and three for Tc and Re.

Unusual extracomplexes of metalloporphyrins have been obtained[41] by heating $Re_2(CO)_{10}$ and $Tc_2(CO)_{10}$ in decalin†;[41]

† The term "axial complexes" cannot be applied to these complexes of metalloporphyrins as well as many others.

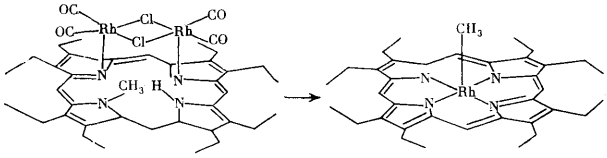
they have the structure



(II)

Formally these MP cannot be called extracomplexes. Their structure resembles that of the intermediate formed in many instances in the coordination of porphyrins to certain metal salts[78].

The synthesis of compound (III) from *N*-methyloctaethylporphin and $[Rh(CO_2)Cl]$, the product being converted on slight heating in chloroform or in the course of chromatography on silica gel into methylrhodium-octaethylporphin (IV),



(III) (IV)

i.e. a compound which is not an extracomplex of rhodium but combines the properties of a complex and an organometallic compound, has been described[46]. Numerous similar instances are now known. In conclusion we should note that the extracomplexes of iron- and cobalt-porphyrins merits particular attention in view of their catalytic activity, which is undoubtedly associated with extracoordination. These complexes have been examined in fair detail[53].

III. STEREOCHEMISTRY OF THE EXTRACOMPLEXES OF METALLOPORPHYRINS

The influence of the nature of the central atom as well as the structure of the porphyrin molecule and the extraligand on the M–extraligand bond length and on the position of the metal atom relative to the plane of the coordinating nitrogen atoms of the porphyrin molecule is examined below. These structural factors determine the physicochemical properties of the extracomplexes of metalloporphyrins.

The structure of many complexes has been determined by X-ray diffraction (Table 1). Table 1 lists the M–extraligand bond lengths for certain monoligand (tetragonal pyramid) and biligand (distorted octahedron) extracomplexes of porphyrins (Fig. 1).

It is known that the central atoms in MP capable of existing without an extraligand are located in the plane of the molecule (for example, Ni, Cu, and Pd). On the other hand, the formation of monoligand extracomplexes[33,39,79–94] leads to the displacement of the metal atoms from the plane of the porphyrin molecule, the deformation of the porphyrin skeleton, and in many instances the non-equivalence of the $M-N_{porph}$ bonds (where N_{porph} is a porphyrin nitrogen atom) in the solid phase. Depending on the nature of the complex, the metal atom is displaced from the plane of the porphyrin ring by 0.2–0.6 Å. It is noteworthy that, despite the apparent abundance of the results listed in Table 2, the dependence of the displacement of the metal atom from the molecular plane on the nature of the porphyrin, the central atom, and the extraligand virtually cannot be described in general terms in view of the lack of data in which only one of the above factors is varied.

Table 1. The metal–extraligand bond lengths in the extracomplexes of porphyrins.

Extracomplex	$M-L_1$ bond	$M-L_1$ bond length, A	$M-L_2$ bond	$M-L_2$ bond length, A	δ**, A	Refs.
(NO)FeTPP	Fe-NO	1.717	–	–	0.211	79
(N)FeTPP	Fe-N	1.661	–	–	0.32	80
$(SC_6H_4NO_2)$FePP	Fe-S	2.32	–	–	0.43	81
$(SC_6H_4$-*p*-$NO_2)$FePP	Fe-S	2.324	–	–	0.448	82
(Cl)FePP	Fe-Cl	2.218	–	–	0.575	83
(OCH_3)FeMP	Fe-O	1.842	–	–	0.456	84
$O(FeTPP)_2$	Fe-O	1.763	–	–	0.50	85
(2-CH_3-im)FeTPP	Fe-N	2.136	–	–	0.42	86
$(pip)_2$FeTPP	Fe-N	2.127	Fe-N	2.127	–	101
(py)(CO)FeTPP	Fe-CO	1.777	Fe-N	2.10	0.02	27
(N-CH_3-im)(NO)FeTPP	Fe-NO	1.734	Fe-N	2.180	0.07	96
$(im)_2$FeTPP	Fe-N	1.957	Fe-N	1.991	0.009	97
$(im)_2$FeOAEP	Fe-N	2.01	Fe-N	2.01	–	102
$(1\text{-}CH_3\text{-im})_2$FePP	Fe-N	1.966	Fe-N	1.988	–	8
(1-CH_3-im)[$(CH_3)_3$ COO^-]. .(CO)FePP	Fe-N	2.05	–	–	-0.03	100
(Cl)CoTPP	Co-Cl	2.149	–	–	0.05	33
(1-CH_3-im)CoTPP	Co-N	2.157	–	–	0.13	87
(1-CH_3-im)CoOAEP	Co-N	2.150	–	–	0.13	88
$(im)_2$CoTPP	Co-N	1.906	Co-N	1.945	–	30
$(pip)_2$CoTPP	Co-N	2.060	Co-N	2.060	–	103
[1,2-$(CH_3)_2$-im]CoTPP	Co-N	2.216	–	–	0.15	89
(Cl)Co(N-CH_3TPP)	Co-Cl	2.242	–	–	0.558	90
(NO_2)(3,5-lut)CoTPP	Co-NO_2	1.948	Co-N	2.036	–	104
(Cl)(py)CoTPP	Co-py	1.978	Co-Cl	2.251	0	105
$(pip)_2$CoTPP	Co-N	1.987	Co-N	1.987	0	106
$(3\text{-}CH_3\text{-py})_2$CoOAEP	Co-N	2.386	Co-N	2.386	0	111
(3,5-CH_3-py)CoTPP	Co-N	2.161	–	–	0.14	100
$(im)_2$ClCoOAEP	Co-im	1.99				
(Cl)MnTPP	Mn-Cl	2.363	–	–	0.27	100
(1-CH_3-im)MnTPP	Mn-N	2.192	–	–	0.5	95
(py)ClMnTPP	Mn-N	2.444	Mn-Cl	2.467	0.12	39
$(N_3)(CH_3OH)$MnTPP	Mn-N_3	2.176	Mn-O	2.329	–	98
(py)ZnTpyP	Zn-N	2.143	–	–	0.33	107,108
(py)ZnOAEP	Zn-N	2.200	–	–	0.31	93
$(im)_2$Ni(4-N-CH_3py TPP)	Ni-N	2.160	Ni-N	2.160	–	100
$(py)_2$RuOAEP	Ru-N	2.089	Ru-N	2.100	–	109
(CO)(py)RuTPP	Ru-N	2.193	–	–	-0.08	47
(H_2O)MgTPP	Mg-O	2.099	–	–	0.27	99
$(py)_2$MgAEP	Mg-N	2.34			0.31	94
(O_2)TiOAEP	Ti-O	1.829	Ti-O	1.822	–	100
$[(CO)_3Re]_2$TPP	Re-CO	1.855	Re-CO_3	1.855	–	94
$[(CO)_3Tc]_2$TPP	Tc-CO	1.892	Tc-CO_3	1.892	–	41

* Abbreviations: H_2MP = mesoporphyrin; H_2TpyP = tetrapyridylporphyrin; lut = lutidine; pip = piperidine; py = pyridine [TPP = tetraphenylporphyrins; PP = protoporphyrin IX; OAEP = octoethylporphyrin].

** Here δ is the degree of displacement of the metal atom from the plane of the four nitrogen atoms.

The displacement of the central atom from the molecular plane has been attributed[91,94] to the considerable resistance of the porphyrin ligand to external deforming influences, the incomplete charge transfer from the porphyrin to the central atom, and the repulsion of the electron shells of the extraligands and the nitrogen atoms of the macroring.

From the standpoint of the chemistry of coordination compounds, the displacement of the central atom in the extracomplexes of metalloporphyrins under the influence of the extraligand can be due to three main causes: (1) the stepwise nature of the complex formation, (2) the interaction of the force fields of the metal and the first extraligand entering the complex, and (3) the repulsion of the electron shells of the extraligand and the π-electron cloud of the porphyrin macroring. The contributions of these individual factors to the geometry of the extracomplex can vary markedly as a function of the configuration of the porphyrin molecule and the nature of charge of the metal and the extraligand.

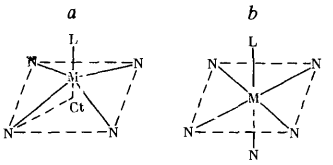


Figure 1. a) Monoligand extracomplex; b) biligand extracomplex.

Table 2. Magnetic properties of certain metalloporphyrins.

Electronic configuration of metal ion	Complex*	Coordination number	μ_{eff}, μ_B	Temp. range**	No. of unpaired electrons	Refs.
d^8	Ni	4	0	*N*	0	240
d^8	$(py)_2$Ni(diac)DP	6	3.45	*R* (*S*)	2	241
d^7	CoMP	4	2.89	*N*	1	240
d^6	(H_2O)(Cl)CoHP	6	0.23	*N*	0	240
d^6	(H_2O)(Cl)RhMP	6	0.05	*R*	0	74
d^6	$(H_2O)_2$FePP	6	4.83—5.02	*R* (*S*)	4	242
d^6	(py)(CO)FePP	6	0	*R* (*S*)	0	243
d^6	(CO)(Cl)IrHP	6	0	*R*	0	74
d^5	(Cl)FePP	5	5.88	*N*	5	244
d^5	$(im)_2$(Cl)FeTPP	6	2.36	*H*	1	245
d^5	$(py)_2$MnHP	6	5.9	*R* (*S*)	5	182
d^5	(C_6H_5Cl)phTPP	6	1.95	*R*	1	74
d^4	(H_2O)(Cl)MnHP	6	4.88	*N*	4	182
d^3	(H_2O)MnHP	6	2.0	*R* (*S*)	1	182

* Abbreviations: HP = haematoporphyrin; (diac)DP = diacetyldeuteroporphyrin.

** Here *R* = room temperature, *N* = temperature range 80 to 300 K, *H* = temperature range 4.2–50 K, and *S* = solution.

It has been suggested[91] that large extraligands, resembling the chloride ion, always cause a marked breakdown of the planarity of the coordination unit of the metalloporphyrin; small extraligands may not distort significantly the planar configuration of the MP. This postulate is valid for ClMnTPP and ClFePP, but it does not hold for ClCoTPP, in which the displacement of Co from the molecular plane is very slight. The latter can be explained by the fact that the cobalt ion in the complex is of the low-spin type and therefore has a comparatively small effective radius. On the other hand, the iron complex is of the high-spin type; its antibonding molecular orbitals, formed with participation of the d_{z^2} and $d_{x^2-y^2}$ orbitals of the metal, are filled, which leads to an increase of the effective radius and to the displacement of the central atom from the plane of the porphyrin[95].

The most significant displacement from the molecular plane is caused by the entry (substitution) of the first extraligand. The entry (substitution) of the second extraligand either diminishes the displacement from the molecular plane[27,96-99] or, as a rule, reduces it to zero[8,41,47,100,101-111] when both extraligands are of the same type (Table 2).

On the basis of ideas concerning the radius of the central cavity of the porphyrin, which determines the distance between each nitrogen atom and the centre of the molecule (Ct) (Fig. 1), Hoard[112] concluded that the metal can be located in the plane formed by the four nitrogen atoms, provided that the metal–nitrogen bond length is equal to the Ct–N distance (it amounts to $\leq 2.015 \pm 0.007$ Å). For example, according to Rifkind[113], the high-spin iron complexes (the Fe–N bond length is 2.061 ± 0.012 Å) cannot be planar, while the low-spin complexes (Fe–N = 1.91 Å) can be planar. However, the Fe–N bond length in the complex $Cl(pip)_2$FeTPP is 2.127 Å (Table 2), which does not lead to the displacement of the Fe from the plane of the ring[96].

Data for complexes of iron-containing porphyrins with proteins and other bioligands have been analysed in two reviews[113,114].

IV. PHYSICAL PROPERTIES OF THE EXTRACOMPLEXES

The typical electronic absorption spectra of porphyrins and metallo-porphyrins are their most important characteristics. Absorption spectroscopy is most widely used in the study of processes associated with extracoordination[5,9,14,25,45,47,81,82,91,114-137], due to the considerable possibilities of the method. Absorption spectroscopy is most frequently used to follow the formation of extracomplexes in solutions, to determine the number of extraligands combined, and to measure the stability of the extracomplexes.

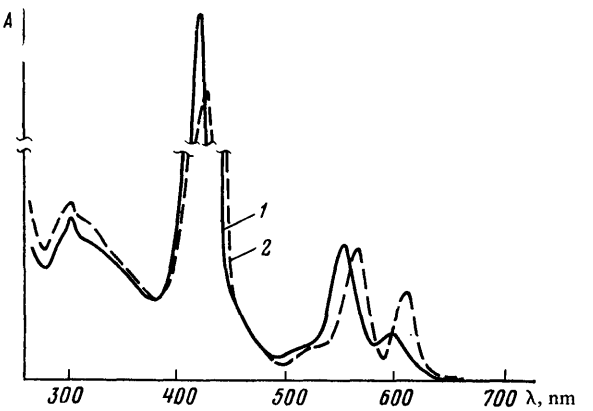


Figure 2. Electronic absorption spectra of ZnTPP (curve *1*) and its extracomplex (DMSO)ZnTPP (curve *2*) in CCl_4 at 25 °C.

A theoretical discussion of the absorption spectra of porphyrins and metalloporphyrins has been described in a monograph[138] and partially by Berezin[1]. However, the spectroscopy of the extracomplexes of porphyrins have been hardly discussed in the above publications. There have been a number of studies specially devoted to the electronic spectra

of the extracomplexes of porphyrins and phthalocyanines[14,36,91,139,140]. The positions and intensities of the absorption bands have been published[37,114] for a large number of extracomplexes of octaethylporphin.

The absorption spectra of metalloporphyrins in the range 350–750 nm consists as a rule of three bands[138]: the Soret band located in the near ultraviolet and two bands in the visible part of the spectrum (Fig. 2). The absorption bands of the MP are due to the $\pi-\pi^*$ transitions in the porphyrin molecule, which are described satisfactorily in terms of the four-orbital Simpson–Platt–Gouterman model[141,142]. The addition of extraligands is accompanied by a 5–35 nm shift of the absorption bands (Fig. 2). The magnitude of the shift and its direction (bathochromic or hypsochromic) depend on the nature of the central atom of the MP, the extraligand, and the structure of the porphyrin.

It is interesting to reproduce the essential feature of a brief analysis of the bathochromic and hypsochromic shifts of the absorption bands of the extracomplexes based on Berezin's data[1]. The extracomplexes of metalloporphyrins constitute one of the groups of mixed complexes. The characteristics of the formation of complexes with a mixed coordination sphere and the characteristics of the compatibility of the ligands in these complexes have been analysed in detail[143]. In the inner coordination sphere ligands of a similar electronic type (for example, σ-donor, π-acceptor, and electrostatic) are most compatible. It is therefore to be expected that π-ligands such as pyridine, imidazole, CN^-, dimethyl sulphoxide (DMSO), CO, O_2, and others of a similar type with both σ-donor and π-acceptor properties will enter more readily the coordination spheres of porphyrin complexes.

Allowance for only the electronic interaction of the extraligand with the MP makes it possible to use the concept of the electronic effects of coordination in planar macrocyclic complexes developed by Berezin[1,144] and to achieve a simpler treatment of the changes in the properties of MP on extracoordination of ligands; this approach is justified in many instances. According to it, for metals with an unfilled d shell the extraligands with suitable π orbitals can enter into a competitive interaction with the dxy, dxz, and dyz orbitals of the metals. As a result, the $d_\pi-p_\pi$ metal–porphyrin interaction is weakened due to the $d_\pi-p_\pi$ interaction of the metal with the extraligands and the role of the metal–porphyrin σ-interaction increases. The coordination of π-acceptor ligands should therefore result in a hypsochromic shift of the first band in the electronic spectra of MP, provided that the extraligands are indeed involved in the π-interaction with the metal atom[3]. The changes in the electronic spectra show that there is not only an electrostatic MP–ligand interaction but also a donor–acceptor interaction between the ligand and the metal atom[138].

In those cases where the central metal atom in the porphyrin complex has closed stable electronic orbitals (the overall orbital moment and the spin are zero), the formation of dative metal–ligand π-bonds becomes virtually impossible. Such cases occur in the metalloporphyrins of Mg^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, etc., where the interaction is limited to the σ-binding of the extraligand by the d^2sp^3 orbitals or ion–dipole attraction. In both cases the extraligand increases the electron density at the metal atom and decreases the degree of its σ-interaction with the porphyrin, so that one should expect a bathochromic shift of the first band in the electronic absorption spectrum of the complex.

The above interpretation of the spectra does not conflict with experiment, provided that the geometrical parameters of the coordination centre of the MP, particularly the coordinates of the metal and the nitrogen atoms linked to it, are not altered. If a displacement of the metal from the plane of the N atoms or the opposite movement is observed in extracoordination, an unambiguous solution of the problem of the nature of the spectroscopic changes in the extracoordination is still difficult. Thus examples of both hypsochromic[125] and bathochormic[122] shifts of the first band in the spectra of cobalt complexes of porphyrin are known. A hypsochromic shift of the first band has been observed for the iron complexes[137].

Despite numerous studies devoted to extracoordination to porphyrins, there are still no systematic studies of the dependence of the absorption spectra of extracomplexes on the nature of the central atom, the extraligand, and the porphyrin under comparable conditions. It is therefore at present difficult to establish rigorous correlations between the M–N bond lengths, the band shifts in the electronic absorption spectra, and the thermodynamic parameters of the extracoordination reaction.

A number of studies by other spectroscopic methods have appeared recently in the literature. EPR has been used for the extracomplexes of cobalt-, iron-, and manganese-porphyrins. Problems associated with the determination of the stoichiometry of the mono- or bi-ligand complexes formed[32,145] and of the spin state of the central atom[82,146–148] have been solved mainly by EPR, which also proved to be an effective method for the detection of cobalt-oxygen complexes[32,121,145,147].

It has been shown by EPR [121] that at −45 °C in air in the presence of imidazole or benzimidazole, CoPP forms a 1:1 complex of the type $(L)(O_2)(CoPP)$, which rapidly decomposes at room temperature with formation of $(L)CoP(O_2)PCo(L)$. It is believed[121] that bridged complexes should be characteristic of cobalt extracomplexes. On the basis of a study of the EPR spectra of CoPP in dimethylformamide (DMF), Stynes and Ibers[149] concluded that the greater the basicity of the extraligand the smaller the capacity of cobalt for oxidation. This conclusion is probably not general[145].

NMR has been used to determine the thermodynamic and kinetic parameters of the extracoordination reaction (see Sections V and VI), to determine the structure of the extracomplex[41,47,150], and to investigate the exchange of extraligands[151]. It has been correctly stated[152,153] that the calculation of K_{st} from NMR data is complicated by the solvent–solute interaction. In general a change in the nature of the extraligands is reflected to a greater extent in the chemical shifts of the protons of the methyl and α-methylene groups and of the meso-protons of the paramagnetic complexes. These data do not allow a distinction to be made between contact and pseudocontact shifts, which hinders the estimation of the effects of extracoordination and association[114]. It has been suggested[114] that the resulting contact shifts depend on the degree of type of interaction between iron and the nitrogen atoms of porphyrins, which depend in their turn on the differences in the binding of the central atom to the extraligands.

Infrared spectra have been used mainly to identify extracomplexes and extraligands. Analysis of the infrared spectra of haemins have led to the conclusion[114] that the nitrogen atom is displaced from the plane of the porphyrin ring by 0.5 Å or more.

Lack of space precludes a detailed examination of all the spectroscopic data for the extracomplexes of porphyrins. Numerous EPR [32,35,82,121,131,135,146–149,154–160], NMR [20,23,38,41,47–49,52,114,150,151,161–171], infrared spectroscopic[9–13,137,172–177], Raman spectroscopic[178–180], and Mössbauer spectroscopic[21,30,82,114,181–186] studies as well as studies based on magnetic circular dichroism spectra[187–189] have been made on porphyrin extracomplexes. The spectroscopic methods yield much useful information about porphyrins, but the lack of

systematic specific investigations hinders a general survey of these data.

The magnetic properties of metalloporphyrins and their extracomplexes are of considerable interest, since they make it possible to determine directly the oxidation state of the central metal atom. Magnetic properties depend significantly on the presence of extraligands in the molecule. Table 2 lists the magnetic properties of certain metalloporphyrins. The results of magnetic measurements have been discussed in detail in the literature[152,153].

V. KINETICS OF THE FORMATION OF THE EXTRACOMPLEXES

Information about the state of extraligands and the nature of their bonds with the metal atom in the extracomplex can be obtained by studying the kinetics of the formation and dissociation of these complexes. Several tens of studies on the kinetics of the formation of extracomplexes of metalloporphyrins and phthalocyanines have been published recently.

Blyumenfel'd[190] established for the first time (on the basis of the rate of substitution of one protein by another in a *gem*-protein complex saturated with O_2 and CO) that the rate of elimination of globin from the oxygenated protohaem (O_2). .FePP is limited by the rate of elimination of O_2, i.e. by the rate of the reaction

$$(O_2)\text{FePP} \rightleftharpoons O_2 + \text{FePP}. \qquad (6)$$

The rate constant for the reaction proved to be $k_V = (5 \pm 2) \times 10^5\ s^{-1}$; such a high rate is evidence for a low strength of the Fe–O_2 covalent bond. The activation energy for the reaction

$$(\text{globin})\text{FePP} + O_2 \rightarrow (\text{globin})O_2\text{FePP} \qquad (7)$$

is close to zero.

On the other hand, for the reverse reaction, it is 21 ± 1.5 kcal mol^{-1}, which is due to the simultaneous abstraction of O_2 and protein imidazole residue from the Fe atom. The considerable possibilities of the kinetic method for the investigation of phenomena based on extracoordination were demonstrated in the same study[190].

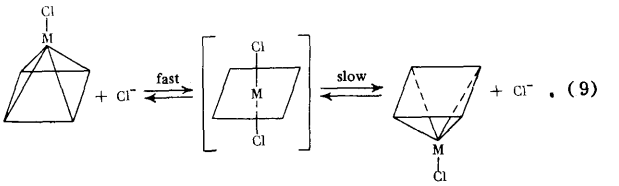
The imidazole exchange in low-spin iron(II) complexes of porphyrins (tetraphenylporphyrin, octaethylporphyrin, and protoporphyrin) has been studied[151] by ^1H NMR. Depending on the nature of the porphyrin, the rate of the exchange reaction

$$(\text{N–CH}_3\text{im})_2\text{FeTPP} + \text{N–CH}_3\text{im}^* \underset{\tau_{-1}}{\overset{\tau_1}{\rightleftarrows}} (\text{N–CH}_3\text{im})^*(\text{N–CH}_3\text{im})^*\text{FeTPP} + \text{N–CH}_3\text{im} \qquad (8)$$

can vary by an order of magnitude, which proves that the binding of imidazole to FePP is covalent.

It has been observed[191] that, under the influence of the extraligand, the metalloporphyrins ClFeTPP(p-CH_3)$_4$ and ClFeOEP undergo inversion with the rate constants of 15×10^2 and 60 s^{-1} respectively. It follows from these data that the rate of inversion determines the strength of the extracoordination of the second extraligand: as a result of the reduced effective charge on FeOEP compared with FeTPP, the strength of the binding of Cl^- to the former is smaller, the fraction of $(Cl)_2$FeOEP is small, and the rate of inversion is low.

An S_N2 mechanism has been proposed for the process



(9)

The rate of inversion was investigated later[20] and the activation parameters were calculated for a series of porphyrins; the data presented in Table 3 indicate the presence of solution of mono- and bi-ligand extracomplexes and show that their stabilities are different. Evidently the inversion reactions are virtually isentropic and the differences between their rates are caused mainly by the differences between the activation enthalpies for the inversion process, i.e. are associated with the stability of the extracomplexes. It is noteworthy that studies similar to that described above[20] can prove useful for the understanding of the detailed mechanisms of the formation and dissociation of porphyrin complexes, particularly with metals such as iron, cobalt, and manganese.

Table 3. Activation parameters for the inversion reaction (6).[20]

Extracomplex	extra-ligand	k^{298}, $m^{-1}\ s^{-4}$	$\Delta G^{\neq}$, kcal mol^{-1}	$\Delta H^{\neq}$, kcal mol^{-1}	$-\Delta S^{\neq}$, e.u.
(Cl)FeTPP(p-CH_3)$_4$	Cl	$(5.6\pm1.4)\cdot10^2$	14.2±1.2	9.1±0.8	17±4
(I)FeTPP(p-CH_3)$_4$	I	$(5.9\pm1.2)\cdot10^3$	12.2±0.6	6.5±0.3	19±2
(Cl)FeOAEP	Cl	$(5.8\pm1.2)\cdot10$	15.0±1.0	8.8±0.5	21±2
(I)FeOAEP	I	$(9.0\pm1.6)\cdot10^2$	13.2±0.4	7.2±0.2	20±2

The self-reduction of Fe^{3+} to Fe^{2+} has been observed in the interaction with ClFeTPP with piperidine in $CDCl_3$.[192] In the presence of the cyanide ion and oxygen, continuous oxidation-reduction of iron takes place.

The kinetics and thermodynamics of the substitution of O_2 as an extraligand by an excess of the main extraligand in $(L)(O_2)$FeTPP, where L = pyridine piperidine, or 1-methylimidazole, have been investigated[193]:

$$(L)(O_2)\text{FeTPP} \xrightarrow[k_V]{\text{slow}} (L)\text{FeTPP} + O_2\ , \qquad (10)$$

$$(L)\text{FeTPP} + L \xrightarrow{\text{fast}} (L)_2\text{FeTPP}. \qquad (11)$$

For the extraligands enumerated, reaction (10) is characterised by the following rate constants respectively: $k_V = 4.3 \times 10^{-3}$, 2.3×10^{-3}, and $0.17 \times 10^{-3}\ s^{-1}$. The corresponding sequence based on the variation of the rate constants for the elimination of O_2 is due to the decrease of the π-donor activity of the central Fe(II) atom, which takes place under the influence of the change in the type and strength of the Fe–L bond and the effective charge on the iron atom. It also follows from the above data[193] that the strength of the binding of O_2 is determined not only by the π-acceptor but also by the σ-donor properties of extraligands.

In a study of the kinetics and thermodynamics of the binding of CO and O_2 to $(L)_2$FeTPP, Weschler et al.[19] used the same extraligands as in the previous study[193]. The reaction

proceeds in accordance with the equations

$$(L)_2FeTPP \rightleftharpoons (L)FeTPP + L; \quad (12)$$

$$(L)FeTPP + O_2 \rightleftharpoons (L)(O_2)FeTPP; \quad (13)$$

$$(L)FeTPP + CO \rightleftharpoons (L)(CO)FeTPP. \quad (14)$$

The study of the rate of the process as a function of the O_2 and CO concentrations Weschler et al.[19] to suggest a dissociative mechanism with formation of the extracomplex L(Fe). TPP. The rate of formation of the complexes with O_2 and CO decreases in the sequence pyridine > piperidine > 1-methylimidazole due to the increasing strength of σ- and π-binding of the extraligands.

It follows from the above data[19,193] that the strengthening of the π-donor properties of the extraligand in processes similar to reactions (10)–(14) leads to a decrease of the strength of the M–O_2 bond in the extracomplex. However, in a study of the interaction of O_2 with FePP in the presence of 2-picoline, 2-methylimidazole, and t-butyl alcohol, Wagner and Kassner[116] concluded that the coordinating properties of the extraligands are insignificant for the binding of O_2 and that ligands of the type of imidazole are not unique extraligands in this process. This conclusion is probably erroneous, since it has been shown in a number of studies[1,194] that π-binding determines the competition between the extraligands for *d* electrons (the *trans*-influence discovered by Chernyaev[195] plays a significant role here).

The electronic nature of the *trans*-influence, examined from modern standpoints in a number of studies, for example by Bersuker[196], can serve as the basis of the treatment of extracoordination to iron-porphyrins[1]. Comparison of the properties of imidazole with those of other nitrogen-containing protein residues led to the conclusion[194] that none of the latter creates more favourable conditions for the addition of O_2 than imidazole.

The reaction of $(pip)_2FePP$ with CO has also been studied by other workers[197,198], but fundamentally new information was not obtained. The substitution of water in diaquoiron(III)- and diaquocobalt(II)-haematoporphyrins by CN^- and SCN^- ions has been described[151,153,199]. The kinetics of the binding of CN^- and imidazole by haemin in micelles have been investigated[200]. A polarographic study has been made[201] of ClFePP in the presence of nitrogen-containing bases (4-cyanopyridine, 4-acetylpyridine, pyridine, 4-phenylpyridine, 4-aminopyridine, piperidine, pyrazole, benzimidazole, 5,6-dimethylimidazole, and imidazole). This study is interesting in connection with the observed linear relation between the pK_B of the nitrogen-containing bases and the rate of electron transfer. The correlation has been explained by the change of ligand environment and the spin state of iron.

Several interesting studies have been made on iron-phthalocyanines[202–206]. The kinetics of the reaction

$$(DMSO)_2FePc + 2im \rightleftharpoons (im)_2FePc + 2DMSO \quad (15)$$

have been studied. It was observed that the substitution of the first DMSO molecule is the rate-limiting stage and that even at a high imidazole concentration the reaction is of second order[205].

The reactions of FePc with tri-n-butyl phosphite [$P(OBu)_3$] and tri-n-butylphosphine (PBu_3) have been reported[206]. The reaction products are low-spin bi-ligand extracomplexes. The kinetics of the substitution reaction

$$[\{P(OBu)_3\}_2FePc] + 2PBu_3 \rightarrow (PBu_3)_2FePc + 2P(OBu)_3 \quad (16)$$

have been investigated. The rate of elimination of $P(OBu)_3$ from $[P(OBu)_3]_2FePc$ is 5000 times greater than the rate of elimination of imidazole from $(im)_2FePc$. Schweigart[206] attributes this finding to the greater *trans*-effect of $P(OBu)_3$ compared with imidazole on the grounds that the substitution of $P(OBu)_3$ by imidazole leads to $[P(OBu)_3](im)FePc$.

The kinetics of the substitution of chlorine by the OH^- group in dichlorosilicon-phthalocyanine have been investigated[207]:

$$Cl_2SiPc(solid) + 2OH^- \rightarrow (HO)_2SiPc(solid). \quad (17)$$

The rate constant for the substitution reaction in 0.1M NaOH solution is 6×10^{-6} s^{-1}, $E = 15.6$ kcal mol^{-1}, and $\Delta S = -19$ e.u. It is suggested that the low rates of substitution of chlorine in the extracomplex of silicon-phthalocyanine are due to the sharp decrease of the positive charge on the silicon atom owing to the strong coordinate σ-bond and the reverse dative Si ← N π-bond. The latter is formed by filling the vacant d_π orbital of silicon with the p_z electrons of chlorine, which reduces sharply the tendency of the Si atom towards nucleophilic substitution reactions.

There have been several studies on the kinetics of the substitution of extraligands in extracomplexes of cobalt[124,208,209]. The conclusions reached do not differ fundamentally from those described above. Reactions involving the substitution of extraligands in extracomplexes of manganese have been described in detail in Boucher's review[210].

Thus the above data show that numerous studies, usually isolated and scattered, have been devoted to the kinetics of the substitution of extraligands in extracomplexes of porphyrins. Large-scale systematic investigations are as yet lacking; the need for such investigations is entirely evident.

VI. THERMODYNAMICS OF THE EXTRACOORDINATION REACTION

The extracoordination reaction in solution

$$MP + L_n \rightleftarrows (L)_n MP \quad (18)$$

is as a rule investigated by electronic absorption and emission spectroscopy. It is readily reversible, which makes it possible to displace the equilibrium in the required direction by a moderate alteration of the concentration of the extraligand, the nature of the solvent, and temperature. Studies on stability are usually carried out by the isothermal saturation method. There have been investigations[211,212] in which the thermodynamic parameters of reaction (18) were determined calorimetrically.

The methods for the calculation of the constants do not differ from those generally adopted for the determination of the stepwise stability constants of the usual complexes[213]. The method proposed by Miller and Dorough[130] is most frequently used. The number of added ligands is found as described by Bent and French[214] and from the decrease of weight on heating the extracomplex *in vacuo*[129]. The latter method is suitable only for porphyrin molecules resistant to thermal degradation. There exist data for the thermodynamic parameters of reaction (18) for the Fe^{2+}, Fe^{3+}, Co^{2+}, Co^{3+}, Zn^{2+}, Ni^{2+}, Hg^{2+}, Cd^{2+}, Cu^{2+}, Mn^{2+}, Mg^{2+}, and VO^{2+} complexes of porphyrins with a large number of extraligands of different types.

One of the first studies[130] was devoted to pyridine complexes in benzene. The stability of pyridine complexes of metalloporphyrins is due to a number of factors, which have been examined[1]. According to the published[130] stability constants K_S, the monoligand extracomplexes of porphyrins can be arranged in the sequence Zn > Cd > Hg > VO. The pyridine complex of VO-porphyrin with H_2TPP has also been

included in this sequence[153], but we were unable to find its stability constant K_S in the literature. It follows from the above data[130] that the hydrogenation of the porphyrin ring leads to appreciable stabilisation of the pyridine complexes of Mg- and Zn-porphyrins; only Mg-porphyrins form a relatively stable dipyridine complex[130]. It has been shown that zinc also forms bi-ligand extracomplexes of a similar type with certain extraligands[215,216]. Baker et al.[5] observed the formation of a dipiperidine complex of Ni-mesoporphyrin and a monopiperidine copper complex. The influence of the nature of the extraligand on the stability of the extracomplexes has been examined in several studies[6,125,129,217-218].

Table 4 presents the logarithms of the stability constants of the monoligand extracomplex of chlorophyll a (MgChl) in benzene[6]. The constants were estimated from the fluorescence intensity, which increases as the extraligand is added to the chlorophyll solution in absolutely dry benzene. The stability of the extracomplexes is associated with the increase of the electron-donating capacity of the ligand. It is noteworthy that the data in Table 4 do not reflect the true stability constants, since the development of fluorescence need not be caused solely by the deaggregation of the associated chlorophyll species due to extracoordination. However, these data do reflect correctly the sequence in the variation of stability. The complexity of the phenomenon may be caused by the operation of several mechanisms of the formation and decomposition of the MgChl associated species[1]. Table 6 shows that the Mg atom in MgChl coordinates oxygen and nitrogen-containing ligands equally effectively.

Table 4. The stability constants of monoligand extracomplexes of chlorophyll *a* in benzene (6).

Extraligand	$\lg K_S$	Extraligand	$\lg K_S$
Dimethylaniline	1.0	Quinoline	4.1
Phenol	1.2	Benzylamine	4.4
Aniline	1.7	Water	4.5
n-Octyl alcohol	3.7	n-Heptylamine	5.2
Benzyl alcohol	3.5		

The formation of complexes of various substituted pyridines with Fe-porphyrins has been investigated[6]. It has been pointed out[129] that the stability constants K_S vary in inverse proportion to the basicity of the extraligand. It has been observed that there is only a tendency towards an increase of stability with decrease of the basicity of the extraligand, but a rigorous correlation has not been found. This complex dependence reflects the fact that the stability of the extracomplexes of iron-porphyrins is determined both by σ- and π-binding of the ligands. The data obtained have been discussed by Falk[6], who notes, in particular, the influence of steric factors on the binding of certain substituted pyridines by the central atom, which may be non-axial.

The stability constants K_S of 4-substituted pyridine complexes of MgDP have been published[129] and a correlation has been observed between the basicity of the substituted pyridine and the stability of the extracomplex. Analogous relations have been observed for ZnTPP, CdTPP, and HgTPP [217] as well as ZnTPP and NiTPP in $CHCl_3$ and benzene[218]. A correlation was observed in the above studies between K_S and the Hammett constants. This type of correlation has also been established for CoPP.[125]

An attempt has been made[129] to find a relation between the stability of the pyridine extracomplexes of Mg-porphyrin and the structure of the porphyrin molecule (Table 5). Table 5 lists the thermodynamic parameters of the reaction

$$(py)MgP + py \rightleftharpoons (py)_2MgP. \quad (19)$$

A difference has been observed between the equilibrium constants, but nothing definite has been established concerning the problem of the influence of the structure of the porphyrin molecule on extracoordination. The estimate of the error of the thermodynamic parameters obtained, quoted by Storm et al.[129], shows that the values of ΔH and ΔS for reaction (19), involving different porphyrins, are probably within the limits of experimental error. The influence of the porphyrin structure on the addition of the second extraligand is slight, owing to the weakness of the LMP—L coordination interaction. It is seen in relation to 2,4-dinitrodeuteroporphyrin[129] that even the introduction of two nitro-groups causes little change in K_2 and ΔH.

Table 5. Thermodynamic parameters of reaction (9) in 2,6-lutidine.

P	K_2	ΔG, kcal mol^{-1}	$-\Delta H$, kcal mol^{-1}	$-\Delta S$, e.u
Mesoporphyrin IX d.m.e.*	0.070	1.60	3.98	18
Actioporphyrin II (H_2AEP)	0.068	1.62	2.92	15
Protoporphyrin IX d.m.e.	0.242	0.84	4.25	17
Deoxophylloerythrin m.m.e.	0.074	1.56	2.55	14
Dinitrodeuteroporphyrin IX d.m.e.	0.326	0.68	3.99	15
Mesoporphyrin IX dicholesteryl ether	0.142	1.16	3.77	16
Tetraphenylporphin	0.161	1.08	2.37	11
Dichlorodeuteroporphyrin IX d.m.e.	0.282	0.76	3.90	15
Deuteroporphyrin IX d.m.e.	0.228	0.85	3.89	16

* Here d.m.e. = dimethyl ester [and m.m.e. = monomethyl ester].

A weak dependence of the thermodynamic parameters of extracoordination to zinc-porphyrins on the porphyrin structure has been observed in a study of the equilibrium in the extracoordination of DMSO [215,216,219]. The addition of DMSO to the zinc complexes takes place stepwise:

$$ZnP + DMSO \rightleftharpoons (DMSO)ZnP; \quad (20)$$

$$(DMSO)ZnP + DMSO \rightleftharpoons (DMSO)_2ZnP. \quad (21)$$

The nature of the plots of the absorbance A against c_0^L (the concentration of the extraligand) (Fig.3) is the same for all the complexes investigated. The first DMSO molecule adds in the DMSO concentration range up to 1.3×10^{-3} M and the second molecule adds on further increase of the ligand concentration. The number of added extraligands (n) in solution has been determined by the Bent—French method[214].

However, one should note that $n = 1$ has been found in a series of studies[130,218,220-221] of the extracoordination to Zn-porphyrins using several extraligands; this is probably due to the inadequate number of experimental points over a wide range of concentrations.

The influence of the structure of the porphyrin molecule on the thermodynamic parameters of the extracoordination reaction has been investigated by Walker et al.[222], who published data for a series of Ni^{2+} and VO^{2+} complexes of *p*- and

m-derivatives of tetraphenylporphin; unfortunately, complete thermodynamic characteristics have been published only for two porphyrins. The second equilibrium constants in the reaction of piperidine with nickel-tetraphenylporphyrin[222] indicate a significant influence of the substituents in the phenyl residues of tetraphenylporphin on the K_S for the extracomplexes of the Ni^{2+} compound. The authors[222] note that the extent of this influence depends on the d_π electrons in the central atom: it is greater for $Ni^{2+}(d^8)$ than for $VO^{2+}(d^1)$. The observation of a correlation between K_S and the Hammett and Taft constants led the authors[222] to the conclusion that there exists a moderate conjugation between the phenyl residues and the macroring. They believe that the roles of the conjugation and inductive effects for *para*-substituted tetraphenylporphins are approximately the same; for *meta*-substituted tetraphenylporphins, the inductive effect predominates.

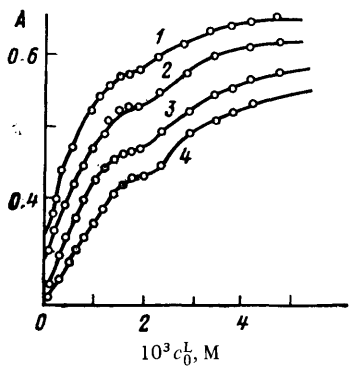


Figure 3. Dependence of A on c_0^L for (DMSO)ZnTPP at different temperatures (°C): *1*) 15; *2*) 25; *3*) 35; *4*) 45.

It is noteworthy that the conclusion that there is conjugation between the macroring and the benzene rings in tetraphenylporphyrins is based on shaky foundations. It can be regarded as premature, since it has not been confirmed by either spectroscopic or kinetic data[1]. The increase of the equilibrium constant K_2 for the binding of piperidine by nickel-tetraphenylporphyrins with enhancement of the electron-accepting properties of *para*-substituents ($NO_2 > CN > OCOCH_3 > Cl$—Table 10) can be readily accounted for by the increase of the effective charge on the nickel atom as a result of the weakening of the σ-donor properties of the corresponding tetraphenylporphin derivatives, which is caused by the inductive effect of the $-C_6H_4X$ groups in the molecule.

One must note that well-founded conclusions concerning the influence of the molecular structure of metalloporphyrins on the nature of their interaction with extraligands and other types of mutual influence of atoms in metalloporphyrins cannot be reached on the basis of the constants for the addition (particularly the second constants!) of extraligands in the absence of reliable numerical data for the entropies and enthalpies of extracoordination.

In their reaction with piperidine, the VO^{2+} complexes are less sensitive to the nature of the substituent in the benzene ring of the tetraphenylporphin[222]. They form only "monoligand" extracomplexes. The location of the vanadium atom outside the molecular plane leads to a change in the degree of overlap of its *d* orbitals with the π orbitals of the porphyrin, which the authors[223] believe to cause a decrease of the "sensitivity" of vanadium-porphyrins to the nature of the substituents in the benzene rings. Furthermore, nickel is capable of back π-bonding (interaction of d_π orbitals with the π^* orbitals of the porphyrin). On the other hand, in the case of V^{4+} its single *d* electron is located in the d_{xy} orbital[224,225] and cannot form a stable bond with the π^* orbitals of the porphyrin ring.

The hypothesis of the authors of an interesting and on the whole useful study[222] concerning the identical degrees of solvation of the complex in the extracoordination process appears doubtful; for example, the quantitative data obtained in our laboratory reveal a significant dependent of ΔH_{solv} on the structure of the porphyrin[219].

The thermodynamic parameters of the formation of extracomplexes of ZnTPP with tetramethylthiourea, tetramethylurea, and triphenylphosphine in benzene have been determined[221]. The increase of ΔH (kcal mol^{-1}) has been observed in the sequence S (−5.6) > O(−6.5) > P(−7.7). The methods of calculation of the equilibrium constant for the extracoordination reaction were critically analysed in the same study[221] and preference was given to the method of Rose and Drago[226].

The equilibrium constants for the coordination of the vanadyl group VO to porphyrins of different structure have been published[223,227,228] (Table 6). Unfortunately the lack of thermodynamic parameters hinders the analysis of the data obtained, which are of considerable interest.

Table 6. The stability constants of monopyridine extracomplexes at 25 °C in $CHCl_3$.

MP	10^2K_S	Refs.	MP	10^2K_S	Refs.
VOAEP*	1.99	227	VOHP	1100	223
VOMP	5.21	228	VOTpyP	1120	228
VODP	7.30	228	$VODP(Br)_2$	1125	228
VOPP	9.13	228	$VODP(CH_3CO)_2$	3330	228

* Solvent—dioxan.

The use of vanadyl complexes of porphyrins is of interest in connection with the presence of the =O group in a single extraposition and also in connection with the possibility of the formation of the "monoligand" complex only. The dependence of K_S on the nature of functional substituents can be clearly traced in a series of porphyrins (Table 6). Electron-donating substituents (in H_2AEP and H_2MP) increase the electron density of the vanadyl ion and K_S is reduced compared with H_2DP. Electron-accepting substituents (in H_2PP, H_2HP, H_2TpyP, $H_2DP(Br)_2$, etc.) lead to an increase of K_S owing to the decrease of the electron density at the vanadyl ion.

Several studies have been published in recent years on the thermodynamics of extracoordination (Table 7) to various Co-porphyrins[121,123,125,161,209,229-231]. A sharp increase of the number of similar studies is apparently to be expected in the immediate future in connection with the extremely interesting ability of the cobalt complexes to combine reversibly with oxygen when the molecule contains another, particularly polymeric, extraligand. The main difficulty arising in the joint examination of these studies is in the first place the different reaction conditions. The marked dependence of the results of the measurements on the nature of the solvent

observed in a number of investigations[117,149,211,218] necessitates caution in comparing data obtained in different solvents.

The results of a study of cobalt-protoporphyrin are of considerable interest[121,125]. The extracoordination of eight extraligands to CoPP was investigated[125] (Table 12). It was established that there is no simple correlation between any thermodynamic parameter and the basicity of the ligand. The thermodynamic parameters of the addition of the second extraligand were not obtained, because the authors[125] were quite rightly afraid of introducing large amounts of extraligand capable of altering the structure of the solvent; the accompanying effects can lead to an erroneous interpretation of the results. The data obtained[125] showed that DMF is a "poore" extraligand for Co-porphyrins and can be used as a "neutral" solvent for the investigation of the extracoordination. The substitution of an alkyl in pyridine has only a slight influence on the complex-forming capacity of the latter, while the CN group causes a sharp decrease of this capacity. A similar behaviour was observed for imidazole, which is a somewhat weaker extraligand for the cobalt complex than pyridine. The identical complex-forming properties of pyridine and piperidine clearly indicate a major role of both σ- and π-binding in extracoordination to cobalt-porphyrins.

The interaction of CoTPP(p-CH_3)$_4$ with a series of π-acceptors and π-donors has been investigated by NMR in $CDCl_3$ (Table 7).[161] Thermodynamic parameters have been found for trinitrobenzene as an extraligand. The virtually complete identity of the K_S for acceptors and donors indicates, according to La Mar and Viscio[150], the ability of the metalloporphyrin to exhibit the properties of a π-acceptor or a π-donor, depending on the conditions. However, this claim does not appear convincing in the absence of fundamental thermodynamic characteristics of the extracoordination reaction.

It has been found[123] for phosphorus-, sulphur-, and arsenic-containing extraligands that the coordinating capacity diminishes in the sequence (Table 11) $P(C_4H_9)_3 \gg P(OCH_3)_3 > P(C_6H_5)_3 > S(CH_3)_2 > As(C_6H_5)_3$, while the K_S are correlated with the pK_B of the ligands. These results led the authors to the conclusion that σ-binding plays a dominant role for the above extraligands, i.e. the role of the d_π–d_π interaction between cobalt and the above ligands is small.

The formation of complexes by CoTPP and CoTPP(p-OCH_3)$_4$ with DMSO in CCl_4 has been investigated by a spectroscopic method[230]. It was established that two DMSO molecules are added in steps (Table 7). CoTPP and CoTPP(p-OCH_3)$_4$ were found to exhibit a significant difference in the extracoordination reaction with DMSO. The introduction of p-OCH_3 groups into the benzene rings alters significantly the enthalpy (increases it by 6 kcal) and entropy (increases it by 17 e.u.) of coordination. The stability constant then decreases almost by a factor of 2.5 (Table 7); the authors[230] attributed its decrease to the increase of the electron density in the porphyrin macroring and at the cobalt atom as a consequence of the greater electron-donating capacity of the $C_6H_4OCH_3$ group compared with the phenyl residue. However, this conclusion was reached without taking into account solvation and steric factors and cannot be regarded as well-founded. It is seen from the data in Table 7 how much the entropy can change in isotypical extracoordination reactions.

Interesting data on the extracoordination of nitrogen-containing heterocycles to ethoxycarbonyl derivatives of porphin (ECP complexes of Co^{2+} and Cu^{2+}) were obtained by Ginzburg et al.[231] Extracoordination is accompanied by a decrease of entropy from −7 to −12 e.u. (for pyridine), depending on the number of ethoxycarbonyl groups (Table 7). The enthalpy then decreases from −7 to −9 kcal mol^{-1}. Somewhat greater values of ΔH, ΔS, and stability constants are characteristic of the extracoordination of piperidine. Overall, the extracoordination to the ECP complexes of cobalt resembles that for CoTPP.

Table 7. Thermodynamic parameters of the extracoordination reaction involving cobalt-porphyrins in toluene.

Extraligand	K_S	$-\Delta H$, kcal mol^{-1}	$-\Delta S$, e.u.	Method of determination of K_S	Refs.
		CoPP*			
DMF	15	7.9	21	SPT	125
4-Cyanopyridine	1 738	10	19	SPT	125
Pyridine	6 025	6.9	6	SPT	125
4-t-Butylpyridine	7 079	9	13	SPT	125
Imidazole	4 365	7.9	10	SPT	125
1-Methylimidazole	5 011	10.7	19	SPT	125
4-Aminopyridine	10 000	8.1	9	SPT	125
Piperidine	6 760	10.4	17	SPT	125
		CoTPP(p-CH_3)$_4$**			
Trinitrobenzene****	17.5	5.7	14	NMR	161
Trinitrotoluene	3.3	—	—	NMR	161
Dinitrobenzene	2.9	—	—	NMR	161
Tetramethyl-p-phenylenediamine	10.2	—	—	NMR	161
		CoMP***			
$P(C_6H_5)_3$	30.4	7.0	17	SP	123
$P(C_4H_9)_3$	12 000	13.3	27	SP	123
$P(OCH_3)_3$	45.1	6.9	15	SP	123
$S(CH_3)_2$	22.5	4.5	9	SP	123
$As(C_6H_5)_3$	3.5	5.2	15	SP	123
		CoTPP**			
DMSO*****	13 800	13.8	27	SP	230
		CoTPP(p-OCH_3)$_4$**			
DMSO*****	5900	8.0	10	SP	230
		Co1ECP***			
Pyridine	3388	6.8	7	SP	231
		Co2ECP***			
Piperidine	9549	6.0	3	SP	231
Pyridine	6456	8.8	13	SP	231
		Co3ECP***			
Piperidine	15 135	8.3	7	SP	231
Pyridine	2 457	7.5	8	SP	231
		Co4ECP***			
Piperidine	12 882	5.4	1	SP	231
Pyridine	4 677	8.5	12	SP	231

* 296 K.
** 298 K.
*** 293–299 K.
**** Solvent–$CDCl_3$.
***** Solvent–CCl_4, $K_2 = 430$ (for CoTPP) and $K_2 = 320$ [for CoTPP(p-OCH_3)$_4$]. Abbreviations: SPT = spectrophotometric titration; SP = spectrophotometric method; 1ECP = ethoxycarbonylporphyrins; 2ECP = di(ethoxycarbonyl)porphyrin; 3ECP = tri(ethoxycarbonyl)porphyrin; 4ECP = tetra(ethoxycarbonyl)porphyrin.

In contrast to the cobalt complexes, the copper complexes of ethoxycarbonylporphyrins coordinate pyridine and piperidine with greater difficulty (the values of lgK_S decrease from 0.2 to −0.8) and with smaller entropy changes (−ΔS changes from 16 to 24 e.u. for piperidine).[231] There is virtually no dependence on the number of ethoxycarbonyl groups.

The most numerous data on extracoordination have been obtained for iron-porphyrins. Studies on iron-porphyrins have been carried out for more than three decades. The first extensive investigations of the interaction of ferrous

and ferric protoporphyrins with hydroxide and cyanide ions as well as pyridine were carried out by Schak and Clark[232] in 1947.

The iron atom in porphyrin complexes has an especially high affinity of anions of the type of CN^-. The oxidation state of the initial iron atom plays a significant role in this. Thus the overall equilibrium constant for the addition of ligands in the extracomplexes $[(CN)_2FePP]^-$ is $K_{1,2} = 1.4 \times 10^{12}$, while the constant for $[(CN)_2FePP]^{2-}$ is $K_{1,2} = 8 \times 10^9$. At the same time the equilibrium constants for the dipyridine complex are $K_1 = 0.8$ and $K_2 = 5 \times 10^7$. The relative affinities of different types of ligands for Fe^{3+}-porphyrins vary in the sequence $CN^- \gg$ imidazoles $\gg$ pyridine[233], which indicates a significant role for π-binding of the extraligands by the iron-porphyrin. The accumulation of the negative charge in the porphyrin macroring then leads to destabilisation of the system. Anionic complexes are therefore more stable for Fe^{3+}-porphyrins and less stable for Fe^{2+}-porphyrins[1].

Since the mobility of *d* electrons diminishes with increase of the positive charge on the central atom, ferric porphyrins become less capable, relative to ferrous porphyrins, of the extracoordination of molecules (of the type of pyridine and oxygen) tending to form dative π-bonds. This ability is restored when one of the extraligands is a powerful electron pair donor. Mixed complexes of Fe^{3+}-porphyrins with cyano- and pyridine groups are therefore more stable than the corresponding Fe^{2+}-porphyrins {$K_{1,2} = 3.6 \times 10^{12}$ for (CN)(py)FePP and $K_{1,2} = 8 \times 10^{10}$ for $[(CN)(py)FePP]^-$ have been found}. Mixed π-ligands then entail a significant gain of the free energy ΔG compared with homogeneous ligands (2py, $2CN^-$).[1]

The central atoms in ferric and ferrous porphyrins exhibit a high affinity also in relation to other nitrogen-containing molecules as well as oxygen containing ligands (H_2O, OH^-, H_2O_2, CO, O_2). The study of the extracomplexes with H_2O and OH^- in an alkaline medium is greatly complicated by the dimerisation and greater degree of aggregation of metalloporphyrins, which makes the measurement of the thermodynamic parameters of extracoordination significantly more difficult[1]. This can probably explain the fact that only the values of K_S have been determined in the majority of studies on extracoordination equilibria[28,29,116,162,234].

An interesting study[117] was devoted to the thermodynamics of the extracoordination of pyridine and its substituted derivatives to the Fe^{2+}-porphyrins of the protoporphyrin group in benzene:

$$FeP + 2L \rightleftharpoons (L)_2FeP. \qquad (22)$$

The authors investigated the dependence of the thermodynamic parameters obtained from spectroscopic data on the nature of the extraligand and the structure of the porphyrin.

Thermodynamic parameters for the iron(II) and iron(III) complexes of 2,4-dicysteine-substituted mesoporphyrin have been determined spectrophotometrically[235] in aqueous solutions. In contrast to other ligands, extracoordination takes place stepwise in this instance. In terms of the changes in ΔH for the Fe^{3+}- and Fe^{2+}-porphyrins, the extraligands investigated can be arranged in the following sequences: CN^- > histidine > imidazole > pyridine; CN^- > pyridine > histidine > imidazole > *N*-acetyl-DL-methionine. The thermodynamic parameters of extracoordination obtained have been attributed[235] to changes in the degree of solvation of iron-porphyrin in a hydrophobic cavity within the haemoprotein and to the influence of the conformational changes in the aminoacid residues. This hypothesis has been confirmed by the values of ΔH and ΔS obtained for ferric cytochrome *c*.[236,237]

The stability of haemin in the extracoordination of histidine and imidazole to a series of peptides has been studied[28,29]. The values of $\lg K$ varied with the nature of the atomic environment of histidine in the range from 7.41 to 8.32. The authors[28] arrived at the interesting conclusion that the stability of the extracomplexes depends to a large extent on steric factors, i.e. on the bulk of the groups adjoining histidine. It has also been established[29] that the stability of the extracomplexes and the strength of the coordinate bond depend on the nature of the porphyrin system (on the basicity of the porphyrin) and the length and degree of branching of the extraligand chain. Table 8 indicates the limits of the variation of $\lg K_S$ for Fe-porphyrins with a series of histidine-containing ligands. Regrettably, these interesting communications[28,29] do not contain complete thermodynamic data.

Table 8. The limits of variation of $\lg K_S$ for the extracoordination of histidine-containing extraligands to Fe-porphyrins in chloroform[28,29].

MP	$\overset{+}{F}$eAEP(III)	$\overset{+}{F}$eMP d.m.e.	$\overset{+}{F}$eDP	$\overset{+}{F}$ePP d.m.e.	$\overset{+}{F}$ePP
$\lg K_S$	6.0—6.08	6.2—6.84	6.70—7.10	7.08—7.32	8.25—8.54

Among studies devoted to Fe-porphyrins, mention should also be made of that of Anusiem and Lumry[212], primarily because of the choice of the method of investigation: the thermodynamic parameters of the extracoordination of the azide ion to ferric haemoglobin were determined calorimetrically in water over a wide range of pH. The electrochemical reduction of the iron(III) complexes of a series of porphyrins has been investigated by cyclic voltammetry in the presence of substituted bipyridyls[238], forming extracomplexes with $K_S = 1 \times 10^{-3}$ for $\overset{+}{F}$eOAEP and 1.8×10^4 for $\overset{+}{F}$eTPP.

The influence of trinitrobenzene as a π-acceptor on the thermodynamics of the extracoordination of *N*-methylimidazole to (Cl)FeTPP was studied by ^1H NMR;[163] the authors suggest that trinitrobenzene can interact with the central atom and can reduce the affinity of the complex for a second *N*-methylimidazole molecule. The stability constants K_{S2} for the reaction of Fe-tetra-arylporphyrins with substituted imidazole and pyridine were determined by NMR [164] and the formation of a biligand extracomplex was discovered. Comparison of the observed values with the K_S obtained previously from electronic spectra led the authors[164] to the conclusion that the NMR method is suitable (subject to some limitations) for the determination of the stability constants and the stoichiometry of the formation of extracomplexes. It is noteworthy that, in the determination of the temperature variation of K_S by NMR, a large error is introduced due to the characteristics of the method, in the first place and high concentration of the metalloporphyrin, which causes its association.

It follows from Table 9 [164] that the influence of substituents in the *para*-position of the benzene rings of FeTPP on the values of K_{S2} is very insignificant. The nature of the halogen in the porphyrin complex has a significant influence on the values of K_{S2}; here K_{S2} varies in the sequence I > Br $\gg$ Cl. The dependence of K_{S2} on the nature of the extraligand is not correlated with pK_B. The authors[164] obtained the approximate value $\Delta H \approx -26$ kcal mol^{-1} for 1-methylimidazole and $\Delta H = -15$ kcal mol^{-1} for 1-methylbenzimidazole. The

authors explain the difference between the ΔH by steric factors preventing extracoordination, i.e.the maximum overlap of the iron and nitrogen orbitals in the case of 1-methylbenzimidazole.

Table 9. The influence of the structure of the porphyrin and of the halogen on the K_{S2} of the iron-porphyrin complexes with 1-methylimidazole in $CDCl_3$ at 25 °C.[164]

Complex	K_{S2}
(Cl)FeTPP(*p*-OCH_3)	$(4.0\pm0.6)\cdot10^3$
(Cl)FeTPP(*p*-CH_3)	$(3.0\pm0.4)\cdot10^3$
(Cl)FeTPP	$(1.4\pm0.7)\cdot10^3$
(Cl)FeTPP(*p*-Cl)	$(0.65\pm0.10)\cdot10^3$
(Br)FeTPP(*p*-CH_3)	$\gtrsim10^6$
(I)FeTPP(*p*-CH_3)	$>10^6$
(Cl)FeOAEP	$(0.66\pm0.13)\cdot10^3$
(Cl)FeTPP*	25 ± 5
(Br)FeTPP(*p*-CH_3)	$(2.4\pm0.5)\cdot10^3$

*Temperature—45 °C; extraligand—1-methylbenzimidazole.

Analysis of the thermodynamic parameters of the extracoordination reactions is frequently difficult, because the values of K_S, ΔH, and ΔS were obtained under non-standard conditions. The choice of solvent exerts an extremely powerful influence on the parameters of the extracoordination reaction, which has been shown in relation to Fe-porphyrins[211,239] and Cu-porphyrins[231].

Cole et al.[211] justly assumed that, when account is taken of the solvation, the extracoordination equation must be written as follows:

$$Fe^{2+}PP\,(solv)_{n_1} + 2\,L\,(solv)_{n_2} \rightleftarrows (L)_2Fe^{2+}PP\,(solv)_{n_3} + n\,(solv)\ . \qquad (23)$$

It follows from Eqn.(23) that the nature of the interaction of the metalloporphyrin can be significantly different in solvents of different types. It has been shown for the reaction of FePP with pyridine and its substituted derivatives in various solvents that the changes in ΔH and ΔS on changing the solvent can be significantly greater than the changes introduced by the structure of the porphyrin and the nature of the extraligand. Depending on the nature of the solvent, the entropies vary by up to 50 e.u. and the ΔH by up to 17 kcal mol^{-1}.

Cole et al.[211] examined the possible energy contributions to ΔH: (1) the formation of a π-complex; (2) the formation of a charge-transfer complex; (3) hydrophobic interaction; (4) dipole orientation forces; (5) dispersion interaction; (6) hydrogen bonding. The postulated contributions to ΔS are due to the following factors: (1) hindered rotation of the molecule owing to the attachment of a second ligand; (2) restricted rotation due to the π-bonding of iron to the extraligand; (3) the formation of a solvate complex, etc. Analogous results have been obtained[231] for copper complexes of ethoxycarbonylporphyrins in reactions with nitrogen-containing heterocycles.

In a study of the interaction of (Cl)FeTPP with imidazole, Kedderis et al.[239] obtained virtually identical values of all the thermodynamic parameters for a series of solvents (acetone, chloroform, methylene chloride, and ethyl acetate). The errors quoted for the values of ΔH are puzzling; whereas the errors in ΔS are consistent with the accuracy of the method, those for ΔH are too low (for the spectrophotometric method) at least by a factor of 10. The authors[239] were unable to explain the discrepancy with the results of Cole et al., but they attempted to relate it to the different charges on Fe in the systems investigated[211,239].

Comparison of the data in Table 9 [239] leads to the conclusion that the free energies of extracoordination reactions involving iron-porphyrins and their enthalpy and entropy components depend markedly on the structure of the porphyrin and the nature of the extraligand and the solvent. Low values of ΔH show that they include the effects of the solvation of the reactant in extracoordination to Fe-porphyrins, which can be inferred from the very low entropies. These data demonstrate clearly the important role of the π-bonding of extraligands to $Fe^{2+}P$.

The data presented for the thermodynamics of extracoordination demonstrate a series of interesting and practically important relations for the metalloporphyrins of certain metals. However, the lack of systematic studies (in which one or several variables are varied, while keeping a number of factors constant) rules out the possibility of wider generalisations and conclusions necessary for the solution of problems of technical and enzyme catalysis on metalloporphyrins.

---oOo---

It follows from the data presented that there exist factors favouring the formation of stable extracomplexes of metalloporphyrins. They include the following: (1) the increase of the effective positive charge on the central metal atom; the σ-electron-donating and π-electron-accepting capacities of the ligands; the latter is important in extracoordination to low-spin metal complexes whose *d* orbital is more than half-filled; (3) the weakening of the solvation and acid–base interaction of the extraligands with the medium; (4) the decrease of the steric hindrance to extracoordination from the side of the extraligand. The last condition is particularly significant for the formation of biligand extracomplexes of porphyrins.

REFERENCES

1. B.D.Berezin, "Koordinatsionnye Soedineniya Porfirinov i Ftalotsianina" (Coordination Compounds of Porphyrins and Phthalocyanine), Izd.Nauka, Moscow, 1978.
2. A.N.Terenin, "Fotonika Molekul Krasitelei i Rodstvennykh Soedinenii" (Photonics of the Molecules of Dyes and Related Compounds), Izd.Nauka, Leningrad, 1967.
3. P.Williams, Chem.Rev., **56**, 299 (1956).
4. A.N.Sidorov, Doctoral Thesis, Institute of Physical Chemistry, Academy of Sciences of Ukrainian SSR, Kiev, 1969.
5. E.W.Baker, M.S.Brookhart, and A.H.Corwin, J.Amer. Chem.Soc., **86**, 4587 (1964).
6. J.Falk, "Porphyrins and Metalloporphyrins", Elsevier Publ., Amsterdam, 1964.
7. H.Fischer, A.Treibs, and K.Zeile, Z.physiol.Chem., **193**, 138 (1930).
8. R.G.Little, K.R.Dymock, and J.A.Ibers, J.Amer. Chem.Soc., **97**, 4532 (1976).
9. J.W.Buchler and K.L.Lay, Z.Naturforsch., **30b**, 385 (1975).
10. T.Yoshida, T.Ozaki, Y.Shintani, and H.Watanabe, J.Inorg.Nuclear Chem., **38**, 1879 (1976).
11. S.McCoy and W.S.Caughey, Biochemistry, **9**, 2387 (1970).

12. L.Vaska and H.Nakai, J.Amer.Chem.Soc., **95**, 5431 (1973).
13. T.Kobayashi, F.Kukorawa, and N.Uyeda, Bull. Inst.Chem.Res.Kyoto Univ., **53**, 186 (1975).
14. B.W.Dale, Trans.Faraday Soc., **65**, 331 (1969).
15. J.E.Baldwin, T.Klose, and M.Peters, Chem.Comm., 881 (1976).
16. J.O.Alben, W.H.Fuchsman, C.A.Beaudreau, and W.S.Caughey, Biochemistry, **7**, 624 (1968).
17. M.Sadasivan, H.J.Eberspaecher, W.H.Fuchsman, and W.S.Caughey, Biochemistry, **8**, 534 (1969).
18. I.A.Cohen, D.A.Summerville, and S.R.Su, J.Amer. Chem.Soc., **98**, 5813 (1976).
19. C.J.Weschler, D.L.Anderson, and F.Basolo, J.Amer. Chem.Soc., **97**, 6707 (1975).
20. R.Snyder and G.La Mar, J.Amer.Chem.Soc., **98**, 4419 (1976).
21. R.Taube, Pure Appl.Chem., **38**, 427 (1976).
22. J.P.Collman and C.A.Reed, J.Amer.Chem.Soc., **95**, 1782 (1973).
23. G.La Mar and F.A.Walker, J.Amer.Chem.Soc., **95**, 1782 (1973).
24. D.Dolphin, J.R.Sams, T.B.Tsin, and K.L.Wong, J. Amer.Chem.Soc., **98**, 6970 (1976).
25. C.E.Castro, Bioinorg.Chem., **4**, 45 (1974).
26. T.Sakurai, Karaku Chemistry, **29**, 976 (1974).
27. S.M.Peng and J.Ibers, J.Amer.Chem.Soc., **98**, 8032 (1976).
28. V.P.Chernyshev, E.I.Filippovich, and R.B.Evstigneeva, Zhur.Obshch.Khim., **41**, 2561 (1971).
29. V.N.Lazgina, E.I.Filippovich, G.N.Sakharova, and R.P.Evstigneeva, Zhur.Obshch.Khim., **44**, 2051 (1974).
30. V.N.Luzgina, E.I.Filippovich, A.F.Vanin, and R.P.Evstigneeva, Zhur.Obshch.Khim., **45**, 212 (1975).
31. V.N.Luzgina, E.I.Filippovich, A.F.Vanin, R.P.Evstigneeva, and L.I.Fainshtein, Zhur.Obshch.Khim., **47**, 2125 (1977).
32. F.Cariati, D.Galizzioli, F.Morazzoni, and C.Busetto, J.Chem.Soc., Dalton Trans., 556 (1975).
33. T.Sakurai, K.Yamamoto, H.Naito, and N.Nakamoto, Bull.Chem.Soc.Japan, **49**, 3042 (1976).
34. J.W.Lauher and J.A.Ibers, J.Amer.Chem.Soc., **96**, 4447 (1974).
35. L.D.Rollman and S.I.Chan, Inorg.Chem., **10**, 1978 (1971).
36. N.Datta-Gupta, J.Inorg.Nuclear Chem., **33**, 4219 (1971).
37. J.W.Buchler, G.Eikelman, L.Puppe, K.Rohbock, H.H.Scheehage, and D.Weck, Annalen, **745**, 135(1971).
38. K.Yamamoto, Sci.Pap.Inst.Phys.Chem.Res., **70**, 71 (1976).
39. B.Gonzales, J.Kouba, S.Yee, C.A.Reed, J.F.Kirner, and W.R.Scheidt, J.Amer.Chem.Soc., **97**, 3247 (1975).
40. L.J.Boucher, J.Amer.Chem.Soc., **90**, 6640 (1968).
41. M.Tsutsui, C.P.Hrung, D.Ostfeld, T.S.Srivastava, D.L.Cullen, and E.F.Meyer, J.Amer.Chem.Soc., **97**, 3952 (1975).
42. D.Ostfeld, M.Tsutsui, C.P.Hrung, and D.C.Conway, J.Amer.Chem.Soc., **93**, 2548 (1971).
43. M.Tsutsui and C.P.Hrung, Annalen, New York, Acad. Sci., **239**, 140 (1974).
44. A.M.Abeysekera, R.Grigg, J.Trocha-Grishaw, and V.Viswanatha, Tetrahedron Letters, 3189 (1976).
45. H.Ogoshi, J.Setsune, T.Omura, and Z.Yoshida, J. Amer.Chem.Soc., **97**, 6461 (1975).
46. H.Ogoshi, T.Omura, and Z.Yoshida, J.Amer.Chem. Soc., **95**, 1666 (1973).
47. F.Hopf, P.O'Brien, W.R.Scheidt, and D.G.Whitten, J.Amer.Chem.Soc., **97**, 277 (1975).
48. S.S.Eaton, G.R.Eaton, and R.H.Holm, J.Organometal.Chem., **39**, 179 (1972).
49. M.Tsutsui, D.Ostfeld, and L.Hoffman, J.Amer.Chem. Soc., **93**, 1820 (1971).
50. C.P.Wong, R.F.Venteicher, and W.Horrocks, J.Amer. Chem.Soc., **96**, 7149 (1974).
51. C.P.Wong and W.Horrocks, Tetrahedron Letters, **31**, 2637 (1975).
52. W.Horrocks and C.P.Wong, J.Amer.Chem.Soc., **98**, 7157 (1976).
53. J.W.Buchler, in "Porphyrins and Metalloporphyrins" (Edited by K.M.Smith), Elsevier, Amsterdam, 1975, p.160.
54. C.Marisondi, W.Swift, and D.K.Straub, J.Amer.Chem. Soc., **91**, 5205 (1969).
55. J.W.Buchler and H.H.Schneehage, Z.Naturforsch., **28b**, 433 (1973).
56. P.Mohr and W.Scheler, Europ.J.Biochem., **8**, 444 (1969).
57. R.G.Little, B.M.Hoffman, and J.A.Ibers, Bioinorg. Chem., **3**, 207 (1974).
58. J.W.Buchler, L.Puppe, K.Rohbock, and H.H.Schneehage, Annalen, New York, Acad.Sci., **206**, 116 (1973).
59. M.Tsutsui, M.Ichikawa, F.Vohwinkel, and K.Suzuki, J.Amer.Chem.Soc., **88**, 854 (1966).
60. M.Tsutsui, R.A.Velapoldi, K.Suzuki, F.Vohwinkel, M.Ichikawa, and T.Koyano, J.Amer.Chem.Soc., **91**, 6262 (1969).
61. T.S.Srivastava and E.B.Fleisher, J.Amer.Chem.Soc., **92**, 5518 (1970).
62. E.B.Fleischer, R.Thorp, and D.Venerable, Chem. Comm., 475 (1969).
63. M.Tsutsui and C.P.Hrung, J.Amer.Chem.Soc., **95**, 5777 (1973).
64. B.C.Chow and I.A.Cohen, Bioinorg.Chem., **1**, 57 (1971).
65. G.W.Sovocool, F.R.Hopf, and D.G.Whitten, J.Amer. Chem.Soc., **94**, 4350 (1972).
66. J.J.Bonnet, S.S.Eaton, G.R.Eaton, R.H.Holm, and J.A.Ibers, J.Amer.Chem.Soc., **95**, 2141 (1973).
67. T.S.Srivastava, L.Hoffman, and M.Tsutsui, J.Amer. Chem.Soc., **94**, 1385 (1972).
68. M.Tsutsui, D.Ostfeld, J.N.Francis, and L.Hoffman, J.Coord.Chem., **1**, 115 (1971).
69. D.Cullen, E.Meyer, T.S.Srivastava, and M.Tsutsui, Chem.Comm., 584 (1972).
70. J.W.Faller and J.W.Sibert, J.Organometal.Chem., **31**, C5 (1971).
71. D.Cullen, E.Meyer, T.S.Srivastava, and M.Tsutsui, J.Amer.Chem.Soc., **94**, 7603 (1972).
72. E.B.Fleischer and N.Sadasivan, Chem.Comm., 159 (1967).
73. N.Sadasivan and E.B.Fleischer, J.Inorg.Nuclear Chem., **30**, 591 (1968).
74. E.B.Fleischer and D.Lavallee, J.Amer.Chem.Soc., **89**, 7132 (1967).
75. B.R.James and D.V.Stynes, J.Amer.Chem.Soc., **94**, 6225 (1972).
76. Z.Yoshida, H.Ogoshi, T.Omura, E.Watanabe, and T.Kurosaki, Tetrahedron Letters, **11**, 1077 (1972).
77. D.Ostfeld, M.Tsutsui, C.P.Hrung, and D.C.Conway, J.Coord.Chem., **2**, 101 (1972).
78. B.D.Berezin and O.I.Koifman, Uspekhi Khim., **42**, 2007 (1973) [Russ.Chem.Rev., No.11 (1973)].
79. W.R.Scheidt and M.E.Frisse, J.Amer.Chem.Soc., **97**, 17 (1975).

80. W.R.Scheidt , D.A.Summerville, and I.A.Cohen, J.Amer.Chem.Soc., **98**, 6623 (1976).
81. S.Koch, S.C.Tang, R.H.Holm, R.B.Frankel, and J.A.Ibers, J.Amer.Chem.Soc., **97**, 916 (1975).
82. S.C.Tang, S.Koch, G.C.Papaefthymiou, S.Foner, R.B.Frankel, J.A.Ibers, and R.H.Holm, J.Amer. Chem.Soc., **98**, 2414 (1976).
83. D.F.Koenig, Acta Cryst., **18**, 663 (1965).
84. J.L.Hoard, H.J.Yamor, and W.S.Caughey, J.Amer. Chem.Soc., **87**, 2312 (1965).
85. A.B.Hoffman, D.M.Collins, V.W.Day, E.B.Fleischer, T.S.Srivastava, and J.L.Hoard, J.Amer.Chem.Soc., **94**, 3620 (1972),
86. B.M.Hoard and W.R.Scheidt, Proc.Nat.Acad.Sci. U.S., 71, 1578 (1974).
87. W.R.Scheidt, J.Amer.Chem.Soc., **96**, 90 (1974).
88. R.G.Little and J.A.Ibers, J.Amer.Chem.Soc., **96**, 4452 (1974).
89. P.N.Dwyer, P.Madura, and W.R.Scheidt, J.Amer. Chem.Soc., **96**, 4815 (1974).
90. O.P.Anderson and D.K.Lavallee, J.Amer.Chem.Soc., **98**, 4670 (1976).
91. L.J.Boucher, Annalen, New York, Acad.Sci., **206**, 409 (1973).
92. V.W.Day, B.R.Stults, E.L.Tasset, and R.S.Marianelli, Inorg.Nuclear Chem.Letters, 11, 505 (1975).
93. J.L.Hoard and W.R.Scheidt, Proc.Nat.Acad.Sci., U.S., **70**, 3919 (1973).
94. J.L.Hoard, Science, **174**, 1295 (1971).
95. J.L.Hoard, G.H.Cohen, and M.D.Glick, J.Amer. Chem.Soc., **89**, 1992 (1967).
96. W.P.Scheidt and P.Piciulo, J.Amer.Chem.Soc., **98**, 1913 (1976).
97. D.M.Collins, R.Countryman, and J.L.Hoard, J.Amer. Chem.Soc., **94**, 2066 (1972).
98. J.F.Kirner and W.R.Scheidt, Inorg.Chem., **14**, 2081 (1975).
99. G.R.Little and J.A.Ibers, J.Amer.Chem.Soc., **95**, 8583 (1973).
100. D.L.Cullen and E.F.Meyer, Acta Cryst., **B32**, 2259 (1976).
101. L.J.Radonovich, A.Bloom, and J.L.Hoard, J.Amer. Chem.Soc., **94**, 2073 (1972).
102. A.Takenaka, Y.Sasada, E.Watanabe, H.Ogoshi, and A.Yoschida, Chem.Letters, 1235 (1972).
103. W.R.Scheidt, J.A.Cunningham, and J.L.Hoard, J. Amer.Chem.Soc., **95**, 8289 (1973).
104. J.A.Kaduk and W.R.Scheidt, Inorg.Chem., **13**, 1875 (1974).
105. T.Sakurai, K.Yamamoto, N.Seino, and H.Katsuta, Acta Cryst., **B31**, 2514 (1975).
106. W.R.Scheidt, J.Amer.Chem.Soc., **96**, 84 (1974).
107. V.W.Day, B.R.Stults, E.L.Tasset, R.O.Day, and R.S.Marianelli, J.Amer.Chem.Soc., **96**, 2650 (1974).
108. B.R.Stults, V.W.Day, E.L.Tasset, and R.S.Marianelli, Inorg.Nuclear Chem.Letters, **9**, 1259 (1973).
109. J.F.Kirner, J.Garofalo, and W.R.Scheidt, Inorg. Nuclear Chem.Letters, 11, 107 (1975).
110. R.Guilard, M.Fontesse, and P.Fourman, Chem. Comm., **5**, 161 (1976).
111. R.G.Little and J.A.Ibers, J.Amer.Chem.Soc., **96**, 4440 (1974).
112. J.L.Hoard, in "Structural Chemistry and Molecular Biology" (Edited by A.Rich, N.Davidson), San Francisco, 1968, p.573.
113. D.M.Rifkind, "Neorganicheskaya Biokhimiya" (Inorganic Biochemistry), Izd.Mir, Moscow, 1972, Vol.2, p.271.
114. V.Koi, "Neorganicheskaya Biokhimiya" (Inorganic Biochemistry), Izd.Mir, Moscow, 1972, p218.
115. B.B.Wayland and L.W.Olson, J.Amer.Chem.Soc., **96**, 6037 (1974).
116. G.S.Wagner and R.J.Kassner, J.Amer.Chem.Soc., **96**, 5593 (1974).
117. S.J.Cole, G.C.Curthoys, and E.A.Magnusson, J. Amer.Chem.Soc., **92**, 2921 (1970).
118. E.Tsuchida, K.Honda, and H.Sata, Inorg.Chem., **15**, 352 (1976).
119. C.K.Chang and D.Dolphin, J.Amer.Chem.Soc., **97**, 5948 (1975).
120. H.Ogoshi, H.Sugimoto, and Z.Yoschida, Tetrahedron Letters, 4481 (1976).
121. D.V.Stynes, H.C.Stynes, J.A.Ibers, and B.R.James, J.Amer.Chem.Soc., **95**, 1142 (1973).
122. T.J.Beugelsdijk and R.S.Drago, J.Amer.Chem.Soc., **97**, 6466 (1975).
123. T.Takayanagi, H.Yamamoto, and T.Kwan, Bull.Chem. Soc.Japan, **48**, 2618 (1975).
124. K.R.Ashley, M.Berggren, and M.Cheng, J.Amer. Chem.Soc., **97**, 1422 (1975).
125. D.V.Stynes, H.C.Stynes, B.R.James, and J.A.Ibers, J.Amer.Chem.Soc., **95**, 1796 (1973).
126. R.F.Pasternak and G.R.Parr, Inorg.Chem., **15**, 3087 (1973).
127. C.O.Beuder, R.Bonnett, and R.G.Smith, J.Chem. Soc., 345 (1969).
128. W.S.Caughey, R.Deal, B.D.McLees, and J.O.Alben, J.Amer.Chem.Soc., **84**, 1735 (1962).
129. C.B.Storm, A.H.Corwin, R.R.Arelano, M.Martz, and R.Weintraub, J.Amer.Chem.Soc., **88**, 2525 (1966).
130. J.R.Miller and G.D.Dorough, J.Amer.Chem.Soc., **74**, 3977 (1952).
131. B.M.Hoffman, C.J.Weschler, and F.Basolo, J.Amer. Chem.Soc., **98**, 5473 (1976).
132. W.L.Hinze and J.H.Fendler, J.Chem.Soc.Dalton, Trans., 1469 (1976).
133. E.B.Fleischer, J.M.Palmer, T.S.Srivastava, and A.Chatterjee, J.Amer.Chem.Soc., **93**, 3162 (1971).
134. P.Hambright and M.K.Rishnamurthy, J.Inorg.Nuclear Chem., 37, 557 (1975).
135. J.D.Stong and C.R.Hartzell, Bioinorg.Chem., **5**, 219 (1976).
136. I.Collamati, C.Ercolani, and G.Rossi, Inorg.Nuclear Chem.Letters, **12**, 799 (1976).
137. J.H.Wang, A.Nakahara, and E.B.Fleischer, J.Amer. Chem.Soc., **80**, 1109 (1958).
138. G.P.Gurinovich, A.N.Sevchenko, and K.N.Solov'ev, "Spektroskopiya Khlorofilla i Rodstvennykh Soedinenii" (The Spectroscopy of Chlorophyll and Related Compounds), Izd.Nauka i Tekhnika, Minsk, 1968.
139. H.Kobayashi and Y.Yanagawa, Bull.Chem.Soc.Japan, **45**, 450 (1972).
140. H.Kobayashi, T.Higuchi, Y.Kaizu, H.Osada, and M.Aoki, Bull.Chem.Soc.Japan, **48**, 3137 (1975).
141. M.J.Gouterman, J.Mol.Spectrosc., **6**, 138 (1961).
142. S.J.Chantrell, C.A.McAuliffe, R.W.Munn, and A.C.Platt, Coord.Chem.Rev., **16**, 259 (1975).
143. Ya.G.Fridman (Editor), Symposium, "Ustoichivost' Smeshennykh Kompleksnykh Soedinenii v Rastvorakh" (Stability of Mixed Complexes in Solutions), Izd.Ilim, Frunze, 1971, p.11.
144. B.D.Berezin, Izv.Vys.Ucheb.Zaved., Khim.i Khim. Tekhnol., 11, 537 (1974),
145. R.P.Evstigneeva, "Problemy Sol'vatatsii i Kompleksoobrazovaniya (Mezhvuzovskii Sbornik)" [Problems of Solvation and Complex Formation (Intercollegiate Collected Volume)], Ivanovo, 1978, p.74.

146. H.Uenoyama and K.Sakai, Spectrochim.Acta, **A31**, 1517 (1975).
147. K.Yamamoto and T.Kwan, Bull.Chem.Soc.Japan, **45**, 664 (1972).
148. J.P.Collman, T.N.Sorrell, and B.M.Hoffman, J.Amer. Chem.Soc., **97**, 913 (1975).
149. H.C.Stynes and J.A.Ibers, J.Amer.Chem.Soc., **94**, 125 (1972).
150. G.La Mar and D.B.Viscio, J.Amer.Chem.Soc., **96**, 7354 (1974).
151. G.La Mar and F.A.Walker, J.Amer.Chem.Soc., **94**, 8607 (1972).
152. P.Hambright, Coord.Chem.Rev., **6**, 247 (1971).
153. P.Hambright, Coord.Chem.Rev., **46**, 1207 (1977).
154. F.A.Walker, J.Magnet.Res., **15**, 201 (1974).
155. B.Wayland and M.E.Abd-Elmageed, J.Amer.Chem. Soc., **96**, 4809 (1974).
156. P.W.Lay and W.S.Lin, J.Inorg.Nuclear Chem., **37**, 2389 (1975).
157. T.Takayanadi, K.Yamamoto, and T.Kwan, Chem. Pharm.Bull.(Japan), **20**, 2721 (1972).
158. B.B.Wayland and D.Mohajer, Inorg.Nuclear Chem. Letters, **9**, 633 (1973).
159. B.B.Wayland and D.Mohajer, J.Amer.Chem.Soc., **93**, 5295 (1971).
160. C.Mengersen, J.Subramanian, J.H.Fuhrhop, and K.M.Smith, Z.Naturforsch., **29a**, 1827 (1974).
161. G.P.Fulton and G.La Mar, J.Amer.Chem.Soc., **98**, 2119 (1976).
162. J.T.Wang, H.J.Ych, and D.F.Johnson, J.Amer.Chem. Soc., **97**, 1968 (1975).
163. G.La Mar, J.D.Satterlee, and R.V.Snyder, J.Amer. Chem.Soc., **96**, 7137 (1974).
164. J.D.Satterlee, G.La Mar, and J.S.Frye, J.Amer. Chem.Soc., **98**, 7275 (1976).
165. S.S.Eaton and G.R.Eaton, Inorg.Chem., **15**, 134 (1976).
166. J.W.Faller and J.W.Sibert, J.Organometal.Chem., **31**, C5 (1971).
167. J.C.Chang, T.P.Das, and D.Ikenberry, Theoret. Chim.Acta, **35**, 361 (1974).
168. E.Goldammer and H.Zorn, Molec.Phys., **32**, 1423 (1976).
169. S.S.Eaton, G.R.Eaton, and R.H.Holm, J.Organometal. Chem., **32**, C52 (1971).
170. E.Goldammer and H.Zorn, Z.Naturforsch., **31b**, 242 (1976).
171. H.A.O.Hill and K.G.Morallee, J.Amer.Chem.Soc., **94**, 731 (1972).
172. J.P.Collman, J.I.Brauman, and K.S.Suslick, J.Amer. Chem.Soc., **97**, 7185 (1975).
173. W.Hendrich, Roczn.Chem., **41**, 743 (1967).
174. H.Ogoshi, E.Watanabe, Z.Yoshida, J.Kinkaid, and K.Nakamoto, Inorg.Chem., **14**, 1344 (1975).
175. J.W.Buchler and P.D.Smith, Angew.Chem., **86**, 820 (1974).
176. J.Collman, R.R.Gagne, H.Gray, and W.Hare, J. Amer.Chem.Soc., **96**, 6522 (1974).
177. L.J.Boucher, J.Amer.Chem.Soc., **90**, 6640 (1968).
178. T.G.Spiro and J.M.Burke, J.Amer.Chem.Soc., **98**, 5483 (1976).
179. J.Kinkaid and K.Nakamoto, Spectrosc.Letters, **9**, 19 (1976).
180. T.Kitagava, Y.Kyogoky, T.Iizuka, and M.I.Saito, J.Amer.Chem.Soc., **98**, 5169 (1976).
181. N.W.G.Debye and A.D.Adler, Inorg.Chem., **13**, 3037 (1974).
182. L.M.Epstein, D.K.Straub, and C.Maricondi, Inorg. Chem., **6**, 1720 (1967).
183. W.H.Woodruff, D.H.Adams, T.G.Spiro, and T.Yonetani, J.Amer.Chem.Soc., **97**, 1695 (1975).
184. D.Dolphin, J.R.Sams, T.B.Tsin, and K.K.Wong, J.Amer.Chem.Soc., **98**, 6970 (1976).
185. C.Maricondi, W.Swift, and D.K.Straub, J.Amer. Chem.Soc., **91**, 5205 (1969).
186. M.A.Torrens, D.K.Straub, and L.M.Epstein, J.Amer. Chem.Soc., **94**, 4162 (1972).
187. C.Djerassi, L.Seamans, and A.Moscowitz, J.Chem. Soc., Perkin Trans.II, 1706 (1974).
188. R.E.Linder, G.Barth, E.Bunnenberg, C.Djerassi, L.Seamans, and A.Moskowitz, J.Chem.Soc., Perkin Trans.II, 1712 (1974).
189. M.C.Hsu and R.W.Woody, J.Amer.Chem.Soc., **93**, 3515 (1971).
190. L.A.Blyumenfel'd, "Gemoglobin i Obratimoe Prisoedinenie Kisloroda" (Haemoglobin and the Reversible Addition of Oxygen), Izd.Sovetskaya Nauka, Moscow, 1957.
191. G.La Mar, J.Amer.Chem.Soc., **95**, 1662 (1973).
192. J.D.Gaudio and G.La Mar, J.Amer.Chem.Soc., **98**, 3014 (1976).
193. C.J.Weschler, D.L.Anderson, and F.Basolo, Chem. Comm., 757 (1974).
194. Symposium, "Struktura i Svyaz'" (Structure and Bonding), Izd.Mir, Moscow, 1969.
195. I.I.Chernyaev, Izv.Inst.Platiny Akad.Nauk SSSR, No.4, 261 (1926).
196. I.E.Bersuker, "Elektronnoe Stroenie i Svoistva Koordinatsionhykh Soedinenii" (The Electronic Structure and Properties of Coordination Compounds), Izd. Khimiya, Leningrad, 1976.
197. D.W.Stynes and B.R.James, Chem.Comm., 325 (1973).
198. E.F.Caldin and B.Hasinoff, J.Chem.Soc.Faraday Trans., 71 (1975).
199. E.B.Fleischer, S.Jacobs, and L. Mestichelli, J. Amer.Chem.Soc., **90**, 2527 (1968).
200. J.M.Simplicio, K.Schwenzer, and F.Maenpa, J.Amer. Chem.Soc., **97**, 7319 (1975).
201. L.A.Constant and D.G.Davis, J.Electroanal.Chem., **74**, 85 (1976).
202. J.G.Jones and M.V.Twigg, Inorg.Chem., **8**, 2120 (1969).
203. H.P.Bonnet, J.G.Jones, and M.V.Twigg, Inorg. Chim.Acta, **4**, 180 (1970).
204. J.G.Jones and M.V.Twigg, Inorg.Chim.Acta, **10**, 103 (1974).
205. J.G.Jones and M.V.Twigg, Inorg.Chim.Acta, 12, 115 (1975).
206. D.A.Schweigart, J.Chem.Soc., Dalton Trans., 1476 (1976).
207. A.S.Akopov, B.D.Berezin, V.N.Klyuev, and A.A.Solov'ev, Zhur.Neorg.Khim., **18**, 965 (1973) [Russ.J.Inorg.Chem., No.4 (1973)].
208. R.F.Pasternak, M.A.Cobb, and N.Sutin, Inorg. Chem., **14**, 866 (1975).
209. R.F.Pasternak and G.R.Parr, Inorg.Chem., **15**, 3087 (1976).
210. L.J.Boucher, Coord.Chem.Rev., 7, 289 (1972).
211. S.J.Cole, G.C.Curthoys, and E.A.Magnusson, J. Amer.Chem.Soc., **93**, 2153 (1971).
212. A.C.I.Anusiem and R.Lumry, J.Amer.Chem.Soc., **95**, 904 (1973).
213. K.B.Yatsimirskii and V.P.Vasil'ev, "Konstanty Nestoikosti Kompleksnykh Soedinenii" (Instability Constants of Complex Compounds), Izd.Akad.Nauk SSSR, Moscow, 1959.

214. H.E.Bent and C.L.French, J.Amer.Chem.Soc., **63**, 568 (1941).
215. O.I.Koifman, T.A.Koroleva, and B.D.Berezin, Koord.Khim., **3**, 1811 (1977).
216. O.I.Koifman, T.A.Koroleva, and B.D.Berezin, Koord. Khim., **4**, 1339 (1978).
217. C.H.Kirksey and P.Hambright, Inorg.Chem., 958 (1970).
218. S.J.Cole, G.C.Curthous, E.A.Magnusson, and J.N.Phillips, Inorg.Chem., **11**, 1024 (1972).
219. O.I.Koifman and B.D.Berezin, "Problemy Sol'vatatsii i Kompleksoobrazovaniya (Mezhvuzovskii Sbornik)" [Problems of Solvation and Complex Formation (Inter-Collegiate Collected Volume)], Ivanovo, 1978, p.124.
220. C.H.Kirksey, P.Hambright, and C.B.Storm, Inorg. Chem., **8**, 2141 (1969).
221. G.C.Vogel and L.A.Searby, Inorg.Chem., **12**, 936 (1973).
222. F.A.Walker, E.Hui, and J.M.Walker, J.Amer.Chem. Soc., **97**, 2390 (1975).
223. P.Hambright, Chem.Comm., 470 (1967).
224. I.Bernal and P.M.Rieger, Inorg.Chem., **2**, 256 (1963).
225. D.Kivelson and S.K.Lee, J.Chem.Phys., **41**, 1896 (1964).
226. N.J.Rose and R.S.Drago, J.Amer.Chem.Soc., **81**, 6138 (1959).
227. J.G.Erdman, V.G.Ramsey, N.W.Kalenda, and W.R.Hanson, J.Amer.Chem.Soc., **78**, 5844 (1956).
228. E.Higginbotham and P.Hambright, Inorg.Nuclear Chem.Letters, **8**, 747 (1972).
229. J.H.Fendler, F.Nome, and H.C.Van Woert, J.Amer. Chem.Soc., **96**, 6745 (1974).
230. O.I.Koifman, T.A.Koroleva, and B.D.Berezin, Trudy IKhTI, **20**, 78 (1976).
231. S.F.Ginzberg, L.P.Brivina, G.V.Ponomarev, and V.V.Khrapov, Koord.Khim., **3**, 1779 (1977).
232. J.Schak and W.M.Clark, J.Biol.Chem., **171**, 143 (1947).
233. R.W.Cowgill and W.M.Clark, J.Biol.Chem., **198**, 33 (1952).
234. K.M.Kadish and L.A.Bottomley, J.Amer.Chem.Soc., **99**, 2380 (1977).
235. H.Goff and L.O.Morgan, Inorg.Chem., **15**, 2069 (1976).
236. E.Margoliash and A.Schejter, Adv.Protein Chem., **21**, 113 (1966).
237. T.A.Moore and C.Greenwood, Biochem.J., **149**, 169 (1975).
238. D.G.Davis and L.M.Bynum, Bioelectrochem.Bioenergetic, **2**, 184 (1975).
239. G.L.Kedderis, F.X.McConville, and J.M.Duclos, J.Inorg.Nuclear Chem., **38**, 1885 (1976).
240. W.P.Hambright, A.N.Thorpe, and C.C.Alexander, J.Inorg.Nuclear Chem., **30**, 3139 (1968).
241. B.D.McLees and W.S.Caughey, Biochemistry, **7**, 642 (1968).
242. N.Aselford and D.P.Mellor, Austral.J.Sci.Res., **5A**, 784 (1952).
243. J.H.Wang, A.Nakahara, and E.B.Fleischer, J.Amer. Chem.Soc., **80**, 1109 (1958).
244. S.Sullivan, P.Hambright, B.J.Evans, A.Thorpe, and J.Weaver, Arch.Biochem.Biophys., **137**, 51 (1970).
245. R.W.Wade, R.Havlin, and C.E.Castro, J.Amer.Chem. Soc., **91**, 7530 (1969).

Ivanovo Institute of Chemical
Engineering

Translated from *Uspekhi Khimii*, **49**, 2418-2441 (1980) U.D.C. 541.64

Polyimides Based on Heterocyclic Monomers

A.L.Rusanov and I.Batirov

Data concerning polyimide macromolecules, containing various heterocyclic fragments in their main chains, which are obtained using monomers incorporating the required heterocyclic systems as well as groups capable of giving rise to such systems, are discussed.
The bibliography includes 189 references.

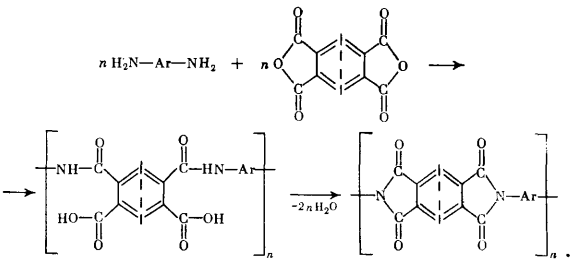
CONTENTS

I. Introduction
II. Polyimides based on monomers containing the required heterocyclic systems 1204
III. Polyimides based on monomers containing groups capable of giving rise to the required heterocyclic systems 1205
1210

I. INTRODUCTION

The vigorous development of new branches of engineering, aviation, cosmonautics, electronics, etc. has imposed increasingly stringent requirements on the polymers employed in these fields. In particular, increasing operating temperatures of polymeric materials are needed—polymeric materials capable of being used at temperatures of 300 °C and above are nowadays of considerable interest. The solution of the problem of synthesising such materials is related directly to the development of new thermostable polymers.

Studies during the last 20 years in the USSR and abroad led to the creation of a series of polymers with high thermal and deformation-strengths[1-9]. In the various examples of new thermostable polymers polyheteroarylenes—polymers containing aromatic heterocycles in the main chains of the macromolecules—are most widely used[1-15]. Despite the great structural variety of the polyheteroarylenes synthesised, only a few of them have emerged from the area of academic research and have acquired industrial importance. Such polyheteroarylenes include in the first place aromatic polyimides—the product of the interaction of aromatic diamines with aromatic tetracarboxylic acid dianhydrides[16,17]:



Polyimides are usually synthesised by a two-stage process involving the interaction of the initial compounds in polar organic solvents, the conversion of the resulting pre-polymers [polyamidoacids (PAA), also referred to as poly(*o*-carboxy)amides] into articles, and thermal cyclisation of the PAA resulting in the formation of articles made of insoluble and infusible polyimides which do not require additional treatment. This method of synthesis of polyimides, which permits the formation of articles from polymers of different structure, has become very common and is nowadays used widely to make polyimide films, fibres, binders, adhesives, varnish coatings, plastics, etc.[16,17].

The majority of the polyimides known at present have been obtained from carbocyclic aromatic monomers, but in recent years polyimides based on heterocyclic monomers have attracted the attention of investigators to an increasing extent.

The great variety of the known heterocycles led to the possibility of formulating completely different projects designed to modify the properties of polyimides:

1. The introduction of highly condensed heterocyclic fragments permitted an increase in the thermal stability and heat resistance of the polyimides.

2. Heterocycles containing bulky side groups have been introduced in order to make polyimides soluble in organic solvents[18-21].

3. The high resistance of the majority of aromatic heterocycles to hydrolysis and the action of nucleophiles compared with imide rings has made it possible to use heterocyclic monomers with a comparatively high molecular weight, which reduced the content of imide rings per unit molecular weight of the polymer, increasing the hydrolytic stability of the polyimides.

Naturally, not every task enumerated above was solved to an equal extent, because all the approaches indicated are formal; nevertheless, definite successes have been achieved in the solution of these problems.

Heterocycles can be introduced into polyimides by employing monomers containing the required heterocycles and also monomers containing groups capable of giving rise to the required heterocyclic systems. Each of these methods has a number of advantages and disadvantages and merits separate consideration.

II. POLYIMIDES BASED ON MONOMERS CONTAINING THE REQUIRED HETEROCYCLIC SYSTEMS

The synthesis of polyimides using monomers containing particular aromatic heterocycles has a significant advantage over the synthesis based on monomers containing groups capable of giving rise to the corresponding heterocyclic systems, which arises because imidisation processes, i.e. cyclisation processes with formation of an imide ring, proceed under milder conditions than the processes leading to the formation of other heterocyclic systems. As a result, this procedure can yield polymers with a higher degree of cyclisation[22,23], i.e. with a less heterounit structure[24-28], which makes it possible to achieve more fully the properties designed into polymers of this type.

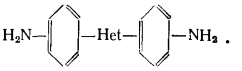
The heterocyclic monomers employed in most studies are isotypical products obtained as a result of complex reactions. This is true also of heterocyclic diamines, particularly of diamines containing azole and benzazole rings, which are synthesised by reactions widely used in the chemistry of polyazoles and polybenzazoles[29-34].

The simplest diamines containing azole rings are of the type

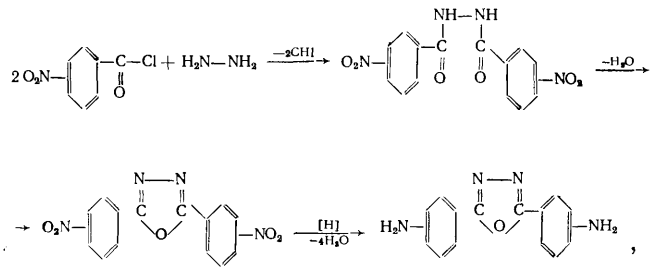
$$H_2N—Het—NH_2 ,$$

some of which (Het = 1,3,4-oxazole, 1,2,4-triazole, 1,3,4-thiadiazole, etc.) have attracted the attention of investigators[35,36] because of the possibility of synthesising from them (by reaction with the dianhydride of pyrazine-2,3,5,6-tetracarboxylic acid) polyimides without hydrogen atoms and possessing as a result an increased thermal stability[37-39]. However, according to some workers[35,36], the low basicity of diamines of this type and the tendency of pyrazine-2,3,5,6-tetracarboxylic acid to decarboxylate precluded the realisation of this possibility. The polyimides obtained had low molecular weights and contained a considerable number of amide fragments formed as a result of the decarboxylation of the PAA; it is noteworthy that these data[35,36] conflict with others[37-39].

More unambiguous results were obtained using azole-containing diamines of the type

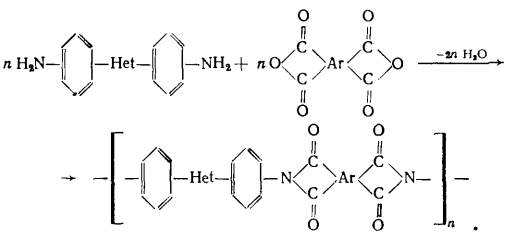


In the series of compounds of this kind the isomeric 2,5-(diaminophenyl)-1,3,4-oxadiazoles[40-47] and 3,5-(diaminophenyl)-4-phenyl-1,3,4-triazoles[41-45,47] are the most common. The former, obtained in accordance with the scheme



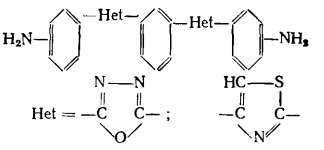
have been most widely used because of their availability.

Poly(*o*-carboxy)amides, the thermal cyclodehydration of which led to polyimides containing 1,3,4-oxadiazole rings, have been synthesised by the reaction of the above diamines with the dianhydrides of aromatic tetracarboxylic acids[41-49]:



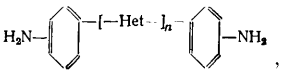
The authors of the above studies do not present data on the basicity of the diamines employed, but the viscosities of the fore-polymers ($\eta_{log} = 1.0-2.0$) indicate a high reactivity of the compounds used. The high molecular weights of the resulting PAA made it possible to obtain from them strong films and fibres, the thermal imidisation of which led to products insoluble in organic solvents and having melting points (485–520 °C) close to the temperatures of the onset of the degradation of these polymers (500–520°).

Polymers of analogous structure, characterised by the same set of properties, have been obtained by a number of other workers[50-52]. The same group of investigators achieved the synthesis of aromatic diamines containing 1,3,4-oxadiazole[51] and thiazole rings[4,45,47] and having the general formula

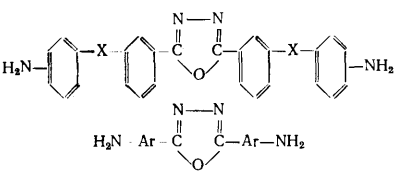


as well as polyimides based on them. Since such diamines are less readily available than di(aminophenyl)-1,3,4-oxadiazoles and the polymers based on them do not have appreciable advantages over the polyimides based on 2,5-(diaminophenyl)-1,3,4-oxadiazoles, these studies were not developed further.

Various modifications of the structure of diamines containing 1,3,4-oxadiazole rings have been carried out in studies[50-52] in which diamines of the following type were synthesised:



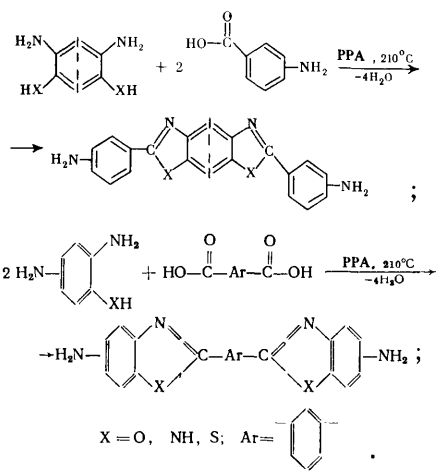
where $n = 2$ or 3 and Het = 1,3,4-oxadiazole or another heterocycle and



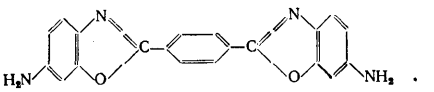
where Ar = naphthyl or a substituted phenyl group and X = O, S, or CH_2. Polyimides based on these diamines were also obtained.

A number of diamines containing benzazole rings were synthesised together with the azole-containing diamines with a symmetrical structure enumerated above. Among these compounds, symmetrical diamines formed in accordance with one

of the following schemes[40,53-59] in polyphosphoric acid (PPA) have come to be most widely used:

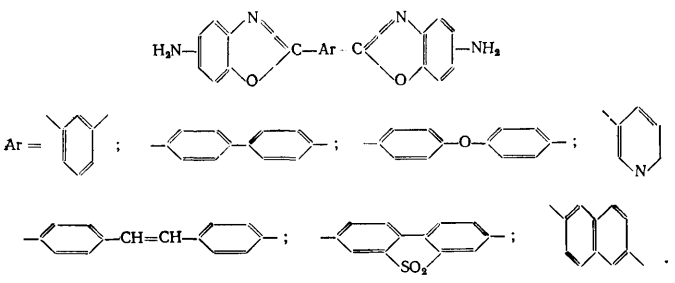


These reactions are employed successfully for the synthesis of diamines containing all three types of the most common benzazole rings—benzoxazole, benzimidazole, and benzothiazole, but, in the series of monomers synthesised, only 2,2-phenylenebis(5-aminobenzoxazole) is promising according to a number of investigators[60]:



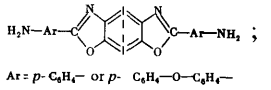
The interaction of this diamine with tetracarboxylic acid dianhydrides under the conditions of a two-phase process yielded high-molecular-weight (the viscosity of the solution of the fore-polymers was $\eta_{log} = 1.24-1.50$) polybenzoxoxazole imides, which can be made into strong elastic films and fibres, best results being obtained when the dianhydride of benzophenone-3,3',4,4'-tetracarboxylic acid is used[22,46,61]. The polymers obtained had high melting points (560–570 °C) and high temperatures for the onset of degradation in the range 560–595 °C (DTGA†, N_2, $\Delta T = 15$ K min^{-1}).

Polymers having comparable thermal characteristics have been obtained on the basis of a series of other benzoxazole-containing diamines having the general formula



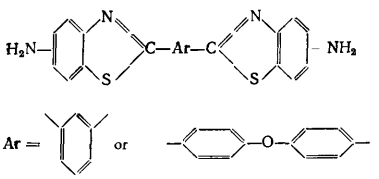
† DTGA = differential thermogravimetric analysis (Ed. of Translation).

Symmetrical benzoxazole-containing diamines derived from bis(*o*-aminophenols) and having the general formula



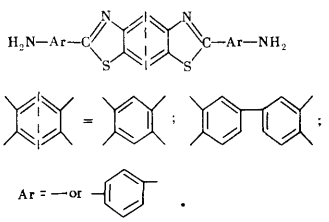
have been used successfully by a number of investigators[22,62-68] to obtain polyimides differing slightly in their characteristics from the polymers discussed above.

Compounds containing benzothiazole rings are much less readily available than the benzoxazole-containing diamines. Compounds of this type, having the general formula

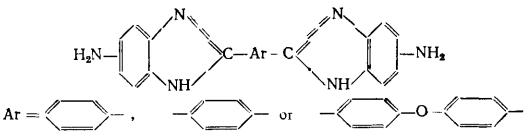


were used by Preston and coworkers[22,46,60] to obtain polyimides on the basis of pyromellitic and benzophenone-3,3',4,4'-tetracarboxylic acids. According to Korshak and Maksimov[69], an appreciable increase in the thermal stability of the systems under consideration might have been expected following the introduction of the benzothiazole ring into the main chains of the macromolecules, but the benzothiazole-containing polyimides did not in fact differ from their benzoxazole-containing analogues[22] and benzothiazole-containing diamines having the above structure have not therefore been widely used in the synthesis of polyimides.

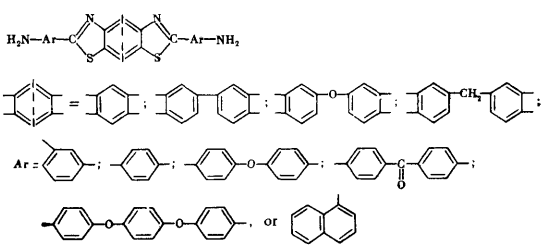
All the above considerations are valid also for benzothiazole-containing diamines having the general formula[22,61,70]



In the series of benzazole-containing aromatic diamines compounds containing benzimidazole rings have attracted most attention. Diamines having the general formula



have been comparatively little used[50], while products based on bis(*o*-phenylenediamines) and having the general formula

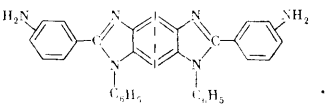


have been used to synthesise polyimides by a number of Soviet and foreign investigators[44,45,47,49,55,57-59,68,71-74].

Detailed studies of polyimides based on benzimidazole-containing diamines[55] showed that, under the classical conditions of the two-stage synthesis of aromatic polyamides, i.e. when a solid dianhydride is added to a solution of the diamine, high-molecular-weight film-forming PAA are formed ($\eta_{log} = 0.48-3.3$). Thermal imidisation of the resulting films at 280–320 °C yielded polyimide films with comparatively high tensile strengths (1225–1900 kgf cm^{-2}), but giving rise to small elongations on rupture (1.5–3.8%).

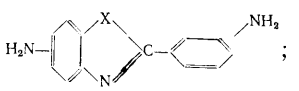
The study of the thermal stability of the polyimides by the DTGA method (air, $\Delta T = 5$ K min^{-1}) showed that weight losses corresponding to 15% are observed in the temperature range 620–630 °C; however, one should note that such high values of the thermal characteristics of benzimidazole-containing polyimides conflict with the results of Preston and Black[45].

Korshak et al.[75] synthesised a series of symmetrical diamines containing *N*-phenylbenzimidazole rings:



The interaction of these diamines with the dianhydrides of aromatic tetracarboxylic acids under the conditions of one- and two-stage polycyclocondensation yielded polyimides containing *N*-phenylbenzimidazole rings[76–79]. In contrast to the polyimides examined above, which are obtained from diamines containing unsubstituted benzimidazole rings, these polymers are in most cases soluble in organic solvents, which makes it possible to make them into articles in the final stage. The polymers obtained in a number of investigations[76–79] exhibited high viscosities ($\eta_{int} = 0.2-2.00$), which makes it possible to convert them into films with interesting electrophysical properties[76]. The polyimides synthesised under the conditions of DTGA ($\Delta T = 5$ K min^{-1}, air) lost 10% of their weight at 520–550 °C and had softening temperatures between 300° and 540 °C depending on their structure.

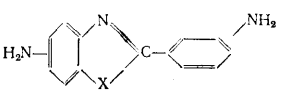
Together with symmetrical benzazole-containing diamines, asymmetric diamines containing benzoxazole, benzimidazole, and benzothiazole rings have attracted much attention[51,80,81]:



X = O; S; NH .

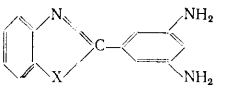
The interaction of asymmetric diamines with the dianhydrides of tetracarboxylic acids under the conditions of a two-stage process gave rise to benzazole-containing polyimides[51,74,80,82–86].

In contrast to the symmetrical diamines examined above, compounds having the general formula



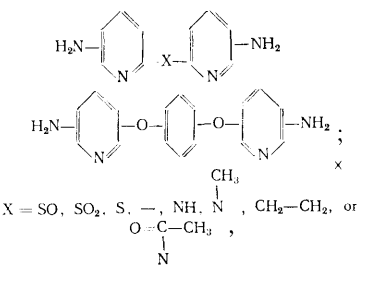
contain amino-groups with non-equivalent nucleophilic properties, which makes it possible to obtain from them polymers with a limited degree of order[82]; the few data available in the literature[87] indicate a comparatively low basicity of such compounds, which is nevertheless sufficient to obtain from them PAA with fairly high viscosity characteristics ($\eta_{log} = 0.6-2.5$). Despite their lack of order, the final structures—polyimides containing benzazole rings—hardly differ from polyimides obtained from symmetrical benzazole-containing diamines: their melting points are in the range 540–575 °C and the temperatures of the onset of their decomposition are in the range 525–575 °C (DTGA, N_2, $\Delta T = 15$ K min^{-1}).

Polyimides based on the benzazole-containing symmetrical and asymmetric diamines listed above contain benzazole heterocycles in the main macromolecular chains, which gives rise to the insolubility of the majority of these polyimides in organic solvents. When the benzazole ring is introduced as a side group into the macromolecular chains of polyimides, which is achieved by employing diamines with a specific structure[51,88]



conditions are created for imparting solubility in organic solvents to polyimides, although information concerning the realisation of this possibility is not available in the literature.

Somewhat less systematic studies have been made on polyimides based on diamines containing six-membered aromatic heterocycles. The simplest diamine of this kind—2,6-diaminopyridine—attracted the attention of a number of research groups[35,36,89–91], but the weak nucleophilic properties of the second amino-group ($pK_{a2} = 1.67$) in this compound constituted a serious obstacle to the synthesis of high-molecular-weight polymers from it. Monomers of the bipyridyl series having the structural formulae

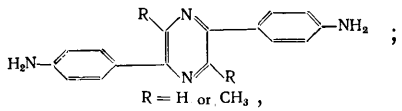


X = SO, SO_2, S, —, NH, N, CH_2—CH_2, or O=C—CH_3 ,
N

which are less readily available but are more nucleophilic compared with 2,6-diaminopyridine, have been used to synthesise polyimides[92,93]. Because of the relatively high nucleophilicities of diamines of this kind, they can interact with the dianhydrides of pyromellitic and benzophenone-3,3′,4,4′-tetracarboxylic acids under the conditions of low-temperature polycondensation in dimethyl sulphoxide (DMSO) to yield high-molecular-weight (η_{log} up to 2.26) film-forming PAA, whose cyclisation *in vacuo* at 190–200 °C for 2–2.5 h yielded polyimides.

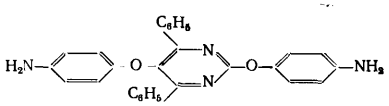
It is of interest to note that, according to the data of Kurita and Williams[92], the introduction of heteroatoms into aromatic rings increases significantly the solubility of polyimides in organic solvents. Polyimides obtained from bipyridyl-containing diamines, incorporating as groups X sulphide, sulphoxide, or sulphone fragments, are readily soluble in dimethylacetamide (DMAA) and *m*-cresol. On the other hand, the thermal stability of polyimides of this kind is appreciably lower than that of their carbocyclic analogues. It may be that these properties of bipyridyl-containing polyimides are due to the unduly mild imidisation conditions, which do not lead to a high degree of completion of this process.

A series of pyrazine-containing diamines having the general formula



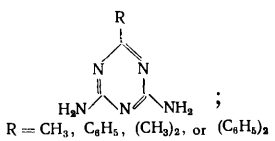
as well as isomeric compounds have been used[94] to obtain polyimides under the conditions of two-stage polycyclocondensation. PAA with logarithmic viscosities in the range 0.22–1.86 have been obtained in DMAA at 20 °C, those with highest molecular weights exhibiting film-forming properties. The thermal imidisation of these products at 250–270 °C led to the formation of polyimides soluble only in sulphuric and methanesulphonic acids and suffering a 5% weight loss (DTGA, N_2, $\Delta T = 5$ K min^{-1}) at 485–595 °C.

Polyimides soluble in amide solvents have been obtained[95] by the interaction of 2,5-bis(4-amino phenoxy)-4,6-diphenylpyrimidine



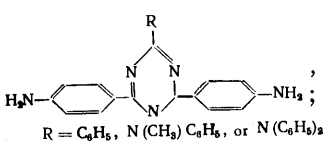
with a series of dianhydrides of aromatic tetracarboxylic acids. The polyimides synthesised exhibit an anomalous thermal stability—their decomposition temperatures do not exceed 310 °C.

Polyimides based on diamines containing symmetrical triazine rings have attracted much attention. The simplest compounds of this series—products having the general formula



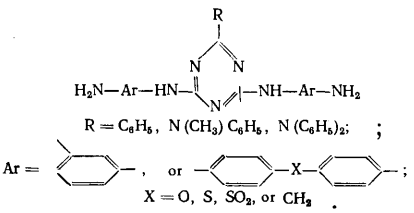
have a weakly nucleophilic second amino-group according to some data[35,36] ($pK_{a2} = 1.90$), which prevents the formation of polyamides with high molecular weights on the basis of these compounds[35,36,96,97]. Nevertheless, polyimides have been successfully synthesised as a result of the two-stage interaction of the above compounds with the dianhydrides of pyromellitic and benzophenone-3,3′,4,4′-tetracarboxylic acids, yielding polyimides which began to lose structure, according to DTGA data[96], at 390–420 °C in air and at 440–460 °C in N_2.

Triazine-containing diamines having the general formula



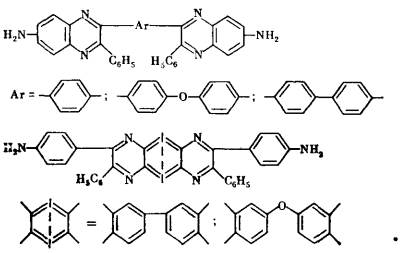
have been used[98,99] to obtain high-molecular-weight film-forming polyimides with high thermal stability and fire resistance.

Analogous results have been achieved by a number of investigators[100–103], who synthesised polyimides from diamines having the general formulae



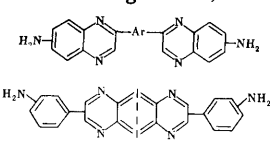
The presence of bulky side groups in the triazine-containing diamines discussed above makes it possible, in principle, to render the final polyimide soluble in organic solvents; however, only some of the investigators concerned have reported the realisation of this possibility[96,100,101].

A much more unambiguous influence of the introduction of a bulky substituent into the diamine molecule on the solubility of polyimides has been traced in the studies by Korshak and coworkers[104–107], who synthesised polyimides from diamines containing quinoxaline rings[107–109]:

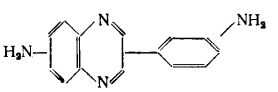


The large set of diamines makes it possible to vary the properties of the final polyamides[105], which combine a high thermal stability with solubility in *m*-cresol, *N*-methyl-2-pyrrolidinone, and the 3 : 1 tetrachloroethane–phenol mixture.

The decisive influence of the phenyl substituent on the solubility of polyimides has been confirmed by the finding that polyimides based on symmetrical diamines containing unsubstituted quinoxaline rings[110,111],

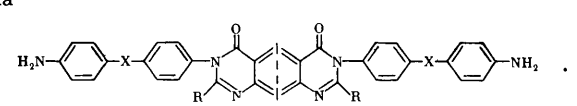


as well as asymmetric diamines having the general formula[77, 110–112]



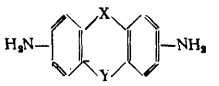
are insoluble in organic solvents.

Results confirming the increased solubility of the final polyimides under the influence of side groups in the diamines have been obtained also using as the starting compounds quinazolinone-containing diamines[113–115] having the general formula



The polyimides obtained from such diamines dissolved in *m*-cresol and exhibited thermal characteristics comparable to those of the usual polyamides.

In the series of diamines containing highly condensed heterocycles (tricyclic and tetracyclic systems) compounds having the general formula



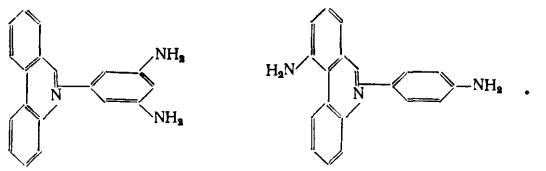
X = O, Y = S, SO_2, or CO; X = SO_2, Y = O, S, SO_2, or CH_2

have attracted most attention. The interaction of diaminophenoxathiine with the dianhydrides of aromatic tetracarboxylic acids yielded polyimides[116-118] with a higher thermal stability than that of polyimides based on di(4-aminophenyl) ether[118].

Polypyromellitimides[119], obtained using 2,7-diaminoxanthone as the initial compound, undergo an appreciable weight loss (under the conditions of DTGA) only at 500 °C.

High-molecular-weight film-forming polyimides have been synthesised by the two-stage interaction of diaminocyclosulphones with the dianhydrides of aromatic tetracarboxylic acids[120].

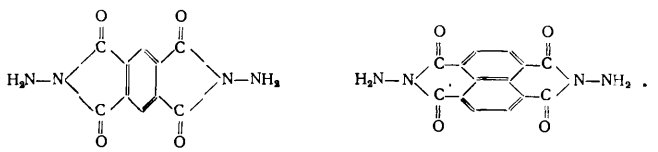
Polyimides based on aromatic diamines containing phenanthridine rings also exhibit high thermal characteristics[121-134]:



It is of interest to note that polyimides obtained from phenanthridine-containing diamines did not dissolve in organic solvents regardless of the location of the heterocycle (in the main chain or as a side group) and of the method of imidisation.

The attempts to employ 3,9-acridine as the monomer[91] did not lead to high-molecular-weight polymers as a consequence of the weak nucleophilic properties of this monomer.

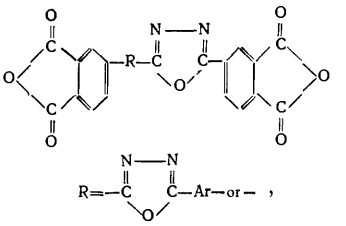
In the series of heterocyclic diamines monomers containing imide rings were of special interest, since one may hope to obtain, by an appropriate selection of those compounds, macromolecules consisting of imide rings only. An attempt to create such structures was undertaken by Dine-Hart[125], who used *N,N'*-diamino(pyromellitimide) and *N,N'*-diamino-(tetracarboxynaphthalene diimide):



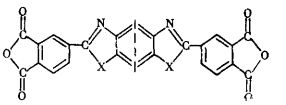
The attempt to synthesise high-molecular-weight polyimides was unsuccessful. Even the feasibility of the above solution of the problem of synthesising high-molecular-weight polymers of this type, capable of being worked, is controversial in view of the weakness of the N–N bonds in the main macromolecular chains.

The structural set of dianhydrides of heterocyclic aromatic tetracarboxylic acids, used to synthesise polyimides, is much smaller than the set of heterocyclic diamines discussed above. In the series of dianhydrides of the tetracarboxylic acids derived from the simplest aromatic heterocycles the dianhydrides of furan-2,3,4,5-tetracarboxylic[126] and thiophen-2,3,4,5-tetracarboxylic acids[100,126,132] attracted attention, but the properties of polyimides based on these monomers have not been studied in detail.

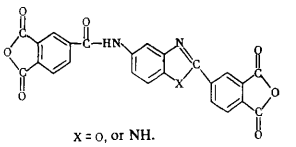
In the series of azole-containing dianhydrides of tetracarboxylic acids only 1,3,4-oxadiazole-containing compounds having the formula[44,133-135]



and in the series of benzazole-containing dianhydrides compounds having the general formulae[136-139]



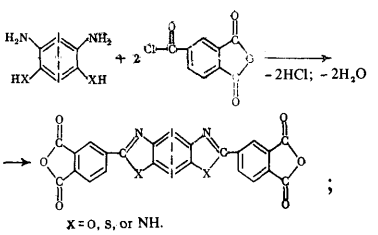
X = O, S, or NH;



X = O, or NH.

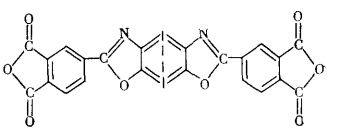
have been widely used.

In most cases, the dianhydrides of tetracarboxylic acids containing azole and benzazole heterocycles can be obtained by the interaction of tetra- or tri-functional nucleophiles with the 4-chloroformyl derivatives of phthalic anhydride[140]:



X = O, S, or NH.

Dianhydrides containing benzoxazole rings[140], particularly compounds having the formula



have been most widely used. Their interactions with di(4-aminophenyl) ether under the conditions of low-temperature polycondensation yielded PAA with $\eta_{log} \geq 0.4$; poly(benzoxazole-imides), obtained by the heat treatment of PAA at 200–380 °C *in vacuo* for 1 h, exhibited high thermal characteristics.

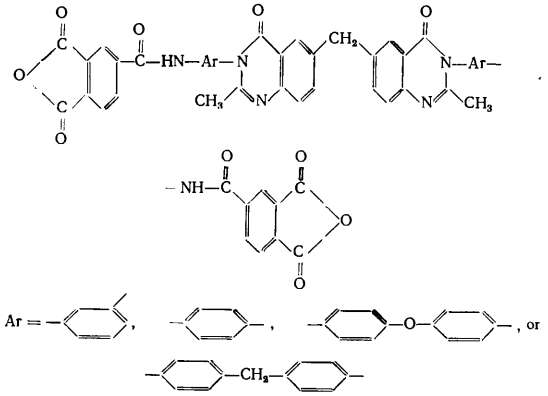
Poly(benzoxazole-imide) films are very strong and last for a long time at 300 °C. The study of the resistance of poly(benzoxazole-imides) to alkalis showed that, on being boiled for 30 min in 10% aqueous solutions of sodium hydroxide, the films hardly changed, their chemical stability being much superior to that of the usual polyimide films.

In the series of dianhydrides of aromatic heterocyclic tetracarboxylic acids containing six-membered heterocycles detailed studies have been made of the dianhydrides of pyridine-2,3,5,6-tetracarboxylic[126,141] and pyrazine-2,3,5,6-tetracarboxylic acids[35-39,90,100,126,127-131,142-146]. The second

dianhydride attracted the attention of numerous investigators in view of the possibility, in principle, of using it to synthesise hydrogen-free polyimides, although, as stated previously, the problem of applying this idea in practice remains open.

The dianhydrides of tetracarboxylic acids containing substituted symmetrical triazine rings[99,147,148] have been used, by analogy with diamines containing identical fragments, to synthesise polyimides soluble in organic solvents[99,147,148].

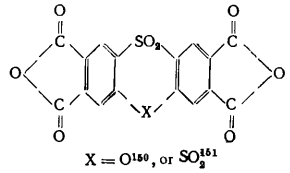
The interaction of the dianhydrides of tetracarboxylic acids containing substituted quinazolinone rings and amide groups and having the general formula



with various aromatic diamines yielded polyimides incorporating amide and quinazolinone groups[149]; these polyimides are soluble in *m*-cresol, but their thermal stability is somewhat lower than that of polyimides obtained from quinazolinone-containing diamines[113-115].

A number of investigators[150,151] attempted to synthesise polyimides from the dianhydrides of tetracarboxylic acids containing highly condensed (tricyclic and polycyclic) heterocycles. The aim in introducing such fragments was usually to increase the thermal stability and heat resistance of the polyimides, which, however, is not achieved in all cases.

When initial compounds having the general formula



were used under the conditions of two-stage processes, polyimides giving rise to strong elastic films and stable up to 440 °C were obtained according to patent data[151].

The syntheses of polymers based on monomers containing heterocyclic units discussed above have not only significant advantages (see above) but also suffer from considerable disadvantages. The latter include the following.

(1) An increased rigidity of the PAA containing certain (particularly highly condensed) heterocycles, which precludes a high solubility of these fore-polymers and a high capacity for being worked into articles.

(2) The reduced reactivity of certain monomers containing aromatic heterocyclic units, which precludes the synthesis of high-molecular-weight polymeric products from these compounds.

In view of the above disadvantages of the method, investigators became interested in monomers, containing groups leading to the final heterocyclic systems, as the initial compounds for the synthesis of polyimides.

III. POLYIMIDES BASED ON MONOMERS CONTAINING GROUPS CAPABLE OF GIVING RISE TO THE REQUIRED HETEROCYCLIC SYSTEMS

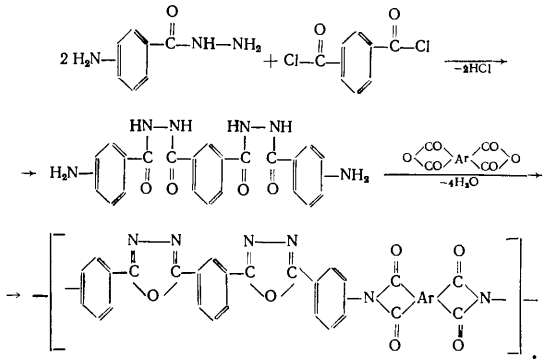
The simplest diamines of this type, containing groups capable of forming the 1,3,4-oxadiazole rings[51] (hydrazide fragments), have been obtained by the interaction of isomeric nitrobenzoic acid chlorides and hydrazides with subsequent mild reduction of the di(nitroaryl)hydrazides.

When the hydrazides of nitrobenzoic acids and the dichlorides of aromatic dicarboxylic acids were used as the comonomers (with subsequent reduction of the nitro-groups), diamines containing two hydrazide groups were obtained[51,152]. The reaction of these compounds with the dianhydrides of pyromellitic and benzophenone-3,3',4,4'-tetracarboxylic acids in DMAA led to the synthesis of PAA containing hydrazide groups, the heat treatment of which led to ordered copolyimido-1,3,4-oxadiazoles[51,152].

Solutions of PAA containing hydrazide fragments had fairly high viscosities ($\eta_{log} = 0.53-0.92$ dl g^{-1}), which made it possible to obtain strong and elastic films from them. Heating the polymers to 150 °C led to their imidisation and the formation of polyimidohydrazides, while heating to higher temperatures (up to 325 °C) resulted in the cyclisation of the hydrazide fragments to the 1,3,4-oxadiazole groups.

A study of the thermal stability of simple copoly(oxadiazole-imides) containing two imide groups per oxadiazole group showed that it is comparable to that of the best polyimide structures, while polymers with the same numbers of imide and oxadiazole rings proved to be less thermally stable[51].

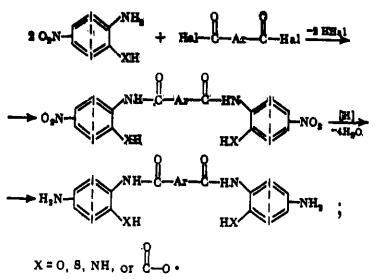
Preston chose a somewhat different approach to the synthesis of diamines containing hydrazide fragments[153,154] using the difference between the nucleophilic reactivities of the amino- and hydrazide groups of *p*-aminobenzohydrazide. The diamines obtained in this way, containing two hydrazide fragments, can be made to react directly with the dianhydride of a tetracarboxylic acid:



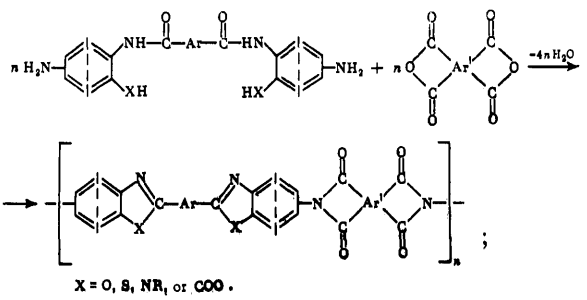
The structure of the resulting diamines is in this case less unambiguous than in the case where nitro-derivatives are used—apparently the interaction of the acid chloride groups can involve partially also the amino-group of the aminobenzohydrazide with formation of amide and amidoimide fragments in the final copolyimido-1,3,4-oxadiazoles, which have an unfavourable effect on various properties of these systems.

A general approach to the synthesis of symmetrical diamines incorporating groups capable of giving rise to benzazole and benzoxazinone rings has been proposed by Kurihara et al.,[155] who achieved the interaction of nitroamines containing various substituents with the dihalides of dicarboxylic acids and the

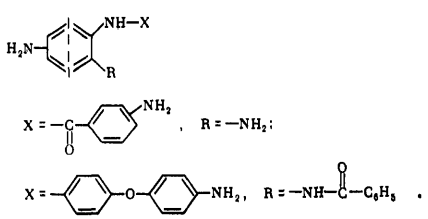
reduction of the resulting dinitro-compounds to the corresponding diamines:



The interaction of the resulting diamines with the dianhydrides of tetracarboxylic acids and subsequent heat treatment of the resulting pre-polymers led to the synthesis of polyimides containing benzoxazole, benzothiazole, benzimidazole, and benzoxazinone rings in the main chains of the macromolecules:



Asymmetric diamines containing groups capable of giving rise to benzimidazole and *N*-phenylbenzimidazole rings have been used[156-158] to synthesise film- and fibre-forming polyimides containing imidazole and *N*-phenylbenzimidazole rings:



A much larger number of studies were designed to synthesise polyimides from the dianhydrides of tetracarboxylic acids containing groups capable of giving rise to various, primarily azole and benzazole, heterocycles. The extensive development of such investigations was due mainly to the fact that the initial compounds can be obtained by a standard procedure involving the interaction of various tetrafunctional compounds, which have found applications in the chemistry of polyazoles[29-32], with the 4-chloroformyl derivatives of phthalic anhydride, which is a derivative of the readily available trimellitic acid[140].

Dianhydrides containing acylamidoxime fragments, capable of giving rise to 1,2,4-oxadiazole rings, have been obtained by the reaction of the bisamidoximes of dicarboxylic acids with the 4-chloroformyl derivatives of phthalic anhydride. The reaction of these compounds with aromatic diamines under the conditions of two-stage polycyclocondensation led to polyimides with 1,2,4-oxadiazole rings[135,160].

Polyimides containing isomeric 1,3,4-oxadiazole rings, whose thermal stability is higher than that of the compounds with 1,2,4-oxadiazole rings, have been obtained by the reaction of dicarboxylic acid dihydrazides with the 4-chloroformyl derivative of phthalic anhydride; the reaction of the dianhydrides containing hydrazide groups, obtained in this way, with diamines and the thermal cyclisation of the resulting copolyhydrazidoamidoacids[161] led to the synthesis of copolyimido-1,3,4-oxadiazoles.

A large series of studies were devoted to the synthesis of dianhydrides containing groups capable of giving rise to benzazole and benzoxazinone rings[162-166]. The interaction of these dianhydrides with aromatic diamines yielded high-molecular-weight (η_{log} up to 1.9) PAA containing groups capable of giving rise to benzazole and benzoxazinone rings; subsequent heat treatment at 250–400 °C converts these PAA into polyimides containing benzoxazole[137,162-175], benzothiazole[162-166,174], benzoxazinone[162-166,175], as well as unsubstituted[162-166,176,177] and *N*-substituted[178] benzimidazole rings.

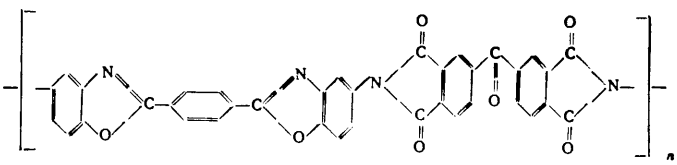
The synthesis of poly(benzoxazoleimides) proceeds most smoothly owing to the ease of the selective acylation of bis(*o*-aminophenols) by the 4-chloroformyl derivative of phthalic anhydride, while the acylation of bis(*o*-phenylenediamines) and bis(*o*-aminothiophenols) by this compound is accompanied by side reactions and ultimately by gel formation. The more nearly ideal structure of poly(benzoxazoleimides) is responsible for their higher thermal characteristics compared with the remaining systems.

A number of studies were undertaken to synthesise copolymers from mixtures of traditional dianhydrides of aromatic tetracarboxylic acids with dianhydrides containing groups capable of giving rise to benzimidazole[179], benzothiazole[180], and benzoxazinone[181] rings.

The fact that almost all reactions using dianhydrides containing groups capable of forming azole, benzazole, and benzoxizinone rings have been carried out without isolating the dianhydrides from the reaction mixture merits attention; this approach is undoubtedly of considerable interest, since it makes it possible to eliminate the laborious and expensive processes involving the isolation and purification of the monomers and hence simplifies the technological synthesis of polymers and also reduces the cost of the latter. Evidently, this approach deserves the widest possible development, particularly in those cases where the syntheses of monomers proceed with a high selectivity and lead to homogeneous initial compounds and not mixtures of products containing various functional groups.

A critical examination of the foregoing data shows that the vast majority of studies on polyimides, obtained from heterocyclic monomers or monomers containing groups capable of giving rise to the required heterocycles, have been purely of their synthesis. Despite the large amount of evidence (particularly in patents) concerning the possibility of obtaining on the basis of polymers of this kind a wide range of materials for all purposes, specific data on the properties of the resulting articles are very few. The properties of materials obtained from polyimides containing azole and benzazole rings, introduced into these polymers as part of the initial diamines, have been examined in greatest detail. In particular, reinforced plastics, obtained using polyimides based on diamines containing 1,3,4-oxadiazole and benzimidazole rings, have been investigated in detail[182,183]. The properties of articles made from polyimides based on diamines and benzoxazole rings have been studied in even greater detail. In particular, fibres whose resistance to thermo-oxidative degradation is superior to that of the poly(*p,p'*-oxydiphenylenepyromellitimide) fibre[186] and the polypyromellitimide fibre based on 2,5-di(*p*-aminophenyl)-1,3,4-oxadiazole

have been obtained[184-189] from the polyimide



synthesised by the reaction of a benzoxazole-containing diamine with the dianhydride of benzophenone-3,3',4,4'-tetracarboxylic acid[187]; the copoly(benzoxazole-imide) fibres have a unique ability to retain acceptable strength characteristics up to temperatures of 500 °C.

REFERENCES

1. V.V.Korshak, "Termostoikie Polimery" (Thermostable Polymers), Izd.Nauka, Moscow, 1969.
2. V.V.Korshak, "Khimicheskoe Stroenie i Temperaturnye Kharakteristiki Polimerov" (The Chemical Structure and Thermal Characteristics of Polymers), Izd.Nauka, Moscow, 1970.
3. A.H.Frazer, "High Temperature Resistant Fibres" (Translated into Russian), Izd.Khimiya, Moscow, 1971.
4. H.L.Lee, D.G.Stoffey, and K.Neville, "New Linear Polymers" (Translated into Russian), Izd.Khimiya, Moscow, 1972.
5. I.E.Kardash and E.N.Teleshov, "Itogi Nauki. Khimiya i Tekhnologiya Vysokomolekulyarnykh Soedinenii" (Advances in Science. The Chemistry and Technology of High-Molecular-Weight Compounds), Izd.VINITI, Moscow, 1971, Vol.3, p.3.
6. C.L.Segal (Editor), "High-Temperature Polymers", Marcel Dekker, New York, 1967.
7. G.F.Pezdirtz and N.J.Johnston, in "Chemistry in Space Research" (Edited by R.Landel and A.Rembaum), Elsevier, New York, 1973.
8. R.J.Cotter and M.Matzner, "Ring-Forming Polymerization", Acad.Press, New York–London, 1972, part B1.
9. R.J.Cotter and M.Matzner, "Ring-Forming Polymerization", Acad.Press, New York–London, 1972, part B2.
10. A.D.Delman, J.Macromol.Sci.-Rev., **C2**(1), 153 (1968).
11. W.W.Wright and W.A.Lee, Progress in High Polymers, **2**, 189 (1968).
12. I.I.Jones, J.Macromol.Sci.-Rev., **C2**(2), 303 (1968).
13. I.I.Jones, Chem.Brit., **6**, 251 (1970).
14. C.S.Marvel, J.Macromol.Sci.-Rev., **C13**(2), 219 (1975).
15. E.S.Krongauz, Uspekhi Khim., **42**, 1854 (1973) [Russ.Chem.Rev., No.10 (1973)].
16. N.A.Adrova, M.I.Bessonov, L.A.Laius, and A.P.Rudakov, "Poliimidy–Novyi Klass Termostoikikh Polimerov" (Polyimides—A New Class of Thermostable Polymers), Izd.Nauka, Leningrad, 1968.
17. C.E.Sroog, J.Polymer Sci., Macromol.Rev., **11**, 161 (1976).
18. V.V.Korshak and A.L.Rusanov, Plast.Massy, No.3, 9 (1978).
19. V.V.Korshak and Ya.S.Vygodskii, Uspekhi Khim., **42**, 1225 (1973) [Russ.Chem.Rev., No.7 (1973)].
20. V.V.Korshak, S.V.Vinogradova, and Ya.S.Vygodskii, J.Macromol.Sci.Rev., **C11** (1), 45 (1974).
21. Ya.S.Vygodskii and S.V.Vinogradova, "Itogi Nauki i Tekhniki. Khimiya i Tekhnologiya Vysokomolekulyarnykh Soedinenii" (Advances in Science and Engineering. The Chemistry and Technology of High-Molecular-Weight Compounds), Izd.VINITI, Moscow, 1975, Vol.7, p.14.
22. J.Preston, W.F.DeWinter, and W.B.Black, J.Polymer Sci., **A-1**, **7**, 283 (1969).
23. V.V.Korshak, G.M.Tseitlin, Ziyad Tarik Al-Haidar, and A.I.Pavlov, Vysokomol.Soed., **A13**, 971 (1971).
24. V.V.Korshak, Uspekhi Khim., **42**, 695 (1973) [Russ. Chem.Rev., No.4 (1973)].
25. V.V.Korshak, Vysokomol.Soed., **A15**, 298 (1973).
26. V.V.Korshak, Acta Chem.Sci.Hungar., **81**, 345 (1974).
27. V.V.Korshak, Vysokomol.Soed., **A19**, 1179 (1977).
28. V.V.Korshak, "Raznozvennost' Polimerov" (The Heterounit Structure of Polymers), Izd. Nauka, Moscow, 1977.
29. A.A.Izyneev, M.M.Teplyakov, V.G.Samsonova, and A.D.Maksimov, Uspekhi Khim., **36**, 2090 (1967) [Russ.Chem.Rev., No.12 (1967)].
30. V.V.Korshak and M.M.Teplyakov, Symposium, "Progress Polimernoi Khimii" (Progress in Polymer Chemistry), Izd.Nauka, Moscow, 1969, p.198.
31. V.V.Korshak and M.M.Teplyakov, St.cerc.chim., **18**, 221 (1970).
32. V.V.Korshak and M.M.Teplyakov, J.Macromol.Sci.-Rev., **C5**(2), 409 (1971).
33. E.S.Krongauz, Doctoral Thesis, Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow, 1968.
34. J.P.Critchley, Progr.Polymer Sci., **2**, 47 (1970).
35. G.B.Vaughan, J.C.Rose, and G.P.Brown, Polymer Prepr., **11**, 339 (1970).
36. G.B.Vaughan, J.C.Rose, and G.P.Brown, J.Polymer Sci., **A-1**, **9**, 1117 (1971).
37. S.S.Hirsch, French P.1150601 (1968); Chem.Abs., **71**, 51178 (1969).
38. S.S.Hirsch, Polymer Prepr., 8, 1155 (1967).
39. S.S.Hirsch, J.Polymer Sci., **A-7**, 15 (1969).
40. J.Preston, J.Heterocycl.Chem., 2, 441 (1965).
41. J.Preston, Polymer Prepr., 6, 42 (1965).
42. J.Preston, Belg.P.650979 (1964).
43. J.Preston, Dutch P.6408298 (1965).
44. J.Preston and W.B.Black, Polymer.Prepr., **6**, 757 (1965).
45. J.Preston and W.B.Black, J.Polymer Sci., **B3**, 845 (1965).
46. J.Preston, "Conference on the Synthesis of Aromatic-Heterocyclic Polymers, Dayton, Ohio, 1967".
47. J.Preston and W.B.Black, J.Polymer Sci., **A-1**, **45**, 2429 (1967).
48. J.Preston and W.B.Black, Polymer Prepr., **9**, 1143 (1968).
49. L.I.Chudina, K.N.Vlasova, S.I.Litovchenko, N.P.Bodryukova, and N.F.Sedova, USSR P.378397 (1970); Byul.Izobret., No.19 (1973).
50. L.W.Frost, French P.1459375 (1966); Chem.Abs., **67**, 22341 (1967).
51. L.W.Frost, G.M.Bower, J.H.Freeman, H.A.Burgman, E.J.Traynor, and C.R.Ruffing, J.Polymer Sci., **A-1**, 6, 215 (1968).
52. R.Salle, B.Sillion, and G.de Gaudemaris, French P. 1488977 (1967); Chem.Abs., **68**, 60075 (1968).
53. J.Preston, W.F.DeWinter, and W.L.Hofferbert, J.Heterocycl.Chem., **5**, 269 (1968).
54. Y.Iwakura, K.Uno, Y.Imai, and M.Fukui, Makromol. Chem., **77**, 41 (1964).

55. T.Kurosaki and P.R.Young, J.Polymer Sci., **C23**, 57 (1968).
56. V.P.Evstaf'ev, G.I.Braz, and A.Ya.Yakubovich, Khim.Geterotsikl.Soed., **6**, 739 (1970).
57. A.I.Kuznetsov, M.I.Bessonov, G.M.Kiseleva, and M.M.Koton, Vysokomol.Soed., **A14**, 2034 (1972).
58. Ch.Mandric, A.I.Pavlov, V.V.Korshak, and I.Zugravescu, Rev.Roum.Chim., **19**, 1783 (1974).
59. V.V.Korshak, A.I.Pavlov, C.Mandric, and I.Zugravescu, Rev.Roum.Chim., **22**, 1521 (1977).
60. J.Preston, H.C.Bach, and J.B.Clements, in "Monomers for Polycondensation" [Edited by J.Steele (tentative spelling, Ed. of Translation)] (Translated into Russian), Izd.Mir, Moscow, 1976, p.428.
61. J.Preston, W.B.Black, and W.F.DeWinter, Polym. Prepr., **9**, 1165 (1968).
62. W.F.DeWinter and J.Preston, US P.3621076 (1971).
63. R.Hirohashi, Y.Hishiki, and S.Ishikawa, Polymer, **11**, 297 (1970).
64. V.V.Korshak, G.M.Tseitlin, Ziyad Tarik Al-Haidar, V.D.Vorob'ev, and L.N.Chudina, USSR P.382651 (1970); Byul.Izobret., No.23 (1973).
65. V.V.Korshak, G.M.Tseitlin, and Ziyad Tarik Al-Haidar, Izv.Akad.Nauk SSSR, Ser.Khim., 2160 (1970).
66. V.V.Korshak, A.V.Vinogradov, V.V.Rode, G.M.Tseitlin, and Ziyad Tarik Al-Haidar, Vysokomol. Soed., **A14**, 1528 (1972).
67. G.M.Tseitlin, V.V.Korshak, V.V.Rode, A.V.Vinogradov, and Z.T.Al-Haidar, J.Polymer Sci., **C3**, 1305 (1973).
68. V.P.Evstaf'ev, G.I.Braz, A.Ya.Yakubovich, and G.F.Shalygin, Vysokomol.Soed., **A13**, 2565 (1971).
69. V.V.Korshak and A.D.Maksimov, "Itogi Nauki. Khimiya i Tekhnologiya Vysokomolekulyarnykh Soedinenii" (Advances in Sciences. The Chemistry and Technology of High-Molecular-Weight Compounds), Izd.VINITI, Moscow, 1971, Vol.3, p.60.
70. S.S.Hirsch, French P.1550044 (1968); Chem.Abs., **71**, 40130 (1969).
71. G.Rabilloud, B.Sillion, and G.de Gaudemaris, French P.1504423 (1967).
72. Y.Iwakura, K.Uno, Y.Imai, and M.Fukui, Japanese P.29034 (1965); Chem.Abs., **64**, 12844 (1966).
73. M.M.Koton, T.M.Kiseleva, and S.N.Nikolaeva, Vysokomol.Soed., **B17**, 18 (1975).
74. B.M.Culbertson, US P.3661849 (1972).
75. V.V.Korshak, A.L.Rusanov, I.Batirov, D.S.Tugushi, and I.Ya.Kolontarov, Dokl.Akad.Nauk Tadzh.SSR, **20**, 9 (1977).
76. V.S.Voishchev, V.A.Beloglazov, B.I.Sazhin, I.Batirov, A.L.Rusanov, and V.V.Korshak, Vysokomol.Soed., **B20**, 259 (1978).
77. I.Batirov, V.V.Korshak, and A.L.Rusanov, Vysokomol.Soed., **A20**, 1036 (1978).
78. V.V.Korshak, A.L.Rusanov, and I.Batirov, Dokl. Akad.Nauk SSSR, **240**, 88 (1978).
79. I.Batirov, Yu.F.Milyaev, and L.N.Balyatinskaya, "Tezisy Mezhdunarodnogo Simposiuma po Makromolekulyarnoi Khimii, Tashkent, 1978" (Abstracts of Reports at the International Symposium on Macromolecular Chemistry, Tashkent, 1978), Vol.3, p.33.
80. J.S.Rodia, US P.3247165 (1966).
81. J.Preston, W.F.DeWinter, and W.L.Hofferbert, Jr., J.Heterocycl.Chem., **6**, 119 (1969).
82. J.Preston, W.F.DeWinter, W.B.Black, and W.L.Hofferbert, J.Polymer Sci., **A-1**, **7**, 3027 (1969).
83. T.Takenaka, E.Nishi, and K.Ohta, Japanese P.1832 (1970); Ref.Zhur.Khim., 20S406 (1970).
84. Y.Imai and H.Utiama, Kobunshi Kagaku, 27, 305 664 (1970); Ekspress-Informatsiya VINITI "Termostoikie Plastiki", No.14, 68 (1971).
85. H.Uchiyama, T.Imai, and M.Uchida, Japanese P.14195 (1973); Ref.Zhur.Khim., 4S367 (1974).
86. N.A.Adrova, V.N.Bagal, A.M.Dubnova, I.Ya.Kvitko, M.M.Koton, N.P.Kuznetsov, and S.S.Florinskii, Vysokomol.Soed., **B15**, 507 (1973).
87. H.G.Bach and H.E.Hinderer, Polymer Prepr., **11**, 334 (1970).
88. A.B.Berezina, A.I.Pavlov, B.B.Berezin, G.M.Tseitlin, and V.V.Korshak, Vysokomol.Soed., **B18**, 187 (1976).
89. L.Z.Jones, F.W.Ochyncki, and F.A.Rackley, Chem.Ind., 1686 (1962).
90. Dutch Appl.298295 (1965); Chem.Abs., **64**, 14386 (1966).
91. K.Kurita and R.L.Williams, J.Polymer Sci., Polym. Chem. Ed., **11**, 3125 (1973).
92. K.Kurita and R.L.Williams, J.Polymer Sci., Polym. Chem. Ed., **11**, 3151 (1973).
93. K.Kurita and R.L.Williams, J.Polymer Sci., Polym. Chem. Ed., **12**, 1809 (1974).
94. Y.Yamazaki, T.Ishikawa, T.Suzuki, and Y.Irie, J.Chem.Soc.Japan, Chem.and Ind.Chem., 502 (1976); Ekspress-Informatsiya VINITI "Termostoikie Plastiki", No.34, 6 (1976).
95. V.V.Korshak, V.P.Namaev, S.V.Vinogradova, Ya.S.Vygodskii, and E.P.Fokin, USSR P.267893 (1969); Byul.Izobret., No.13 (1970).
96. V.I.Azarov, V.V.Fefilov, B.P.Vorob'ev, B.N.Mityukhin, N.P.Antsiferova, and T.V.Devdariani, USSR P.376406 (1971); Byul. Izobret., No.17 (1973).
97. H.Frommelt and D.Hein, BRD P.112138 (1975).
98. R.Seltzer and D.A.Gordon, US P.3729448 (1973).
99. R.Seltzer, D.A.Gordon, and P.D.Sherman, US P.3814719 (1974).
100. R.J.Kray and R.A.E.Winter, US P.3666723 (1972); Chem.Abs., **77**, 62519 (1972).
101. R.J.Kray and R.A.E.Winter, US P.3803075 (1974).
102. Y.Yuki and S.Mouri, J.Chem.Soc.Japan.Chem. and Ind.Chem., 2181 (1974).
103. Y.Yuki and M.Kinoshita, Nippon Kagaku Kaishi, 549 (1977); Chem.Abs., **87**, 39869 (1977).
104. V.V.Korshak, E.S.Krongauz, S.V.Vinogradova, Ya.S.Vygodskii, N.M.Kofman, H.Raubach, H.Frommelt, D.Hein, and B.Falk, USSR P.552333; Byul.Izobret., No.12 (1977).
105. V.V.Korshak, E.S.Krongauz, S.V.Vinogradova, Ya.S.Vygodskii, N.M.Kofman, H.Raubach, H.Frommelt, D.Hein, and B.Falk, Dokl.Akad.Nauk SSSR, **236**, 890 (1977).
106. N.M.Kofman, Candidate's Thesis, Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow, 1977.
107. H.Raubach, H.Frommelt, V.V.Koršak, S.V.Vinogradova, E.S.Krongauz, D.Hein, J.S.Vigodskii, N.M.Kofman, R.P.Travnikova, B.Falk, and R.Becker, Faserforsch.Textiltechn., **28**, 611 (1977).
108. V.V.Korshak, E.S.Krongauz, N.M.Kofman, H.Frommelt, H.Raubach, and D.Hein, USSR P.540461 (1975); Byul.Izobret., No.47 (1977).

109. V.V.Korshak, E.S.Krongauz, A.M.Berlin, H.Raubach, and D.Hein, USSR P.555099 (1974); Byul.Izobret., No.5 (1977).
110. B.M.Culbertson, US P.3630994 (1971).
111. B.M.Culbertson, US P.3637692 (1972).
112. B.M.Culbertson, US P.3661847 (1972).
113. S.Nishizaki and A.Fukami, US P.3674741 (1972).
114. S.Nishizaki and A.Fukami, Japanese P.2434 (1973); Ref.Zhur.Khim., 24S464 (1973).
115. S.Nishizaki and A.Fukami, Kobunshi Ronbunshu, **32**, 445 (1975).
116. F.Bentz and F.Bodesheim, BRD Appl.1811167 (1970); Chem.Abs., **73**, 46064 (1970).
117. T.I.Zhukova, F.S.Florinskii, M.M.Koton, M.I.Bessonov, and L.A.Laius, Vysokomol.Soed., **B16**, 390 (1974).
118. M.Ueda, T.Aizawa, and Y.Imai, J.Polymer Sci., Polym.Chem.Ed., **15**, 2739 (1977).
119. K.K.Mozgova, V.V.Korshak, and S.G.Levitskaya, Plast.Massy, No.10, 14 (1968).
120. F.F.Holub and J.T.Hoback, US P.3539537 (1970).
121. A.Stoenciu, O.Ya.Fedotova, and V.V.Korshak, Trudy Moskov.Khim.-Tekhnol.Inst.im.Mendeleeva, **74**, 130 (1973).
122. A.Stoenciu and O.Ja.Fedotova, Mater.Plast., **40**, No.11, 15 (1974).
123. G.S.Kolesnikov, O.Ya.Fedotova, and R.I.Gramatikati, Trudy Moskov.Khim.-Tekhnol.Inst.im.Mendeleeva, **66**, 209 (1970).
124. O.Ya.Fedotova, R.I.Gramatikati, and G.S.Kolesnikov, Vysokomol.Soed., **B17**, 701 (1975).
125. R.A.Dine-Hart, J.Polymer Sci., **A-1**, **6**, 2755 (1968).
126. E.F.Hoegger, US P.3442861 (1969); Chem.Abs., **71**, 31005 (1969).
127. J.Bateman and D.A.Gordon, US P.3856752 (1974); Chem.Abs., **82**, 140751 (1975).
128. W.M.Edwards, B.P.898651 (1962); Chem.Abs., **58**, 14147 (1963).
129. W.M.Edwards and A.L.Endrey, B.P.903271 (1962); Chem.Abs., **58**, 3520 (1963).
130. W.M.Edwards and A.L.Endrey, B.P.903272 (1962); Chem.Abs., **58**, 3520 (1963).
131. W.M.Edwards and A.L.Endrey, US P.3179630 (1965); Chem.Abs., **63**, 18403 (1965).
132. C.E.Sroog, "International Symposium on Macromolecular Chemistry, Prague, 1965", Preprints, p.155; J.Polymer Sci., **C16**, 1191 (1967).
133. H.Sekiguchi and K.Sadamitsu, Japanese P.21656 (1971); Ref.Zhur.Khim., 1S247 (1972).
134. H.Sekiguchi and K.Sadamitsu, Japanese P.26876 (1973); Ref.Zhur.Khim., 13S384 (1973).
135. Japanese P.14196 (1973); Ref.Zhur.Khim., 5S318 (1973).
136. N.Ida, M.Kurihara, S.Toyama, N.Dokoshi, and Y.Nakanishi, Japanese P.24593 (1970); Ref.Zhur. Khim., 20S322 (1971).
137. N.Yoda and N.Dokoshi, "23rd International Congress on Pure and Applied Chemistry, Boston, 1971" Macromol.Prepr., Vol.2, p.967.
138. N.P.Lyubchenko and B.A.Zhubanov, Izv.Kazakh. SSR, Ser.Khim., **4**, 49 (1972).
139. Japanese P.34697 (1972); Chem.Abs., **78**, 125471 (1973).
140. B.V.Suvorov, B.A.Zhubanov, and S.A.Mashkevich, "Trimellitovaya Kislota i Polimery na Ee Osnove" (Trimellitic Acid and Polymers Based on It), Izd. Nauka, Alma-Ata, 1975.
141. S.Hashimoto and Y.Nagasuna, Kobunshi Kagaku, **24**, 633 (1967); Ref.Zhur.Khim., 10S255 (1968).
142. W.G.Gall, French P.1365545 (1964); Chem.Abs., **62**, 7898 (1965).
143. W.G.Gall, US P.3249588 (1966); Chem.Abs., **64**, 8387 (1966).
144. V.V.Korshak, G.M.Tseitlin, A.I.Pavlov, T.G.Pogorelov, and V.A.Smirnova, Izv.Akad.Nauk SSSR, Ser.Khim., 1900 (1968).
145. V.V.Korshak, G.M.Tseitlin, O.S.Zhuravkov, and A.I.Pavlov, Trudy Moskov.Khim.-Tekhnol.Inst.im. Mendeleeva, **70**, 179 (1972).
146. O.S.Zhuravkov, G.M.Tseitlin, V.V.Korshak, and A.M.Mazgarov, Izv.Vys.Ucheb.Zaved., Khim.i Khim. Tekhnol., **20**, 779 (1977).
147. T.Ishizaki, Japanese P.49-2036 (1974); Ref.Zhur. Khim., 22S399 (1974).
148. D.A.Gordon and R.S.Seltzer, US P.3957726 (1976).
149. A.Fukami, Kobunshi Eonbunshu, **34**, 669 (1977).
150. N.A.Churochkina, Candidate's Thesis, Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow, 1972.
151. H.Melven, US P.3502625 (1970).
152. L.W.Frost, US P.3941749 (1976).
153. J.Preston, "Preprints of the International Symposium on Macromolecules, Helsinki, 1972", 1972, Vol.2, p.735.
154. J.Preston, J.Polymer Sci., Polymer Chem.Ed., **10**, 3373 (1972).
155. M.Kurihara, A.Kobayashi, and M.Yorita, Japanese P.12745 (1971); Ref.Zhur.Khim., 15S40 (1972).
156. S.Minami, Japanese P.28712 (1969); Ref.Zhur.Khim., 17S353 (1970).
157. T.Minami, Japanese P.48-2951 (1973); Ref.Zhur. Khim., 3S303 (1974).
158. S.Minami, Japanese P.48-2954 (1973); Ref.Zhur. Khim., 3S304 (1974).
159. T.Shono, M.Soga, M.Obora, and K.Shiura, Kogyo Kagaku Zasshi, **70**, 1250 (1967).
160. T.Shono, M.Izumi, S.Matsumura, and N.Asano, Japanese P.13473 (1968); Ekspress-Informatsiya. VINITI. "Termostoikie Plastiki", No.4, Abs.120 (1969).
161. N.Dokoshi, M.Kurihara, and N.Ida, Japanese P.19876 (1969); Ref.Zhur.Khim., 15S508 (1970).
162. French P.15227947 (1968); Chem.Abs., **71**, 31059 (1969).
163. N.Dokoshi, S.Tohyoma, S.Fujita, M.Kuruhara, and N.Yoda, J.Polymer Sci., **A-1**, 8, 2197 (1970).
164. M.Yorita, M.Kurihara, S.Toyama, and N.Dokoshi, Japanese P.13115 (1970); Ref.Zhur.Khim., 13S299 (1971).
165. M.Kurihara, A.Kobayashi, and N.Yorita, Japanese P.9264 (1971); Ref.Zhur.Khim., 15S381 (1972).
166. S.Toyama, M.Kurihara, and N.Yoda, Japanese P.27820 (1971); Ref.Zhur.Khim., 10S340 (1972).
167. N.Yoda, M.Kurihara, N.Dokoshi, K.Ikeda, S.Toyama, and I.Nakanishi, Japanese P.19875 (1969); Ref.Zhur.Khim., 15S507 (1970).
168. N.Yorita, M.Kurihara, S.Toyama, N.Dokoshi, K.Ikeda, and I.Nakanishi, Japanese P.13114 (1970); Ref.Zhur.Khim., 13S298 (1971).
169. N.Yorita, N.Dokoshi, S.Toyama, M.Kurihara, K.Ikeda, and I.Nakanishi, Japanese P.13116 (1970); Ref.Zhur.Khim., 13S300 (1971).

170. M.Kurihara, A.Kobayashi, and N.Yorita, Japanese P.24250 (1971); Ref.Zhur.Khim., 6S428 (1971).
171. Japanese P.27320 (1971); quoted after Ref.140.
172. V.V.Korshak, G.M.Tseitlin, Ziyad Tarik Al-Haidar, S.A.Zholaeva, and Ya.S.Vygodskii, USSR P.360352 (1970); Byul.Izobret., No.36 (1972).
173. S.Arai, N.Kotani, N.Yoda, M.Kurihara, and N.Dokoshi, Japanese P.38697 (1974); Ref.Zhur. Khim., 6T119 (1975).
174. M.Kurihara, N.Dokoshi, S.Toyama, K.Ikeda, N.Ida, and Y.Nakanishi, Japanese P.23109 (1969); Ref.Zhur.Khim., 12S411 (1970).
175. N.Ida, M.Kurihara, N.Dokoshi, K.Ikeda, S.Toyama, and Y.Nakanishi, Japanese P.19874 (1969); Ref.Zhur.Khim., 15S506 (1970).
176. N.Dokoshi, M.Kurihara, S.Toyama, K.Ikeda, and N.Ida, Japanese P.19879 (1969); Ref.Zhur.Khim., 15S510 (1970).
177. N.Ida, S.Toyama, N.Dokoshi, M.Kurihara, K.Ikeda, and Y.Nakanishi, Japanese P.131117 (1970); Ref.Zhur.Khim., 13S301 (1971).
178. V.V.Korshak, G.M.Tseitlin, G.M.Cherkasova, and A.L.Rusanov, USSR P.267065 (1969); Byul.Izobret., No.12 (1970).
179. N.Ida, S.Toyama, N.Dokoshi, M.Kurihara, K.Ikeda, and Y.Nakanishi, Japanese P.13349 (1970); Ref.Zhur.Khim., 13S302 (1971).
180. N.Ida, S.Toyama, N.Dokoshi, M.Kurihara, K.Ikeda, and Y.Nakanishi, Japanese P.13350 (1970); Ref.Zhur.Khim., 13S303 (1971).
181. N.Ida, S.Toyama, N.Dokoshi, M.Kurihara, K.Ikeda, and Y.Nakanishi, Japanese P.13351 (1970); Ref.Zhur.Khim., 13S304 (1971).
182. H.A.Burgman, J.H.Freeman, L.W.Frost, G.M.Bower, E.J.Traynor, and C.R.Ruffing, J.Appl.Polymer Sci., **12**, 805 (1968).
183. J.H.Freeman, L.W.Frost, G.M.Bower, E.J.Traynor, H.A.Burgman, and C.R.Ruffing, Polymer Eng. and Sci., **9**, 56 (1969).
184. J.Preston and W.B.Black, Man-Made Fibres, Sci. Technol., **2**, 365 (1968); Chem.Abs., **69**, 3144 (1968).
185. J.Preston, Rubber Plast.Age, **49**, 1124 (1968).
186. J.Preston, W.B.Black, and W.F.DeWinter, Appl. Polymer Symp., No.9, 145 (1969).
187. J.Preston and W.B.Black, Appl.Polymer Symp., No.9, 107 (1969).
188. J.Preston, "Preprinty Mezhdunarodnogo Simposiuma po Khimicheskim Voloknam, Kalinin" (Preprints of the International Symposium on Chemical Fibres, Kalinin), 1974, Vol.7, p.5.
189. J.Preston, Polymer Eng.Sci., **16**, 298 (1976).

Institute of Organoelemental Compounds,
USSR Academy of Sciences, Moscow

Institute of Chemistry,
Academy of Sciences of Tajik SSR,
Dushande